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Role in Prevention of Corona Virus Infection

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Abstract -

Corona virus disease 2019 (COVID-19) is an infectious disease caused by severe acute respiratory syndrome corona virus 2 (SARS-CoV-2). It was first identified in December 2019 in Wuhan, China, and has since spread globally, resulting in an ongoing pandemic. As of 10 May 2020, more than 4.02 million cases have been reported across 187 countries and territories, resulting in more than 279,000 deaths. More than 1.37 million people have recovered. Common symptoms include fever, cough, fatigue, shortness of breath, and loss of smell and taste. While the majority of cases result in mild symptoms, some progress to acute respiratory distress syndrome (ARDS), multi-organ failure, septic shock, and blood clots. The time from exposure to onset of symptoms is typically around five days but may range from two to fourteen days.

Introduction -

The virus is primarily spread between people during close contact, most often via small droplets produced by coughing, sneezing, and talking. The droplets usually fall to the ground or onto surfaces rather than travelling through air over long distances. Less commonly, people may also become infected by touching a contaminated surface and then touching their face. It is most contagious during the first three days after the onset of symptoms, although spread may be possible before symptoms appear and in later stages of the disease. The standard method of diagnosis is by real-time reverse transcription polymerase chain reaction (rRT-PCR) from a nasopharyngeal swab. Chest CT imaging may also be helpful for diagnosis in individuals where there is a high suspicion of infection based on symptoms and risk factors; however, guidelines do not recommend using it for routine screening.

Recommended measures to prevent infection include frequent hand washing, maintaining physical distance from others (especially from those with symptoms), quarantine, covering coughs, and keeping unwashed hands away from the face. In addition, the use of a face covering is recommended for those who suspect they have the virus and their caregivers. Recommendations for face covering use by the general public vary, with some authorities recommending, some recommending against, and others requiring their use. There is limited evidence for or against the use of masks (medical or other) in healthy individuals in the wider community.

According to the World Health Organization, there are no available vaccines nor specific antiviral treatments for COVID-19. On 1 May 2020, the United States gave Emergency Use Authorization to the antiviral remdesivir for people hospitalized with severe COVID-19. Management involves the treatment of symptoms, supportive care, isolation, and measures. The World Health Organization (WHO) declared the COVID-19 outbreak a Public Health Emergency of International Concern (PHEIC) on 30 January 2020 and a pandemic on 11 March 2020. Local transmission of the disease has occurred in most countries across all six WHO regions. It is important to note that no fortune teller, astrologer or architect has predicted the corona at the Indian or international level. The important task in the future is to rid the masses of those who propagate and spread unscientific things. Corona urges us to take a positive view of science and research. The name 'Corona' is now well known. Certainly not in a good sense. Today, the whole world is shocked by the disease 'Covid-19' caused by the corona virus. He has never crossed the boundaries of caste, religion, gender, country. I also put 'direction' in it. In all directions, the Corona has penetrated villages and homes. The architect and the person who built the house on his advice are no exception. I don't think anyone would be

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upset about that.It should be noted that no fortune teller, astrologer or architect has predicted the corona at the Indian or international level. I say this internationally because the so-called world astrologer Nostradamus or Vedokta astrologer is likely to publish something in the future, so I make it clear at the outset. Evidence of Shlokas, Vedas, Puranas is also likely to be given for this prophecy. A corona is a natural disaster that has hit the entire world. Although it originated in China, it is not officially recognized as a Chinese product. It is irresponsible to make any statement without evidence, so China has not yet been officially reprimanded.

Signs and symptoms –

Fever is the most common symptom, although some older people and those with other health problems experience fever later in the disease. In one study, 44% of people had fever when they presented to the hospital, while 89% went on to develop fever at some point during their hospitalization. Other common symptoms include cough, loss of appetite, fatigue, shortness of breath, sputum production, and muscle and joint pains. Symptoms such as nausea, vomiting, and diarrhea have been observed in varying percentages. Less common symptoms include sneezing, runny nose, or sore throat. Some cases in China initially presented with only chest tightness and palpitations. A decreased sense of smell or disturbances in taste may occur. Loss was a presenting symptom in 30% of confirmed cases in South Korea. As is common with infections, there is a delay between the moment a person is first infected and the time he or she develops symptoms. This is called the incubation period. The incubation period for COVID 19 is typically five to six days but may range from two to 14 days, although 97.5% of people who develop symptoms will do so within 11.5 days of infection.

Prevention -

Preventive measures to reduce the chances of infection include staying at home, avoiding crowded places, keeping distance from others, washing hands with soap and water often and for at least 20 seconds, practicing good respiratory hygiene, and avoiding touching the eyes, nose, or mouth with unwashed hands. The CDC recommends covering the mouth and nose with a tissue when coughing or sneezing and recommends using the inside of the elbow if no tissue is available. Proper hand hygiene after any cough or sneeze is encouraged. The CDC has recommended the use of cloth face coverings in public settings where other social distancing measures are difficult to maintain, in part to limit transmission by asymptomatic individuals. The U.S. National Institutes of Health guidelines do not recommend any medication for prevention of COVID 19, before or after exposure to the SARS-CoV-2 virus, outside of the setting of a clinical trial. Social distancing strategies aim to reduce contact of infected persons with large groups by closing schools and workplaces, restricting travel, and cancelling large public gatherings. Distancing guidelines also include that people stay at least 6 feet (1.8 m) apart. There is no medication known to be effective at preventing COVID 19. After the implementation of social distancing and stay-at-home orders, many regions have been able to sustain an effective transmission rate ("Rt") of less than one, meaning the disease is in remission in those areas.

As a vaccine is not expected until 2021 at the earliest, a key part of managing COVID 19 is trying to decrease and delay the epidemic peak, known as "flattening the curve". This is done by slowing the infection rate to decrease the risk of health services being overwhelmed, allowing for better treatment of current cases, and delaying additional cases until effective treatments or a vaccine become available. According to the WHO, the use of masks is recommended only if a person is coughing or sneezing or when one is taking care of someone with a suspected infection. For the European Centre for Disease Prevention and Control (ECDC) face masks could be considered especially when visiting busy closed spaces but only as a complementary measure. Several countries have recommended that healthy individuals wear face masks or cloth face coverings (like scarves or bandanas) at least in certain public settings, including China, Hong Kong, Spain, Italy (Lombardy region), Russia, and the United States.

Those diagnosed with COVID 19 or who believe they may be infected are advised by the CDC to stay home except to get medical care, call ahead before visiting a healthcare provider, wear a face mask before entering the healthcare provider's office and when in any room or vehicle with another person, cover coughs and sneezes with a tissue, regularly wash hands with soap and water and avoid sharing personal household items. The CDC also recommends that individuals wash hands often with soap and water for at least 20 seconds, especially after going to the toilet or when hands are visibly dirty, before eating and after blowing one's nose, coughing or sneezing. It further recommends using an alcohol-based hand sanitizer with at least 60% alcohol, but only when soap and water are not readily available.

Here are the measures you need to take to keep the virus at time:

1. Avoid close contact with people who are sick. Maintain at least three feet distance between yourself and anyone who is coughing or sneezing.
2. Avoid touching your eyes, nose, and mouth.
3. Stay home when you are sick.
4. Cover your cough or sneeze with a tissue, then dispose of the tissue safely.
5. Clean and disinfect frequently-touched objects and surfaces using a regular household cleaning spray or wipe.
6. Wearing a mask is not necessary unless you are taking care of an infected person. The Centers for Disease Control (CDC) does recommend that only infected people wear masks to prevent the spread of the virus.
7. Wash your hands often with soap and water for at least 20 seconds, especially after going to the bathroom, before eating, and after blowing your nose, coughing, or sneezing.
8. If soap and water are not readily available, use an alcohol-based hand sanitiser with at least 60% alcohol. Always wash hands with soap and water when hands are visibly dirty.
9. If you have a fever, cough and difficulty breathing, seek medical attention immediately.
10. Keep in mind the travel advisory set out by the Ministry of Health and Welfare.

Result -

1) Corona in our country. In the new world a virus that will linger in our minds for a long time. Two things that are very important for it are good health and safe perfume. Now your fight is with Corona for at least a year. 'LOCKDOWN' Whether or not you want to go to the critical stage of corona disease, then the following suggestions are very important because if you do not want the infection to be critical, then two things are important immunity and viral load.
2) Corona spreads through the respiratory tract, just as the surface is spread through body clothes, hand objects, mobiles, watches. There is seeing this, I felt it was my responsibility to write this article as a doctor.
3) The first point is better health Eating on time for good health, like eight hours of good sleep, one hour of light exercise at home Keep yourself happy with yoga, rope jumping, spot jogging, pranayama, kapalbhati, anulom-vilom (there are many videos available for this on YouTube). Don't let the stress of studying put pressure on the children at home.
4) Second issue 'Social Distance'. Today we will understand the meaning of this word which is not new to anyone. There should be at least one meter distance between two persons. Afterwards, when I went to a grocery store to buy groceries, there was a very disturbing picture. The shopkeeper and his three colleagues wore masks around their necks for the show without putting a mask on their faces. There was a bottle of sterlium .Some people didn't even bother to wear a mask .Some even took a packet of chips and started eating. At that moment, the shop seemed to be a hot spot for me. What did I have to do in such a situation??? Get out only if the first thing is necessary.

References -

1) Chen N, Zhou M, Dong X, Qu J, Gong F, Han Y, et al. (February 2020). "Epidemiological and clinical characteristics of 99 cases of 2019 novel coronavirus pneumonia in Wuhan, China: a descriptive study". Lancet. 395 (10223):

507–513. doi:10.1016/S0140-6736(20)30211-7. PMC 7135076. PMID 32007143.

2) Han X, Cao Y, Jiang N, Chen Y, Alwalid O, Zhang X, et al. (March 2020). "Novel Coronavirus Pneumonia (COVID-19) Progression Course in 17 Discharged Patients: Comparison of Clinical and Thin-Section CT Features During Recovery". Clinical Infectious Diseases. doi:10.1093/cid/ciaa271. PMC 7184369. PMID 32227091.

3) "Symptoms of Coronavirus". U.S. Centers for Disease Control and Prevention (CDC). 20 March 2020. Archived from the original on 30 January 2020.

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Impact of Covid-19 on Education in India

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Abstract -

It is an attempt to documentize the effects of pandemic on various aspects of society. "COVID-19 is an infectious disease caused by a newly discovered virus named as corona virus.[1] More than 4 million cases have been confirmed worldwide, corona became the cause of nearly three lakhs deaths until the date, and count is increasing. Most of the countries are in grave danger. Therefore, WHO characterized COVID-19 as 'Pandemic'? Corona virus affects the number of countries in a lockdown situation.The increasing number of infectious people and the intensity of spreading COVID-19 creates the pandemic. In order to control the pandemic most of the countries preferred lock down as the safest way and solutions. However, the decision of lock down taken by the authorities directly affects on the socio-economic structure of the country. Moreover, it influences the-future-of-learning.

As compare to other countries in India, the rate of death is lower. The first phase of lock down was declared on 24 March 2020 by the government of India. When the lock down was declared, people were inattentive and heedless. It creates some kind of fear, anxiety and confusion among the people. The wheel of economy was stopped. It forced to shut down all other institutions and enterprises. The pandemic affects not only the enterprises and industry but also the physical and mental health of the people. Various social organizations and the government authorities have been working for day and night to handle the pandemic. The government authorities were successful to control the spread of the infectious disease COVID- 19 and the law and order of the country at the cost of economic slowdown. The social, political, religious, cultural, educational, agricultural, as well as administrative wings have been immobilized for more than 50 days.

Keywords - COVID-19, Pandemic, economy, educational institutions, academics.

Introduction -

This research article is an observation of impact of COVID- 19 on various aspects of the human life. As the researcher has been working in the field of education, it is preferred to discuss on the academic and educational aspects of the society. When the Hon. Prime Minister declared the first phase of lock down on 23rd March 2020 nobody was aware of the future happenings and its impact on human life. Everyone feels insecure and anxious. Nobody knows that how many days and how long the lock down and fearful situation caused by pandemic will persist. When the second phase of lock down was declared then people come to know that the previous was the first phase and when the third phase of lock down was declared then it comes to know that the previous was second phase and henceforth.

The pandemic creates just a war like situation in the world. However, the Indian people have been facing the challenge bravely. "In order to ensure safety of the Faculty members/Teachers/Researchers/Non-teaching staff of educational institutions, under your organization should be permitted and advised to work from home till 31/03/2020".[2] During this lock down period it is observed that various social organization, NGOs, corporate sector and the government authorities have been working hand in hand. Each organization cooperates with the decision taken by the government. The social organizations, NGOs, educational institutions, health experts, media personnel, representatives of the government have been participating eagerly in the work to control and overcome the pandemic. People were making aware of the facts of COVID-19 and its effects on human health and life. Various online awareness

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programs were organized by the government and NGOs to educate the people. The multimedia and television channels play an important role to spread messages as:

- Stay at Home
- Keep safe physical distancing at about 2 meters
- Avoid public gathering.
- Wash hands with any soap for 20 seconds.
- Wearing mask on face.
- Use digital payments.
- Use of ArogyaSetu App.
- Self-isolations.
- How to fight against corona.
- Fight against corona virus and not with the infected person.

These measures have been following by everyone in India. While following these precautionary measures to overcome pandemic, the educational institutions would not run his academic activities. The academic activities were affected by this situation in the country. Its immediate effect is on teaching-learning activities as well as teaching -learning-evaluation pattern and organizing the examination in the month of April –May 2020.

Education and Methods of Teaching -

In India, the education system is traditional and pursuing towards modern and digital. The schooling generally constitutes the most traditional, conservative, rigid, bureaucratic institution since independent India. The aim of education is stated from time by the educational commissions. Since independence, India formed the three education commissions to renovate the colonial education system of the past British India to suit the needs and aspirations of the nation. Apart from the many functions of education, the main function is the development of human resources. The achievement of social and economical development of the nation would be possible through proper education. To achieve these goals priority must be given to universal primary education of eight years, total adult literacy, vocationalization of secondary education and a relevant higher education that can provide ideas for man to shape his future. These ideals of education have been fulfilling by the traditional methods of teaching learning and evaluation. In the course of time, it becomes the system.

Unforeseen Challenges -

The COVID-19 produced many unforeseen and undesirable impacts. As it is stated in, the introductory part that how pandemic affects each field in the country. However, as a researcher it is restricted to discuss on the effects of pandemic on educational and academic fields. The schools and colleges were in a full-fledged planning to conduct various practical and theory examination "Not only the cases of COVID-19 are increasing rapidly around the world, the deadly virus is taking its toll on various schools, colleges and competitive examinations."[3]

In this regard, the education system is shocked and remained silent for a month. Gradually the academicians and government authorities tried to seek solution. As, it is not possible for anyone to reach at the educational institutions for exams. Conducting practical exams is just a thing to say. At most, of the educational level it is important to conduct practical examinations to evaluate knowledge of the aspirants. It is not reliable to judge knowledge of the aspirants only on assignments and theoretical examination.

Psychological Condition of Students' -

As a researcher, it is decided to contact with the students and the stakeholders. Whenever the responses from the students received, it is found that the students were not aware of the examination schedules.The stakeholders and students were very anxious about their future career. They found themselves in the clutches of lockdown and mental stress. They have been scared about their studies and examinations. In addition, the rumors were spread through social media about the examinations schedules and decisions of the authorities. Therefore, the university authorities formed a special center "counseling and guidance centre"[4] for students and stakeholders at various places. The students would sought online counseling and guidance from the experts where they will experience and receive genuinely human climate.

Examinations -

The COVID -19 acutely affects the examinations system in the country. Examinations plays very crucial role in education system. Examinations are the way to test the knowledge and skills of the learner. Examinations are essential in schools and colleges to find out the skills, knowledge and talent the students have achieved. Evaluation system should be used to reflect the index of teacher effectiveness and students' efforts. Examinations reflect the spirit of self-analysis and achievements of the students. The assessment system evaluates the student's ability of learning, analytical power, logical thinking and understanding. Therefore, students prefer to appear for examination as a career and the goal they decided to achieve. However, the circular from "KBC North Maharashtra University Circular"[5] stated that the government authorities have taken a decision to postpone the examination schedule. Moreover, first year, second year examinations were cancelled for three year degree course. Wherever there is a four/ five, year degree course only the last year examination will be organized. In most of the places student assessments are moving online with trial and error basis.

Shifting and Turning -

In connection with the immediate changes in academic affairs, happenings and the phrase 'Work from Home' the researcher get more valuable information and resources from Dr. Vijay Bachhao as an Online Talk "In the history of education, the year 2020 would be recorded as the year of shifting and turning. Up to March 2020, everything is going on smoothly, satisfactory and traditionally excellent in the academic realms." [6] The present day education system has undergone many changes since British Raj in India. However, due to COVID 19, the giant wheel of action stopped and every one remains in a lockdown situation. It affects everyone and each enterprises. Moreover, the education and academic realm has been more objectified by the pandemic. The whole academic scenario has been changed. Everyone is trying to make adjust with the situation. The traditional teaching-learning-evaluation pattern has been substantially shifting to digital and virtual pattern. Everybody seems to be hurried in attending online webinars, FDP, workshops on multimedia enriched e-content development etc. The practicing teachers have been eagerly creating the e-content and uploaded on various digital platforms for the students. The face-to-face teaching and learning method will be shifted to virtual, digital and online teaching – learning method. Even the ministry of MHRD Human Resource Development and UGC have been providing free online courses and teachers training program in order to shift digital and virtual education. Everything has been shifting and turning from offline to online.

Positive Impacts of Pandemic on Education:

While discussing on the effects of pandemic on human life and education system, it is realized that there are some positive aspects of pandemic on education. As the Hon. Prime Minister NarendraModi noted in his speech on 13th of May "India must ensure to be capable on its own."[7] The attitude of Indian people is very positive towards new technology. They are very flexible to adopt the digitalization and its uses. In such a background education, institutes are not behind to adopt the new technology. As it is said that education is one of the fastest growing sectors in India. The use of new technology is a central and driving component of this growth. Lockdown proves to be turning point in the education field. During the lockdown, the schools and colleges organized many webinars on variety of topics. The free online faculty development programs were offered by the universities. Meanwhile Google provides digital platform for the academicians and scholars. Many institutions organized online COVID-19 awareness quizzes and programs. The education could be transformed into industry sector. In a near future, the great businesspersons would be turned towards this profitable industry. The students who have a potential to handle the online education system would be flourished with bright careers. The IT industry will be in a great demand to provide the access to online education system. Then the Indian economy will be gear up. The academic schedule and framework somewhat reshuffled but it would not derail the teaching and learning spirit. The innovative teachers create a digital platform to fulfill the educational interludes between the teachers, students, educational institutes and society.

Conclusion -

To sum up COVID-19 is a challenge, and the teachers and the educational institutes have been facing the challenge successfully. It has been predicted that in future the classroom teaching and learning will be replaced by on line teaching-learning process. COVID-19 has brought a big gap in everyone's life. It can be safely said that the issues and problems aroused during the pandemic would be tackled.The education system in India has a potential to overcome the problems created by COVID-19. Students are the future of the country and teachers have the responsibility to shape them.

References -

1. https://www.who.int/health-topics/coronavirus#tab=tab_1
2. Letter from Govt. of India, Ministry of Human Resource Development, dt. 21StMarch 2020.
3. Times of India.com,TOI-Online/updated, Mar 18,2020.
4. A Letter from the registrar KBC North Maharashtra University Jalgaon, dt. 13/05/2020.
5. A Circular from the Director, Board of Exam and Evaluation, KBCNMU Jalgaondt, 15th May,2020.
6. Dr. Vijay Bachchhao: S.G.Patil College Sakri, On line Talk: 'Pandemic and Educational Changes' on 16/05/2020 at 03-04:20 PM.
7. PM Modi's address to the nation COVID-19.

Comparative X-ray Diffraction Studies on Gel Grown Crystals of Li-tartrate, Cu-tartrate and Mixed Li-Cu tartrate

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Abstract : Natural as well as Gel grown crystals plays an important role in modern technology development. Gel method for the growth of crystals which are insoluble or sparingly soluble in water is the best alternative for the growth of many crystals. Crystals grown by gel method are relatively perfect compared to the other methods. In the present investigation crystals of Li-tartrate, Cu-tartrate and Mixed crystals of Li-Cu tartrate have been grown by single diffusion gel technique. The x-ray diffraction studies of these crystals are carried out in this work. The x-ray diffraction studies on these crystals revels that these crystals belongs to orthorhombic crystal structure system. The lattice parameters of these crystals are calculated and tabulated in this article.

IndexTerms – **Gel method, XRD, Li-Cu tartrate.**

I. INTRODUCTION

It is well established that there are extensive study on tartrate based crystal grown by gel technique, however, we have found that there are few reports on the lithium tartrate based crystal because of its chemical properties [1-4]. Therefore, in the present study, we have investigated the growth mechanism of lithium tartrate, copper tartrate and mixed lithium-copper tartrate crystals. All the three types of crystals were grown by gel method by using single diffusion techniques, the crystal growth procedures and various different parameters affecting the growth of the crystals are discussed. The present paper contains the comparative study of all crystals under investigation regarding their growth and X-ray diffraction study. All results obtained are put at a glance in present paper.

II. GROWTH OF CRYSTALS

The crystals of lithium tartrate, copper tartrate, and lithium-copper tartrate were grown by gel method by using single diffusion technique. Table 1 gives details regarding method and chemicals used, different habits of crystals obtained and their transparency etc. In the present work, we obtained semitransparent, shiny and star shaped lithium tartrate crystals. The copper tartrate crystals were of diamond shaped with bluish color, while the mixed lithium-copper tartrate crystals were whitish blue in color and having a cubic shape. The adopted single diffusion gel technique proved to be beneficial because of it only we successfully obtained well-shaped and good quality crystals. All the well-defined good quality crystals were found below 2 to 3 cm in the gel interface [5-8].

The optimum growth conditions for gel grown crystals established by varying the different parameters like pH of gel, gel setting time, gel density, room temperature etc. are reported in the Table 2 for the all these three crystals. The suitable value of gel density is found to be 1.04 gm /cm^3 and the pH value is 4 to 4.2.

Sr. No.	Type	Method	Chemica l Used	Solvent	Quality	Size (mm)
1	Lithium Tartrate	Gel method using single diffusion techniques	Na_2SiO_3, $C_4H_6O_6$ 2LiCl	Methanol or Ethanol	Opaque, Transparent Good	3 x 1 x 1
2	Copper tartrate	Gel method using single diffusion techniques	Na_2SiO_3, $C_4H_6O_6$ $CuCl_2$	Distilled water	Opaque, bluish color	2.5 x 2 x 1
3	Lithium -copper Tartrate	Gel method using single diffusion techniques	Na_2SiO_3, $C_4H_6O_6$ Cucl + 2LiCl	Methanol or Ethanol	Opaque, good	2 x 2 x 1.5

Table 1 Summary of lithium, copper and lithium-copper tartrate crystals grown by gel technique

Sr. No.	Parameter	Lithium tartrate	Copper tartrate	Copper – lithium tartrate
1	Concentration of tartaric acid	1M, 7ml	1 M, 7ml	1M, 5ml
2	pH of the mixture	4 to 4.2	4.2	3.8 to 4.2
3	Temperature	25 to 30°C	25 to 30°C	20 to 30°C
4	Gel setting time	120 hours	96 hours	96 hours
5	Density of sodium metasilicate solution	1.04 gm/cm^3	1.04 gm/cm^3	1.04 gm/cm^3
6	Period of growth	4 weeks	3-4 weeks	4 weeks
7	solvent	Ethanol or Methanol	Water	Ethanol or Methanol

Table 2 Optimum growth conditions for gel grown tartrate crystals

III. XRD ANALYSIS

The crystals of lithium tartrate, copper tartrate, and mix lithium – copper tartrate were characterized by XRD analysis. From these diffractogram, 'd' values were computed [9]. Figure 1 shows comparative X-ray diffraction pattern of lithium-copper tartrate crystals. From the XRD pattern it is noticed that the peaks obtained at 11.00, 14.80, 25.00, 31.95, and 43.35° are corresponds to the (020), (220), (221), (620), and (312) lattice planes of the copper tartrate crystals, respectively. We also found (101), (021), and (102) lattice planes of lithium tartrate crystals at 2θ of 21.40, 28.81 and 36.51°, respectively. Moreover, apart from the individual lattice planes, we also obtained new peaks at 18.83, 23.11, 26.53, 34.51, 40.78, 48.19, 51.90 and 55.03 degree (2θ) exhibiting the planes (201), (141), (151), (171), (352), (313), (211) and (850), respectively, confirming the formation of lithium-copper tartrate crystals [10-11]. Calculated (hkl) and 'd' values indicate orthorhombic crystals structure of lithium-copper tartrate crystals and having lattice parameters of a = 14.5289 Å, b = 20.8745 Å and c = 6.1806 Å and volume of unit cell, V = 1874.474 (Å)^3, which are summarized in Table 3[12]. The details of the interplaner distance corresponding to each plane is tabulated in Table 4,5 and 6.

Material	Chemical formula	System	Lattice parameters a, b, c, α, β, γ	Volume (Å)^3
Lithium tartrate	$Li_2C_4H_4O_6$	Orthorhombic	a =6.7942Å b=7.9804Å c=5.2386Å α= β = γ= 90°	284.05
Copper tartrate	$CuC_4H_4O_6$	Orthorhombic	a= 17.9058Å b = 16.0728Å c = 4.4232 Å α= β = γ=90°	1272.97
Lithium-copper tartrate	$LiCuC_4H_4O_6$	Orthorhombic	a=14.5289Å b=20.8745Å c=6.1806Å α= β = γ= 90°	1874.47

Table 3 Comparison of Lattice parameters

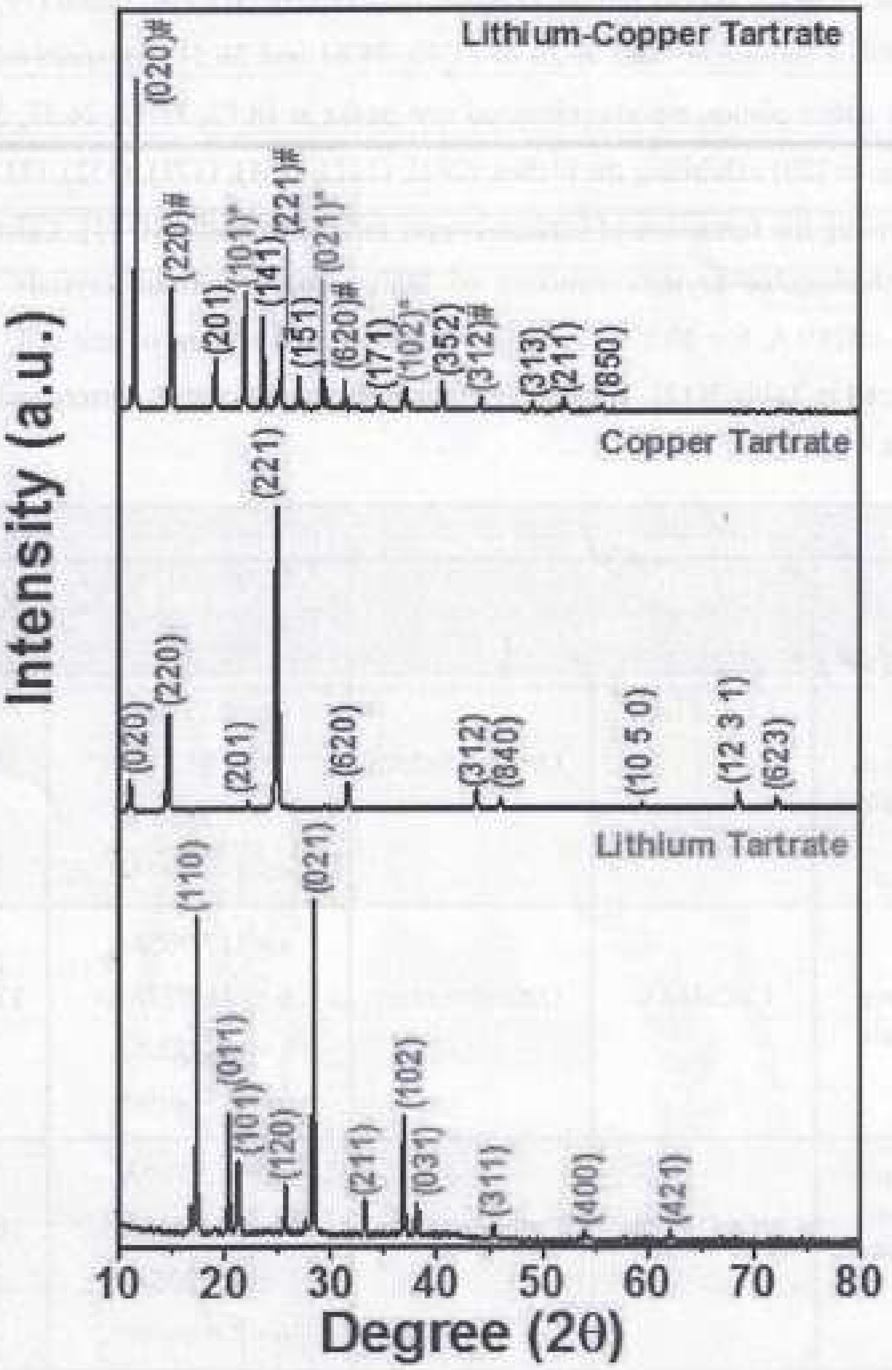

Figure 1 X-ray Diffraction patterns of Li-tartrate, Cu-tartrate and Mixed Li-Cu Tartrate crystals

Peak no.	d-Spacing		Indices	2 θDegree	
	Obs.	Cal.	(h k l)	Obs.	Cal.
1	5.17	5.17	(1 1 0)	17.13	17.13
2	4.37	4.37	(0 1 1)	20.26	20.26
3	4.14	4.14	(1 0 1)	21.40	21.41

4	3.46	3.44	(1 2 0)	25.67	25.69
5	3.15	3.17	(0 2 1)	28.24	28.21
6	2.70	2.68	(2 1 1)	33.08	33.10
7	2.44	2.44	(1 0 2)	36.79	36.71
8	2.37	2.37	(0 3 1)	37.93	37.88
9	2.01	2.01	(3 1 1)	45.05	45.05
10	1.69	1.69	(4 0 0)	53.89	53.90
11	1.49	1.49	(4 2 1)	61.87	61.84

Table 4 Calculated and observed d-spacing of Li-tartrate

Peak	d-Spacing (Å)		Indices	2Θ Degree	
	Obs	Calc.	hkl	Obs	Calc.
1	8.0364	8.0364	(0 2 0)	11.00	11.00
2	5.9804	5.9804	(2 2 0)	14.80	14.80
3	3.9656	3.9656	(2 0 1)	22.40	22.40
4	3.5588	3.5562	(2 2 1)	25.00	25.02
5	2.7945	2.7976	(6 2 0)	32.00	31.96
6	2.0562	2.0567	(3 1 2)	44.00	43.99
7	1.9553	1.9553	(8 4 0)	46.40	46.40
8	1.5642	1.5643	(10 5 0)	59.00	59.00
9	1.3668	1.3671	(12 3 1)	68.60	68.59
10	1.3042	1.3043	(6 2 3)	72.40	72.39

Table 5 Calculated and observed d-spacing of Cu-tartrate

Peak	d-Spacing (Å)		Indices	2Θ Degree
	Obs.	Cal.	hkl	Obs
1	8.4767	8.4767	(0 2 0)	11.00
2	5.9624	5.9624	(2 2 0)	14.80
3	4.7074	4.7074	(2 0 1)	18.83
4	4.1486	4.1749	(1 0 1)	21.40
5	3.8453	3.8452	(1 4 1)	23.11
6	3.5842	3.5070	(221)	25.00

7	3.3569	3.3655	(1 5 1)	26.53
8	3.0962	3.0968	(0 2 1)	28.81
9	2.7945	2.7976	(6 2 0)	31.95
10	2.598	2.5601	(1 7 1)	34.51
11	2.4593	2.4598	(1 0 2)	36.51
12	2.2108	2.2101	(3 5 2)	40.78
13	2.0857	2.0853	(312)	43.35
14	1.8867	1.8880	(3 1 3)	48.19
15	1.7604	1.7601	(2 1 1)	51.90
16	1.6673	1.6654	(8 5 0)	55.03

Table 6 Calculated and observed d-spacing of Li- Cu-tartrate

CONCLUSIONS

The X-ray diffraction revealed the crystallanity of the grown crystals. The crystal structures of all three types of tartrate crystals were found to be orthorhombic. The volume of unit cell is of increasing order for Li, Cu and Li-Cu tartrate.

REFERENCES

[1] Henisch H.K" Crystal growth in Gel"(**1970**)

[2] Henisch H.K. "Crystals in Gel and Liesegang Rings" (**1986**)

[3] Sawant D.K, Patil H.M, Bhavsar,D.S., Patil J.H and Girase K.D."Journal of Scholars Research Library"3 (**2011**) 404-413.

[4] Patil H.M, Sawant D.K, Bhavsar D.S, Patil J.Hand GiraseK.D."Journalof.Therm. Anal.Calorim," 107 (**2012**) 1031.

[5] Krishnakumar Vand Dheivanalar S. "Journal Raman Spectroscopy". 40 (**2009**) 627-631.

[6] Sawant.D.K.Ph.D.Thesis North Maharashtra University,Jalgaon (**2012**).

[7] Sonawane S.S. Ph.D. Thesis J.J.T. University Rajasthan (**2015**).

[8] Ahmad Nazir and Kotru P.N." Journal of Crystal Growth" 24 (**2014**).

[9] Nandre S.J. Ph.D. Thesis North Maharashtra University Jalgaon (**2013**).

[10] Sawant D.K, Patil H.M, Bhavsar.D.S, Patil. J.H and Girase K.D. "Scholars Research Library Archives of Physics Research",2 (**2011**) 67-73.

[11] http://www.rsic.iitb.ac.in/icp-aes.html

[12] Yanes A.C,.Topez T, Stockel J,Peraza J.F and Torres M.E. "Journal Mater Sci." 31(**1996**)2683.

[13] Lopez T, Stockel J,Peraza J.F and Torres M.E. "Crys Res.Technol",30 (**1995**) 677.

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Growth of Lithium Tartrate crystals by Gel Method

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ABSTRACT

Single crystals of Lithium Tartrate were grown by single diffusion gel technique. Methanol used as solvent for lithium chloride .Optimum conditions were established for growth of good quality pure crystals .Effect of various growth parameters such as PH of the gel, concentration of inner reactants, concentration of upper reactants, gel density etc. Were studied .Needle shaped, dendrite crystals were grown.

Keywords: Gel technique, Lithium tartrate, crystals.

INTRODUCTION

Crystal growth by gel technique is one of the technique for growing perfect single crystals [1].Gel growth technique is used for those compounds which are insoluble in water and decompose before melting [2].Good quality single crystals are obtained from gel grown technique due to very slow controlled rate of crystallization and non turbulence during growth .The aim of the present work is to grow good quality single crystals of pure lithium tartrate in sodium metasilicale gel. Some of the researches on the growth of tartrate crystals of various elements having potential applications [3-5].The tartrate crystals has potentials applications such as dielectric ,ferroelectric, piezoelectric [6].Tartrate crystals also enlists nonlinear optical characteristics and find use in transducers ,linear and non linear mechanical devices like crystal oscillators ,resonators etc.

MATERIALS AND METHODS

Experimental:

Silica gel, the growth media was prepared by using tartaric acid and sodium metasilicate with different PH values. The PH of the solution was maintained from 4 to 4.5 by controlled addition of solution of (1 M) sodium metasilicate. After setting of gel, allow the gel which makes the gel harder and also reduces the diameter of capillaries present in the gel (1M) solution of lithium chloride was prepared as a standard solution dissolving lithium chloride in solvent methanol using (1M) this prepared different molar concentration solution of lithium chloride (0.5 to1M) solution of lithium chloride of different concentration used as upper reactant for different test tube The solution often poured slowly with the help of pipette .The higher upper reactant was about 60 to 70% of the gel height in test tube . with time Lithium Chloride diffuses in the gel and crystals of lithium tart ret appears in the gel ,Good quality crystals were observe red in the test tube having upper reactant(LiCl) concentration of 0.8m .Needle shaped ,opaque crystals are seen.

The chemical reactions inside the gel can be expressed as

$$2Licl + C_4O_6H_6 \dashrightarrow (C_4H_4O_6)Li_2 + 2HCl$$

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Table 1. Optimum conditions for growth of lithium tartrate crystals.

Sr.No	Process parameter	Optimum condition
1	Density of sodium meta silicate	1.04gm/cm^3
2	Concentration of Tartaric acid	1M
3	Volume of Tartaric acid	7ml
4	Volume of sodium meta silicate	17ml
5	pH of gel	4.2
6	Concentration of lithium chloride	0.5to1M
7	Temperature	Room temperature

3. Results and Discussion

Crystals of lithium tartrate are whitish, semitransparent and star shaped. Crystals having size 2.5mm x 4.5mm and thickness of about 2.5 to 3mm are obtained. Different parameters such as concentration of reactants, pH of gel, impurities in the solvent, gel setting time, gel aging time etc. have considerable effect on growth rate. Near the interface of gel, dendrite growth is observed due to fast growth rate. However as the reactants percolates through the gel, the controlled reaction occurs below, at the depth of 3 to 4 cm. Hence good quality, semitransparent, well developed faces of crystals are observed. This results due to the decrease in concentration of reactants at the depth of 3 to 4 cm below the gel interface. Table 1 gives the various optimum conditions for lithium tartrate.

5 Conclusions

From systematic investigation on the single diffusion gel growth of the above crystals. Best conditions have been established to get good crystals.

1) Gel method is found suitable for growing lithium tartrate crystals.
2) The growth of lithium tartrate crystals was accomplished by allowing diffusion of lithium chloride solution through silica gel impregnated with tartaric acid in single diffusion gel tube system, with all growth conditions; lithium tartrate crystals assume transparent, opaque, shiny morphology.
3) The crystals obtained in silica gel with average size of 2.5mm x 4.5mm x3mm in single diffusion.
4) Different habits of lithium tartrate crystals can be obtained by changing parameters like gel density, gel aging pH of gel, concentration of reactant etc.

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References:

1) H.k Henisch (1970) Crystal growth in Gels, Pennsylvania State university Press, Pennsylvania.
2) H.K. Henisch (1986) Crystals in Gel and Liesegang Rings, Cambridge University press, Cambridge.
3) H.M Patil, D.K Sawant, D.S Bhavsar, J H Patil, K.D .Girase (2012) J.Therm. Anal .Calorim, 107,1031
4) V.Krishnakumar, S Dheivanalar (2009).J. Raman Spectrisc, 40,627
5) T.Vijaykumari, C .M .Padma, C.k.Mahadevan(2014) Int. J Eng Res. Appl 4(2)47
6) N.S.Patil, P.A.Chaudhari, D.S .Bhavsar(2011),Arch. P Appl Sci. Res.3,272

Effect of Bi doping on Electrical and Gas Sensing Properties of Tin Oxide Thin Film Gas SensorPrepared by Physical Vapour Deposition Method

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Abstract

Pure and doped thin solid films were prepared by Physical Vapour Deposition (PVD) Technique on glass substrates. Temperature of substrates was changed from 50°C to 375°C. Gas sensing properties of the films was tested for various gases for this temperature range using static gas sensing unit. Sensitivities of the undoped and Bi-doped films were measured to be 5.83 and 9.53 respectively. These sensitivities were found at operating temperatures 75°C and 150°C respectively.

Keywords :- Tin oxide, PVD technique, thin films, sensitivity.

INTRODUCTION

Since decades metal oxide semiconductor, like tin oxide, thin films havebeen widely used as gas sensors. Such materials are used for detection of gaseslike acetone, ammonia,methane, H2S with their sensing ability up to a few ppm levels [1–3].These materials sense the target gases by exhibiting change in resistance of the films with reference to the film resistance in the absence of these gases. The ratio of the resistances gives sensitivity of the sensor or sensing material towards the gas under consideration. [3–6].The sensitivity of these materials depends upon operating temperature range also. Therefore, performance of the sensors is tested with variation in its temperature. Generally, sensor performance is observed to be maximum at a particular operating temperature. Many metal oxide semiconducting materials showed these properties.[7–10].Tin oxide is a versatile material which is sensitive to most of the gases and hence is poor selective. To have a good compromise, doped metal oxide thin filmsare being used recently.Selection of the dopant is obviously wantsimproved selectivity towards the target gas, achieve betterstability of the sensing layer over longer durationand athigher operating temperatures. Doping alsoimproves thesensing properties by changing the grain size and structurethrough the introduction of surface defects and impuritylevel. Various synthesis methods such as sol-gel RFsputtering, electrospinning, spray pyrolysis, vacuum evaporation etc. have been employed [11-15].

EXPERIMENTAL DETAILS

In the present work, the tin oxide thin films were prepared by physical vapour deposition method. Pure tin metal was evaporate in vacuum (~10^{-5}torr) onto the pre-cleaned standard glass substrates. The formed thin metal films were then heated in muffle furnace at 150°C for 24 hours for getting oxidized. They were later on annealed 300, 400 and 500°C each for 2 hours. Those film samples annealed at 400°C were observed to show better performances. Hence, all the characterizations were performed for these film samples only. These films were then characterized to study structural, morphological, electrical and gas sensing parameters by XRD, FESEM, and static system [15].XRD patterns were used to determine interplanar spacing, average texture coefficient, lattice parameters etc. FESEM images were analyzed to know average grain size of the film material. Electrical resistance of the film was measured with reference to film temperature by indirect method [15].Graph of film resistance versus temperature enabled us to evaluate TCR of the film material, which in this case was found to be negative, proved semiconducting nature. Another graph, logR versus 1/T was used to determine activation energy by using Arrhenius equation. The same static system was used to measure film resistance in the presence of target gases and sensitivity of the film was calculated at various operating temperatures.

RESULTS AND DISCUSSION

Fig. 1 shows the variation in film resistance with operating temperature. It is found that the film resistance increases after the film was exposed to CO_2 gas. This is because there in increase in oxygen sites on the film surface which reduces conductivity.

Fig.1

Fig.2

Similar trend has been observed in case of Bi-doped thin films also.

Fig. 3

Fig. 3 shows the variation in sensitivity with operating temperature. Bi-doped tin oxide thin films exhibit higher sensitivity over that of undoped thin films. Thus, doping has improved the film performance.

REFERENCES

[1]K. Govardhan1 and Andrews Nirmala Grace, 'Temperature Optimized Ammonia and
Ethanol SensingUsing Ce Doped Tin Oxide Thin Films in a Novel FlowMetric Gas Sensing Chamber', Hindawi Publishing CorporationJournal of SensorsVolume 2016

[2] N. Hongsith, E. Wongrat, T. Kerdcharoen, and S. Choopun,"Sensor response formula for
sensor based on ZnO nanostructures,"*Sensors and Actuators B: Chemical*, vol. 144, no.
1, pp. 67–72, 2010.

[3] S. B. Kondawar, S. P. Agrawal, S. H.Nimkar,H. J. Sharma, and P.T. Patil, "Conductive
polyaniline-tin oxide nanocomposites forammonia sensor," *Advanced Materials Letters*,
vol. 3, no. 5, pp.393–398, 2012.

[4] J. R. Brown, M. T. Cheney, P. W. Haycock, D. J. Houlton, A.C. Jones, and E. W. Williams, "The gas-sensing properties oftin oxide thin films deposited by metallorganicchemical vapordeposition," *Journal of the Electrochemical Society*, vol. 144, no.1, pp. 295–299, 1997.

[5] A.J. Galdikas, V. Jasutis, S. Kačiulis et al., "Peculiarities ofsurface doping with Cu in
SnO_2thin film gas sensors," *Sensorsand Actuators, B: Chemical*, vol. 43, no. 1–3, pp. 140–146, 1997.

[6] M. I. Ivanovskaya, P. A. Bogdanov, D. R. Orlik, A. C. Gurlo,and V. V. Romanovskaya,
"Structure and properties of sol-gelobtained SnO2 and SnO2-Pd films," *Thin Solid Films*,
vol. 296,no. 1-2, pp. 41–43, 1997.

[7] S.D. Bakrania and M. S.Wooldridge, "The effects of the locationof au additives on combustion-generated SnO2 nanopowdersfor CO gas sensing," *Sensors*, vol. 10, no. 7,
pp. 7002–7017, 2010.

[8] E. Comini, G. Faglia, G. Sberveglieri, Z. Pan, and Z. L. Wang,"Stable and highly sensitive gas sensors based on semiconductingoxide nanobelts," *Applied Physics Letters*, vol. 81, no. 10, pp.1869–1871, 2002.

[9] P. Feng, Q.Wan, and T. H. Wang, "Contact-controlled sensingproperties of flowerlike ZnO nanostructures," *Applied PhysicsLetters*, vol. 87, no. 21, Article ID 213111, pp. 1–3, 2005.

[10] D. Zhang, Z. Liu, C. Li et al., "Detection of NO2 down to ppblevels using individual and multiple In2O3 nanowire devices,"*Nano Letters*, vol. 4, no. 10, pp. 1919–1924, 2004.

[11]T. Okuno, T. Oshima, S. Dong Lee, S. Fujita, - Growth of SnO2 crystalline thin films by mist chemical vapour deposition method, Physica status solidi (c), 2011 , *8, 540-542.*

[12] K. Murakami, K. Nakajima, S. Kaneko, - Initial growth of SnO2 crystalline thin films on the glass substrate deposited by the spray pyrolysis technique, Thin Solid Films, 2007, 515, 8632-8636.

[13] T. gui, L. Hao, J. Wang, L. Yuan, W. Jai, X. Dong-Structure and Features of SnO2 Thin Films prepared by RF Reactive Sputtering, Chinese Optic Letters, 2010, 8, 10134-03.

[14]H. S. Randhawa, M. D. Matthews, R. F. Bunshah, SnO2 films by activated reactive evaporation, Thin Solid Films, 1981, 83, 267-271,

[15] K. S.Thakare, S. J. Patil, S. B. Deshmukh, R. Y. Borse, R. R. Ahire, Preparation, Characterization and Gas Sensing Performance of Pure SnO_2 Thin Films Deposited using Physical Vapour Deposition Technique, IRA-International Journal of Technology & Engineering ISSN 2455-4480; Vol.04, Issue 02 (2016) Pg. no. 103-116

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Gas Sensing Studies of Tin Oxide Thin Films Annealed at Different Temperatures

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ABSTRACT

Thin films of Tin oxide (SnO_2) were prepared by physical vapour deposition method. The as-prepared films were further annealed at 300°C, 400°C and 500°C to study the effect of annealing on the physical as well as gas sensing properties of the thin films. Gas sensing performance of annealed SnO_2 thin films was studied for different gases having different concentrations at working temperature of 250°C. Significantly, gas response changes for SnO_2 samples annealed at different temperatures, which is discussed herein.

Keywords: SnO_2 Thin films, PVD technique, XRD, FESEM, EDAX, gas sensing.

Introduction

Monitoring and controlling the toxic gases has become a serious topic not only in industries but also in day to day life. These toxic gases are used either as process gases or generated as byproducts from vehicles, industries, etc. In concern to this, detecting the harmful gases is of prime importance and hence, research in developing gas sensors is at its forefront these days. The semiconductor metal oxide gas sensors like SnO_2, ZnO, WO_3 etc. have been studied due to their range of conducting variability and their strong response to reducing as well as oxidizing gases [1-3].

A variety of thin film preparation methods have been used by the researchers to synthesize metal oxide thin films in various nano-structured forms. Some of the synthesis methods are chemical vapour deposition [4], spray pyrolysis [5], sputtering [6], activated reactive evaporation [7] etc. Physical Vapour Deposition (PVD) method is straight forward and simple one. It has several advantages [8] such as (a) Minimum impurity concentration in the film, (b) sublimation of materials at lower temperature under vacuum, (c) considerably large mean free path of the vapour atoms at lower pressure and hence a sharp pattern of the film is obtained, (d) wide substrate selection. Another advantage of this method is that evaporation yields a large number of films of uniform thickness. The thin film deposition takes place in four stages [9]. In the first stage the formation of the vapor phase from the condensed phase. The transport of atoms or molecules from the source to the substrate constitutes the second stage. The third stage involves the deposition of atoms on the substrate. The final stage involves rearrangement of the atoms on the film to give the desired properties for the product. Moreover, the post treatments like annealing, etc. are important, too in obtaining the desired phases and the stoichiometry. Annealing of films is a necessary step to control grain growth, altering the stoichiometry of the film, introducing dopants and oxidizing the film, inducing compressive stresses in the film are some of the reasons for post-film deposition processing [10-11].

Therefore, in the present paper, we prepared SnO_2 thin films on the thoroughly cleaned glass substrates. The so prepared thin film samples were then heated in muffle furnace for 24 hours to allow maximum oxidation. These samples were further annealed at different temperatures (viz. 300°C, 400°C and 500°C). The gas response of the samples were studied and discussed.

Experimental Details

The pre-cleaned glass substrates were mounted on the specially designed mask arranged at about 15 cm above the evaporator. A tungsten spiral filament used as an evaporator was screwed to two copper electrodes connected to dimmerstat. The 99.999% pure tin (in the form of wire) purchased from Koch-Light Ltd. Haverhill Sulfolk, England was placed in the evaporator. An appropriate amount of current was passed through the tungsten spiral to evaporate tin. Evaporated tin gets deposited on to the substrates [12]. The films formed were then placed in the muffle furnace at 200°C for 24 hours for allowing maximum oxidation of the samples. The samples were then annealed at three different temperatures 300°C, 400°C and 500°C each for 2 hours to get the desired SnO_2 thin films. The thin film samples were examined by XRD (Model-D8 Advance, Make-Bruker AXS GmbH, Berlin, Germany) using CuK_α radiation having wavelength 1.5402 Å. Surface morphology of the samples was analyzed by using FESEM (Model-S4800 Type II, Make-Hitachi HiTechnologies Corporation, Tokyo, Japan) and Elemental composition of the films by energy dispersive spectrophotometer (Model-XFLASH5030 Detector, Make - Bruker Nano GmbH, Berlin, Germany). The film resistance was measured in air and in the target gas atmosphere over the same range of operating temperature (i.e. from 50°C to 375°C).

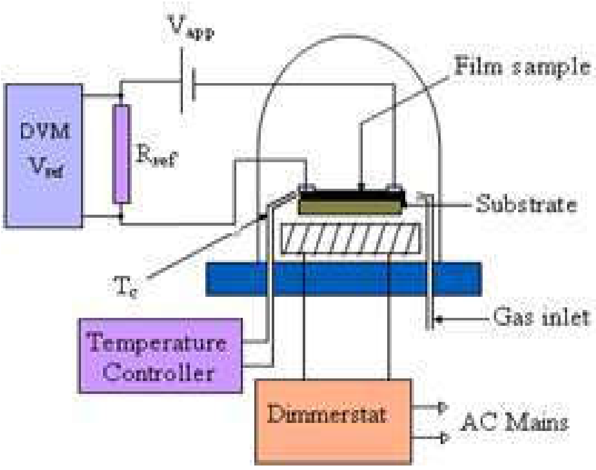

Figure1 Schematics of the Gas sensor unit.

The schematics of experimental arrangement used for this purpose is shown in Fig.1. Gas response was studied for various gases such as acetone, chlorine, CO_2, ethanol, H_2S and NH_3 having different concentrations ranging from 1cc to 15 cc in 15 *l* bell-jar, corresponding to 66.67 to 1000 ppm.

Results and Discussion

Structural, surface morphological and electrical studies were carried out; results were interpreted and systematically tabulated in our previous papers [12, 13]. To avoid repetition, details of only gas sensing studies are given over here.

The gas response studies was carried out by exposing the annealed SnO_2 thin film samples surface to various gases such as acetone, Chlorine, CO_2, ethanol, H_2S and NH_3. For each gas exposure, the change in the resistivity was observed at different operating temperatures i.e., from 50°C to 375°C. Good gas response was obtained for the samples annealed at 400°C, which were further considered for further measurements with these gases at different concentrations.

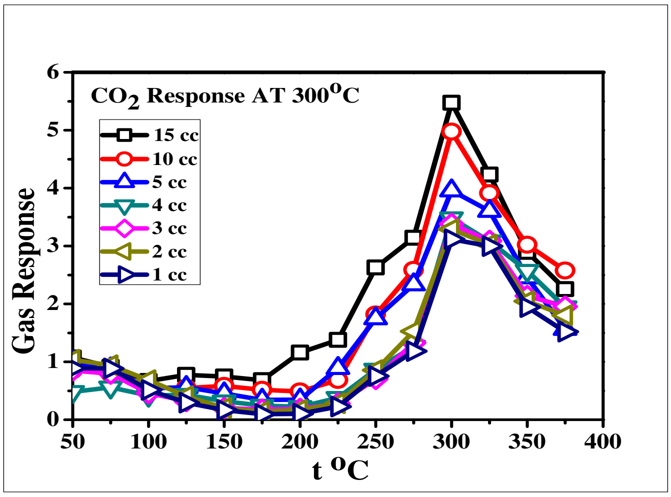

Figure2 (a) Gas response of SnO_2 film samples annealed at 300°C (CO_2 for example).

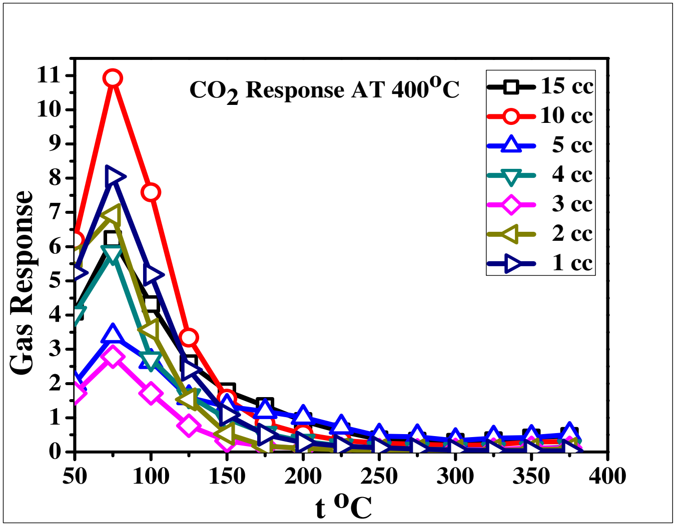

Figure2 (b) Gas response of SnO_2 film samples annealed at 400°C (CO_2 for example).

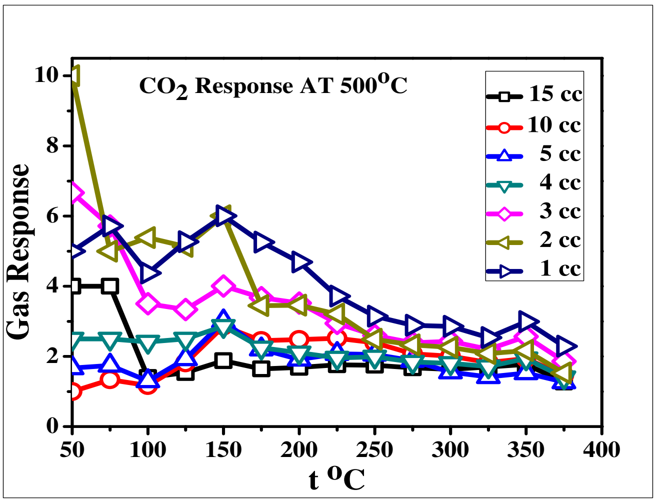

Figure2 (c) Gas response of SnO_2 film samples annealed at 500°C (CO_2 for example).

Fig.2 (a-c) explains relatively smooth gas response curves (e.g for CO_2) of samples annealed at 400°C compared to those annealed at 300 and 500°C.

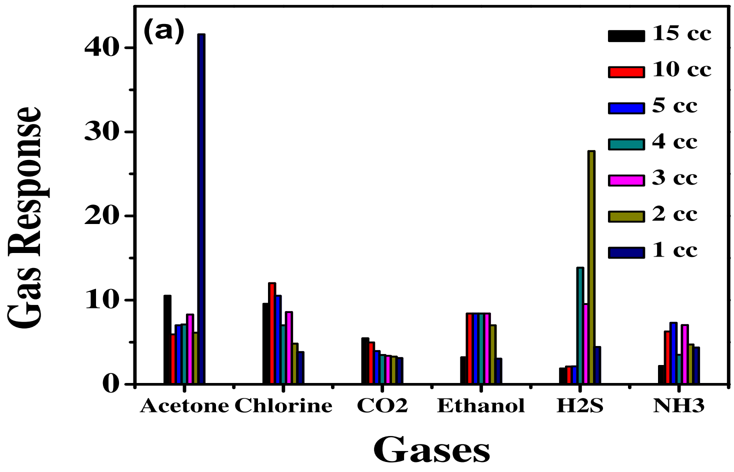

Figure3 (a) Histogram showing selectivity profile of the SnO_2 thin film samples annealed at3 00°C temperature for various gases and their concentrations.

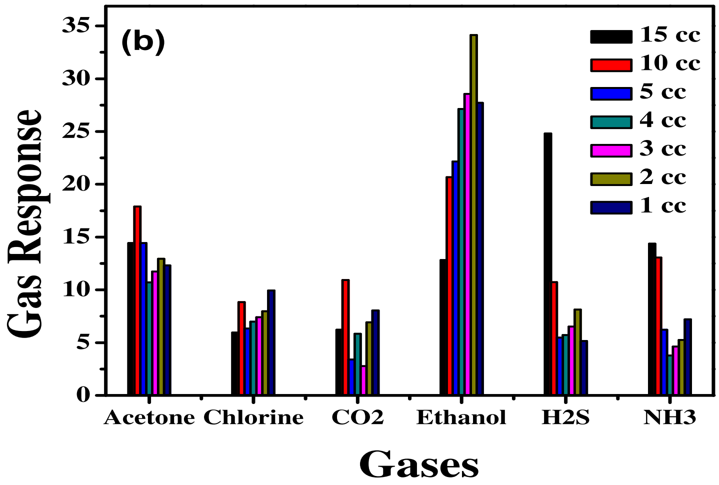

Figure3 (b) Histogram showing selectivity profile of the SnO_2 thin film samples annealed at 400°C temperature for various gases and their concentrations.

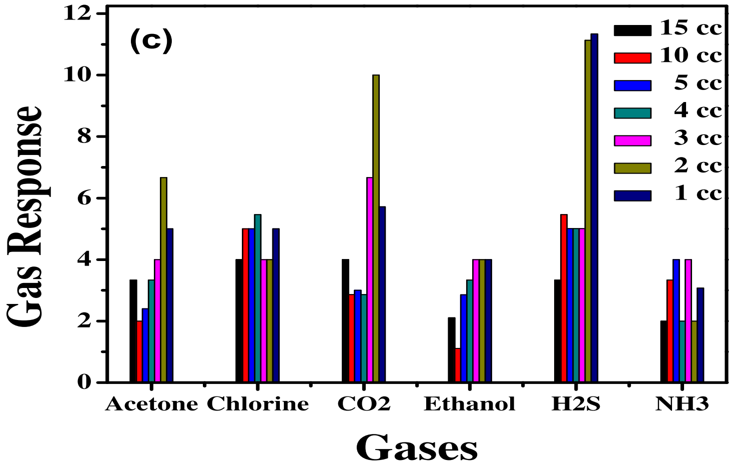

Figure3 (a) Histogram showing selectivity profile of the SnO_2 thin film samples annealed at 500°C temperature for various gases and their concentrations.

Fig.3 (a-c) exhibits the histogram of the annealed SnO_2 samples at 300°C, 400°C and 500°C for different gases and different concentrations, respectively. This indicates that annealing SnO_2 has a strong effect on the gas response properties, which indirectly depends on the oxygen contents, stoichiometry and the morphological evolution of the sample with annealing.

Conclusions

The thin film samples of tin oxide were prepared using the Physical Vapour Deposition technique. The XRD analysis of the samples proved that the film samples were polycrystalline. It is also confirmed from various structural parameters such as crystallite size, degree of crystallinity, texture coefficient etc. obtained for SnO_2 thin films annealed at 400°C. A well compact and irregular shaped grain was also seen for samples annealed at 400°C. Moreover, samples annealed at 400°C indicated rich oxygen contents, thereby increasing the resistivity of the sample. SnO_2 annealed at 400°C showed good gas response towards 2 cc ethanol and moreover good sensor response to all other gases, too. Hence, one can obtain the necessary gas response of a particular gas using a single material and by just manipulating its physical properties with controlled annealing.

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References

[1] Y. Shimizu, E. D. Bartolomeo, E. Traversa, G. Gusmano, T. Hyodo, K. Wada, M. Egashira-Effect of surface modification on NO_2 sensing properties of SnO_2 varistor-type sensors, Sensors and actuators B, vol. 60, 118-124, (1999)

[2] R. H. Bari, S. B .Patil, A. R. Bari, G. E. Patil, J. Ambekar, Spray pyrolysed nano structured ZnO thin film sensors for ethanol gas, Sensors and Transducers, vol.140, (2012)124-132

[3] M. Stankova, X. Vilanova, J. Calderer, I. Gracia, C. Cane, X. Correig- Nanograin WO_3 thin films as active layer for resistive type gas sensors, Journal of Optoelectronics and Advanced Materials, Vol. 7, No.3, (2005)1237-1242,

[4] T. Okuno, T. Oshima, S. Dong Lee, S. Fujita, - Growth of SnO_2 crystalline thin films by mist chemical vapour deposition method, Physica status solidi (c), vol.8, (2011) 540-542,

[5] K. Murakami, K. Nakajima, S. Kaneko, - Initial growth of SnO_2 crystalline thin films on the glass substrate deposited by the spray pyrolysis technique, Thin Solid Films, vol.515, (2007) 8632- 8636,

[6] T. Gui, L. Hao, J. Wang, L. Yuan, W. Jai, X. Dong-Structure and Features of SnO_2 Thin Films prepared by RF Reactive Sputtering, Chinese Optic Letters, vol.8, (2010)10134-03

[7] H. S. Randhawa, M. D. Matthews and R. F. Bunshah, SnO_2 films by activated reactive evaporation, Thin Solid Films, vol. 83, (1981)267-271

[8] K. L. Chopra, Thin Film Phenomena, McGraw-Hills, New York (1969)

[9] Bunshah, R. F., Handbook of Deposition Technologies for Films and Coatings, 2nd ed., Noyes Publications, NJ (Ed.) (1994)

[10] K.S. Sree Harsha, Principles of Physical Vapor Deposition of Thin Films, Elsevier Ltd.

[11] W. Gaede, Ann. Physik., 46 357 (1915)

[12] K. S. Thakare, S. J. Patil, R. Y. Borse and R. R. Ahire -Influence of annealing Temperature on Structural and Electrical Characteristics of Pure SnO_2 Thin Films Deposited by Physical Vapour Deposition Technique, 'Research Journey' International Multidisciplinary E- Research Journal online (2016)15-22

[13] K. S. Thakare, S. J. Patil, S. B. Deshmukh, R. Y. Borse and R. R. Ahire, Preparation, Characterization and Gas Sensing Performance of Pure SnO_2 Thin Films Deposited using Physical Vapour Deposition Technique, IRA-International Journal of Technology & Engineering ISSN 2455-4480; Vol.04, Issue 02 (2016) 103-116

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Structural And Optical Properties of $Cd_xCr_{2-x}S_4$ Thin Films Grown By CBD Method

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ABSTRACT

We report the structural and Optical properties of crystalline Cadmium Chromium sulfide (x= 0.8) thin films was deposited on glass substrate using the chemical bath deposition method. The prepared thin films were characterized by X-ray diffraction analysis; scanning electron microscopy. From UV spectroscopy, the value of fundamental absorption edge from the intercept lies between 1.5528– 3.7083 eV and the corresponding α values were 6.869×10^5 to $1o.4129 \times 10^5$ cm^{-1}. The direct optical energy band gap of this sample was 2.43 eV lying in the range of semi-conducting materials, suitable for solar cell applications.

Key words- CBD, XRD, SEM, absorption coefficient, direct optical band gap.

INTRODUCTION:

Cadmium Chromium sulfide ($CdCr_2S_4$) is a chalcogenide metal sulfide semiconductor of the II-VI group compound semiconductors. The technological interests in polycrystalline based devices are mainly caused by their low production cost [1]The uses of thin film polycrystalline semiconductors have attracted much interest in an expanding variety of application in various magneto-optical and optoelectronic devices [2]. Many techniques have been reported in the deposition of thin films such as evaporation, sputtering, spray pyrolysis; molecular beam epitaxy and photochemical deposition. In these deposition methods there are some problems in each of them [3-4]. Among all, chemical bath deposition (CBD) is simple and low cost technique and is suitable for a large area deposition [5]. Ferromagnetic chalcogenite CdCr2S4 have outstanding properties such as giant magnetoresistance, magnetocapacitive, red shift of the optical absorption edge and giant Faraday rotation, providing for design of devices with various applications [6-8]. Thin films of diluted magnetic semiconductors attract many researchers due to their wide range of applications in various fields. The films of $CdCr_2S_4$ are usually crystallized in cubic structure [JCPDS-77-0677] with lattice constants 10.2 Å [9]. As the trade of fabricating smaller devices continued toward nanoscale technology, new effects related to the small size were realized in producing novel devices, magneto- optical and optoelectronics [10, 11].

In the present study, the chemical bath process is performed by slow release of S^{2-} and controlled free Cd^{2+} and Cr^{2+} react to form $CdCr_2S_4$ nuclei on glass substrate and in the bath solution in form of precipitation. The properties of the deposited thin films basically depend on the deposition parameters such as deposition temperature, complexing agent, thiourea, deposition time, pH value, composition of materials and film thickness. Finally, we report the deposition of $CdCr_2S_4$ thin films and the investigation of the different deposition parameters to obtain uniform film having expected thickness.

MATERILS AND METHODS:

In the present investigation, thin films of $Cd_xCr_{2-x}S_4$ ($X=0.8$) were grown on glass substrate by chemical bath deposition technique. All AR grade (MERCK) chemicals were used for growth of $Cd_xCr_{2-x}S_4$ thin films. For deposition of $Cd_xCr_{2-x}S_4$ solutions of $CdCl_2$, CrO_3 and NH_2-CS-NH_2 were prepared separately of concentration 0.1 M using double distilled water as solvent and were mixed in stoichiometric proportion. EDTA was used as complexing agent. pH of the reaction mixture was adjusted by adding ammonia. The deposition carried out in borosil glass pot of capacity 100ml is used to put chemical reactant in the form of solution is serve as chemical reaction bath. This chemical reaction bath is put inside constant temperature oil bath. The chemical reactant in form of solution is stirred by magnetic stirrer. Well clean glass microslides are dip vertically in the chemical reaction bath by supporting to glass pot of reaction bath. The stirring speed of magnetic stirrer is so adjusted that the solution can stirr slowly during the deposition process. After deposition of $CdCr_2S_4$ thin films, the substrate were taken out and washed with double distilled water and dried in air and finally, preserved in an air tight container. The thickness of deposited thin films was measured by the weight difference technique. The structural properties of the films were analyzed with using Bruker AXS D8 Advanced model X-ray diffractometer (CuK_α radiation; $\lambda = 0.15405$ nm) and grain size was determined from a Scherrer formula. The film surface morphology was investigated using scanning electron microscopy (FE-SEM HITACHI S4800 II). The optical absorption studies were carried out using UV-VIS spectrophotometer (UV-VIS 2400 SHIMADZU) in the 200-800 nm wavelength range.

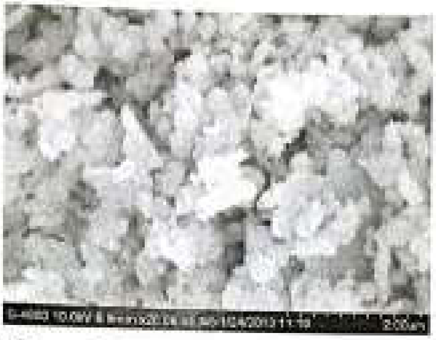
Results and discussion:

X-ray diffraction studies were carried out at room temperature as shown in figure (1). The observed peaks are matching well with reported JCPD'S data card. The XRD pattern shows that

the deposited films are polycrystalline having cubic structure [11, 12, 13] with noticeable growth along the (2 2 0) plane (JCPDS card no. 03-065-7117). In addition the other small peaks viz, (2 2 2), (3 3 1). Table 1. represents the observed and reported XRD data.

Table 1

Planes	2 Theta (degree)		d-spacing values d (^{0}A)	
(h k l)	JCPDS data card	Experiment	JCPDS	Experiment
2 2 2	30.198	30.200	2.95719	2.95575
3 3 1	38.268	38.267	2.35013	2.35108



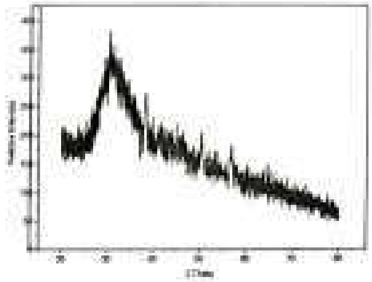


Figure 2 SEM image of $Cd_xCr_{2-x}S_4$ thin film(0.8). Figure 1 XRD of $Cd_xCr_{2-x}S_4$ (X= 0.8)

Figure 2 shows SEM image of $Cd_xCr_{2-x}S_4$ thin film. The particles covered over the surface of substrate are randomly oriented and elongated in different directions with some voids. The grain size measured from SEM images (24–41 nm) was almost same as that of estimated by XRD studies. But, these grain sizes are little bit more than that in XRD observations. This may be due to two or more grains fusing together to form the cluster type of structure.

OPTICAL PROPERTIES:

The optical absorption spectra were obtained in the 355nm-735nm wavelength range by employing a Shimadzu 2450 UV-Visible model of the spectrophotometer. Figure 3 shows the optical absorbance spectra versus wavelength range nm of the film deposited in this work. The fundamental absorption edge is one of the most important features of the absorption spectrum of a semiconductor. The increased absorption near the edge is caused by the transition of electron from the valance band to conduction band. Figure 4 shows the plot of absorption coefficient α against photon energy. The value of fundamental absorption edge from the intercept lies at 1.5599– 3.6674 eV and the corresponding absorption coefficient values were 5.624×10^5 to 9.097×10^5 cm $^{-1}$ supporting direct transition of the material [10]. The higher value of absorption coefficient in the UV region makes the material useful in forming p-n junction, solar cells with other suitable thin film materials for photovoltaic applications [14].

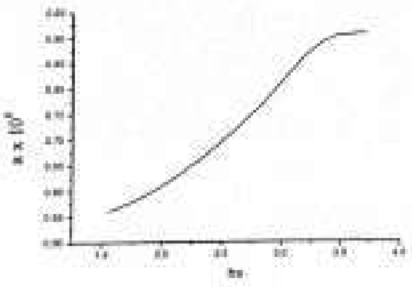


Figure 3 $\alpha \times 10^6$ Vs hγ

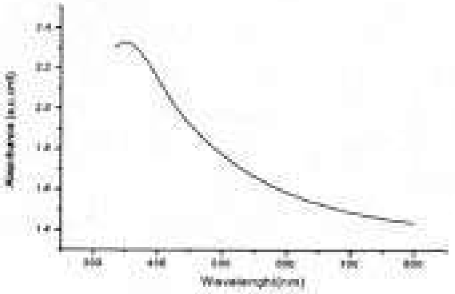


Figure 4 Absorbance (α) V s Wavelength (λ)

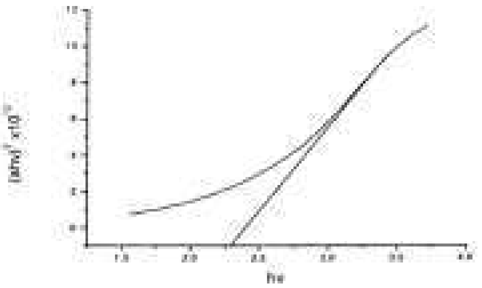


Figure 5 $(\alpha h\nu)^2 x10^{12}$ Vs hγ

The optical band gap of these films has been calculated using the relation (Tauc 1974).

$$\square h\square = A\,(h\square - Eg)^n$$

Where, $h\nu$ is the photon energy, α is the absorption coefficient, Eg the band gap, $n = 2$ for indirect band gap material. Figure 5 shows $(\alpha h\nu)^2$ x 10^{12} verses photon energy (hv) for $Cd_xCr_{2-x}S_4$ thin film, optical band gap was obtained by extrapolating these curve. The direct optical energy band gap of this sample was 2.43 eV. The reported values in literature are 2.23- 2.61 eV [10, 11, 15]. The decrease in band gap energy with increase in film thickness is commonly observed phenomenon in semiconducting thin film [9,10].

CONCLUSION:

The film was deposited successfully by CBD.

1. XRD analysis confirms that the deposited film was polycrystalline in nature.
2. From SEM, the particles are distributed uniformly over the surface of the film with some voids.
3. The direct optical energy band gap of this sample was 2.43 eV.

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REFERNCES:

[1] M.A.Mahdi, S.J.Kasem, J.J.Hassen, A.A. Swadi, S.K.J.A.I-Ani, Int.J.Nanoelectronics and
materials, 2009, 2, 163-172.
[2] S.S.Kale, C.D. Lokhande, Mater.Chem.Phys. 62 (200), 103.
[3] P. P. Sahay, R. K. Nath, S. Tewari, Crys. Res. Technol.**2007**, 42, 275-283.
[4] D. C. Cameron, W. Duncan, W. M. Tsang,Thin Solid Films, **1979**, 58, 69-76.
[5] S. M. Mahdavi, A.Irajizad, A. Azariari and R. M. Tilaki, Scientia Iranica, **2008**, 15(3), 360-
365.

[6] L.Golik, S.M.Grigorovitch, M.I.Elinson, Z.E. Kunkova, V.M.Ukrainskyi, in: Proceeding of
the Third International Conference on Thin Films,Basic Prpblems,Applications and Trends,
Budapest ,Hungary,25-29 August, Paper 7, 1975, p.17.

[7] J.Hemberger, P.Lunkenheimer, R.Fichtl, H.A.Krug von Nidda, V. Tsurkan and A.Loidl,
Nature (London) 434, 364 (2005).

[8] C.P.Sun, C.C.Lin, J.L.Her, C.J.Ho, S.Taran, H.Berger, B.K.Chaudhuri and H.D.Yang, Phys.
Rev.B 79, 214116 (2009).

[9] T.Mahalingam, S. Thanikaikarasan, V. Dhanasekaran, Mariappan, P. Jayamurugan, S. Velumani,
Jin-Koo Rheee; Materials Sci. and Engi. B 174, 2010, 249-252.

[10] V. V. Todkar, R. S. Mane, C. D. Lokhande, Habib M. Pathan, Oh-Shim Joo, Hoeil Chung, J. Of Phys.
And Chem. Of Solids 2008, 69, 1802-1807.

[11] A. M. Salem and ME El-Chazzawi, Semicond. Sci Technol 2004, 19, 236-241.

[12] D. C. Cameron, W. Duncan, W. M. Tsang,Thin Solid Films, **1979**, 58, 69-76.

[13] B.D.Cullity, Elements X-ray Diffraction, Addison-Wesley, 1967, pp-1-80.

[14] H. B. Patil, K. S. Chaudhari, S.V. Borse, Arch. of Sci. Res, 2011, 3(5), 465-470.

[15] □. Akman, H.Karacha, M. □zdemir, Balkan Phy. Letts., 2009, 16, 161037.

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Structural, Optical and Thermoelectrical Properties of Mercury Chromium Sulfide Thin Films Deposited By Novel Chemical Route

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Abstract: *Semiconducting mercury chromium sulfide thin films were deposited on glass substrate using simple, quick chemical bath deposition method using the mixed aqueous solution of mercury chloride, chromium trioxide, thiourea, EDTA and ammonia. The EDTA was used as the complexing agent. The preparative parameters such as temperature, molar concentration, deposition time and thiourea concentration have been optimized. Thin films of* $Hg_xCr_{2-x}S_4$ *(X=0.2) with different thickness were prepared by changing the deposition time at 65* ^{0}*c. The structural, morphological, optical and electrical studies were performed by X-ray diffraction, scanning electron microscopy, UV-VIS spectrophotometer and TEP methods respectively. The films are very adherent to the substrate and cubic structure in nature with the preferential orientation (2 2 0). The optical studies showed a film of direct band gap is 2.13eV. Thermoelectric properties show a positive sign exhibiting P- type semiconducting nature of film.*

Keywords: *Thin film, XRD, SEM, UV, TEP.*

I. Introduction

Mercury chromium sulfide is a chalcogenide metal sulfide semiconductor of the II–VI group compound semiconductors. The technological interests in polycrystalline-based devices are mainly caused by their low production cost [1]. As a ternary Cr-based chalcogenide $HgCr_2S_4$ performed a variety of applications in various magneto-optical and optoelectronics devices [2,3] as well as magnetocapacitive or magnetoelectric effect devices [3–7]. Doping with chromium to HgS window material improves the electrical and optical properties of thin films. Mercury Chromium sulfide is a chalcogenide metal sulfide semiconductor with an insulating structure [8]. Many techniques have been reported in the deposition of thin films such as evaporation, sputtering, spray pyrolysis, molecular beam epitaxy, and photochemical deposition. There is a problem in each of these deposition methods [9, 10]. Amongst all, chemical bath deposition (CBD) is simple, easy to handle, low cost and is suitable for a large area deposition and capable of yielding good quality thin films [11]. The characteristics of chemically deposited $HgCr_2S_4$ thin films by CBD strongly depend on the growth conditions.

In the present study, the chemical bath process is performed by slow release of S^{2-} and controlled free Hg^{2+} and Cr^{2+} react to form $HgCr_2S_4$ nuclei on glass substrate and in the bath solution in the form of precipitation. The growth, structural, surface morphological, optical and thermoelectric properties have been studied.

II. Experimental

In the present investigation, thin films of $Hg_xCr_{2-x}S_4$ (X=0.2) are grown on glass substrate by chemical bath deposition technique. All AR grade (MERCK) chemicals are used for growth of $Hg_xCr_{2-x}S_4$ thin films. For the deposition of $Hg_xCr_{2-x}S_4$ solutions of $HgCl_2$, CrO_3 and NH_2-CS-NH_2 are prepared separately of concentration 0.1 M using double distil water as solvent and mixing them in non-stoichiometric proportion. EDTA is used as complexing agent. pH (10-11) of the reaction mixture was adjusted by adding ammonia. The deposition carried out in borosil glass pot of capacity 100ml is used to put chemical reactant in the form of solution, served as chemical reaction bath. This chemical reaction bath is put under constant temperature oil bath. The chemical reactant in form of solution is stirred by magnetic stirrer. Well cleaned glass microslides are dipped vertically in the chemical reaction bath by providing support to glass pot of the reaction bath. The stirring speed of magnetic stirrer is so adjusted that the solution can stir slowly during the deposition process. After deposition of$HgCr_2S_4$ thin films, the substrate are taken out and washed with double distilled water and dried in air. Finally, they are preserved in an air tight container. Good quality samples were deposited at optimized temperature, time of deposition, speed of solution rotation and pH at 65 ^{0} C, 120 min, 40 rpm and 10 values respectively. The thickness of deposited thin films is measured by the weight difference technique. The structural properties of the films are analyzed by using Bruker AXS D8 Advanced model X-ray diffractometer (CuK_α radiation; λ = 0.15405 nm) and the grain size is determined from the Scherrer formula. The film surface morphology was investigated using scanning electron microscopy (FE-SEM HITACHI S4800 II). The optical absorption studies were carried out using UV-VIS spectrophotometer (UV-VIS 2400 SHIMADZU) in the 200-800 nm wavelength range. Thermoemf of the samples was measured by TEP by "Scientific Equipment and Services, Roorkee".

III. Results and Discussions

3.1. Impact of Preparative Parameters

3.1.1. Impact of Bath Temperature

Figure 1 shows the variation of film thickness with deposition temperature, keeping other parameters constant. The temperature of chemical bath was changed from 40 ^{0} C to 90 ^{0} C with an interval of 5 ^{0} C. It can be seen from Figure 1 that the thickness goes on increasing with bath temperature; it reaches maximum thickness at 65 ^{0} C and further decreases with increase in temperature after 65 ^{0} C [12–15].

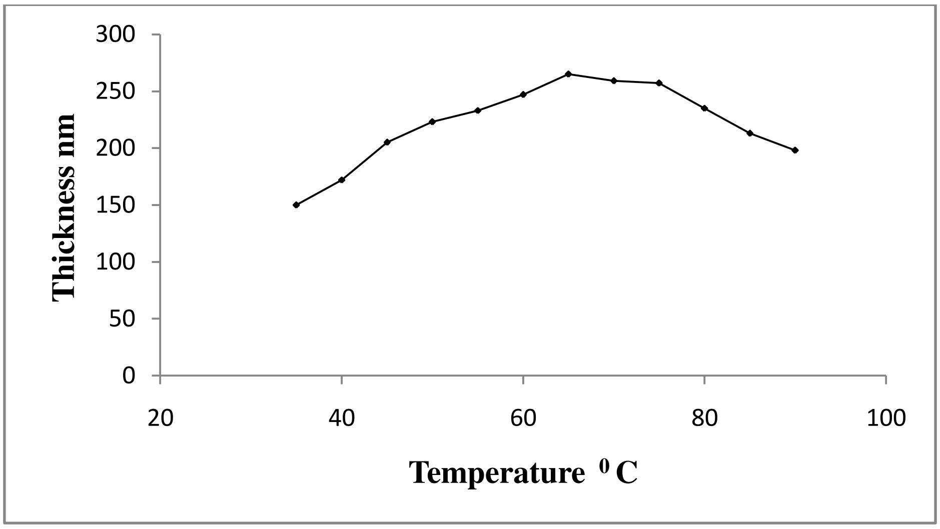

Figure 1: Optimization of solution bath temperature for $Hg_xCr_{2-x}S_4$ (x = 0.2).

3.1.2. Impact of Molar concentration.

Figure 2 shows the variation of film thickness with molar concentration, keeping other parameters constant. The molar concentration of chemical bath was changed from 0.02 M to 0.2 M with an interval of 0.02 M. It can be seen from Figure 2 that the thickness goes on increasing with molar concentration; the film thickness was reached maximum and then it was constant.

3.1.3. Impact of Deposition Time

The impact of deposition time on thickness was studied in Figure 3, keeping the other parameters the same. The thickness of thin film went on increasing with time of deposition, reaching to maximum at 120 minute.

3.1.4. Impact of Thiourea Concentration

Figure 4 shows the variation of film thickness with volume of thiourea, keeping other parameters the same. The volume of thiourea was changed into a bath solution. The maximum and well uniformed thin films were obtained with the addition of 10mL thiourea into a chemical bath solution. pH of the chemical bath solution was 10 at room temperature. Figure 4 indicates that the thickness went on increasing with volume of thiourea reaching to maximum (10mL) and then decreases with further increase in volume of thiourea.

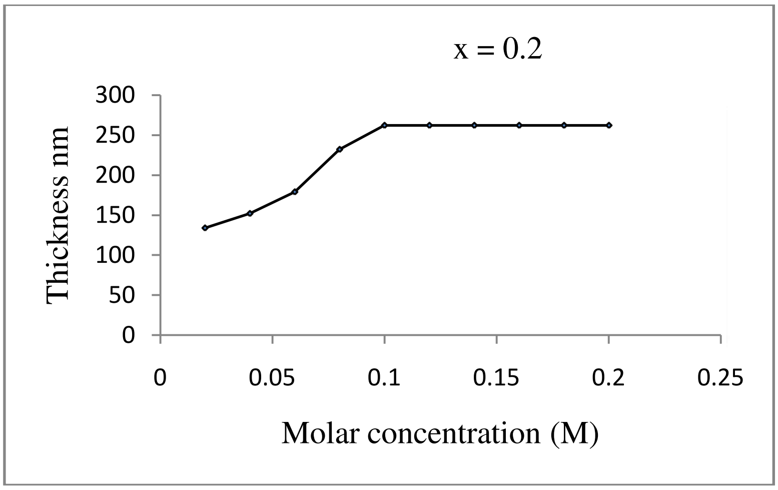

Figure 2: Optimization of molar concentration for $Hg_xCr_{2-x}S_4$ (x = 0.2).

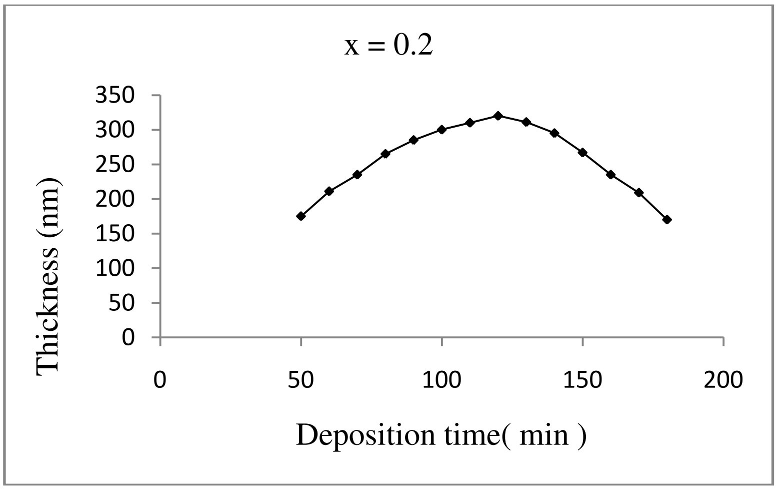

Figure 3: Optimization of deposition time for $Hg_xCr_{2-x}S_4$ (x = 0.2).

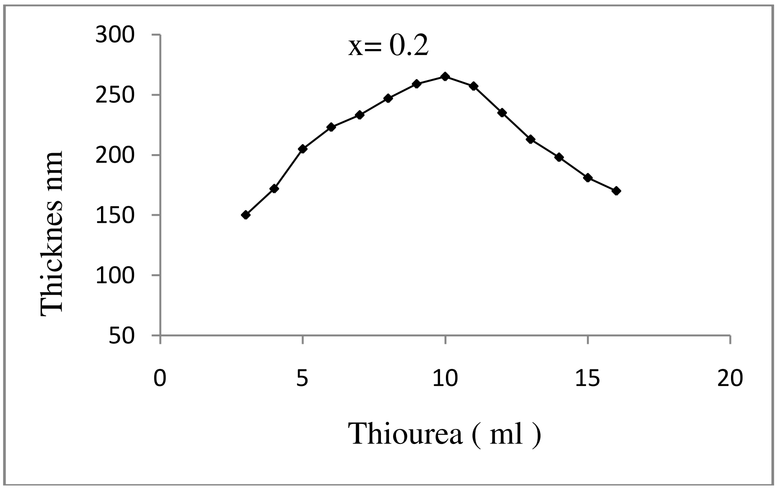

Figure 4: Optimization of thiourea concentration for $Hg_xCr_{2-x}S_4$ (x = 0.2).

3.2 Structural analysis

The structural characterization was studied by using X-ray diffraction. The powder X-ray diffraction is performed using Bruker D8 Advanced model, X-ray diffractometer (CuKα radiation; $\lambda = 0.15405$ nm). The average crystalline size (D) has been calculated from the line broadening using the Scherer's formula: $D = K \lambda/\beta\cos\Theta$, where K is a constant, λ is the wavelength, β is full width at half maximum (FWHM) and Θ is Bragg's angle.

The XRD pattern of the as- deposited $Hg_xCr_{2-x}S_4$ (x = 0.2) thin films with optimum growth parameters was carried out. It is shown in Figure 5. The observed XRD pattern shows cubic crystal structure with noticeable growth along the (220) plane [15-17], in addition to the other small peaks, namely,(3 1 1), (4 2 2), and (4 4 0). Table 1 shows the measured and standard XRD data of d-spacing. There was similarity between measured and standard d-spacing values suggesting the formation of $Hg_xCr_{2-x}S_4$ [18].

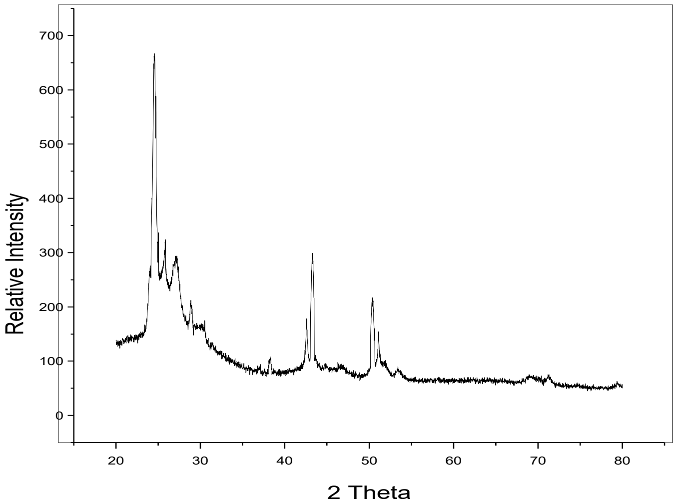

Figure 5 XRD pattern of $Hg_xCr_{2-x}S_4$ (x = 0.2)

Table 1

h k l	2ϴ degree	d Å	
		measured	standard
2 2 0	24.5800	3.61967	3.62000
3 1 1	28.852	3.08123	3.0870
4 2 2	43.2602	2.08982	2.09000
4 4 0	50.3800	1.80983	1.81000

3.3 Surface Morphology

Figure 6 shows SEM image of chemically deposited $Hg_xCr_{2-x}S_4$ (X=0.2) thin film. SEM image, confirmed good quality of film formation. From this micrograph, profound observation reveals well resolved, compact grains with irregular shape are cluster structure to form homogeneous surface morphology on substrate surface without void spaces. The grain size measured from SEM image falling in the nanometer range was almost same as that of estimated by XRD studies.

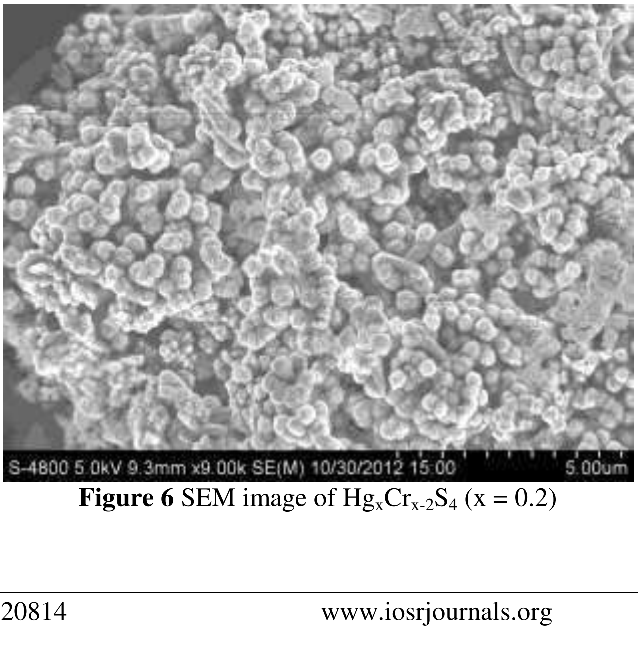

Figure 6 SEM image of $Hg_xCr_{x-2}S_4$ (x = 0.2)

3.4 Optical properties

The optical absorption spectra were obtained in the 335 nm - 800 nm wavelength ranges by employing a Shimadzu 2450 UV-Visible model of the spectrophotometer. Figure 7a shows the optical absorbance spectra versus wavelength range nm of the films deposited in this work. The fundamental absorption edge is one of the most important features of the absorption spectrum of a semiconductor. The increased absorption near the edge is caused by the transition of electron from the valance band to conduction band. Optical energy band gap (E_g) can be calculated using the relation [19].

$$\alpha = \frac{A(hv-Eg)^n}{hv}$$

Where 'A' is a constant and 'hv' is the photon energy and n = 2 for indirect band gap and n = 1/2 for direct band gap.

Figure 7b shows the plot of absorption coefficient α against photon energy. The value of fundamental absorption edge from the intercept lies at 1. 1.5600– 3.6494 eV and the corresponding absorption coefficient values were 5.605 x 10^5 to 9.040 x 10^5 cm^{-1} supporting direct transition of the material [14, 20]. The higher value of absorption coefficient in the UV region makes the material useful in forming p-n junction, solar cells with other suitable thin film materials for photovoltaic applications [21]. Figure 7c shows $(\alpha hv)^2$ x 10^{12} verses photon energy (hv) for $Hg_xCr_{x-2}S_4$ (x = 0.2) thin film, optical band gap was obtained by extrapolating these curve. The direct optical energy band gap of this sample was 2.139eV. The reported values in literature are 2.39- 2.70eV [14, 20]. .

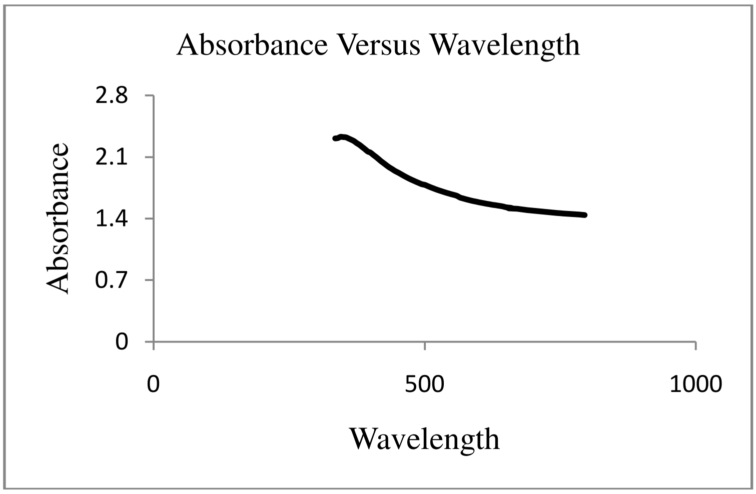

Figure 7 a Absorbance Vs Wavelength

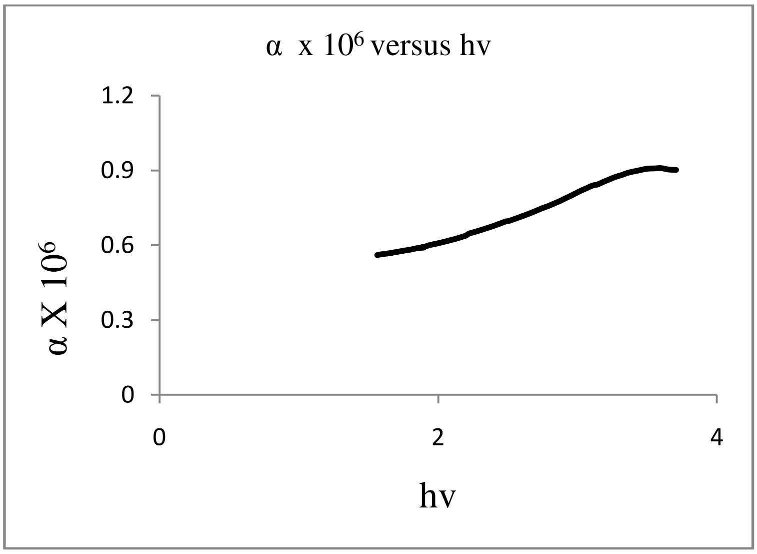

Figure 7b Absorbance coefficient Vs Photon energy

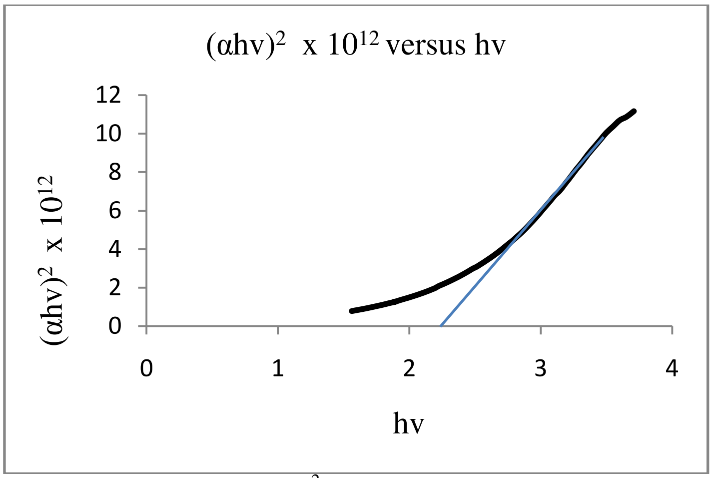

Figure 7c $(\alpha h\nu)^2$ Vs Photon energy(hv).

3.5 Thermoelectric power

In the thermo e.m.f. measurement, the temperature difference causes the transport of carriers from the hot end to the cold end and thus creates an electric field, which gives the thermal voltage. This thermally generated voltage is directly proportional to temperature difference created across the semiconductor. Thermo-emf generated by the $Hg_xCr_{x-2}S_4$ (x = 0.2) thin film was measured in the temperature range 308- 423 k and the graphical representation of thermoemf verses change in temperature is as shown in figure 8. The plot shows that the thermoemf increased with temperature in the sample, which can be attributed to increase in carrier concentration and mobility of charge carriers with temperature. The positive value of thermoelectric emf found over the entire temperature range studied that the majority charge carriers are hole and electron as a minority carriers i.e. p-type behavior.

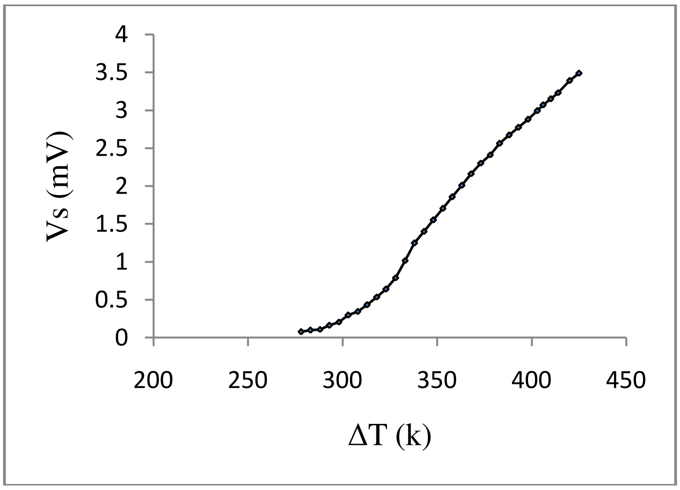

Figure 8 Thermoemf verse ΔT for as-deposited $Hg_xCr_{x-2}S_4$ x = 0.2) thin film onto glass substrate.

IV. Conclusion

$Hg_xCr_{x-2}S_4$ (x = 0.2) thin films have been successfully deposited by the simple and inexpensive chemical bath deposition method. The effect of various preparative parameters such as deposition temperature, molar concentration, deposition time and thiourea concentration on growth process is studied. XRD analysis confirms that the deposited films are cubic in nature. A well defined grains with closed packed structure and homogeneous film was observed by surface morphology. The size of grains mostly falls into nanometer range. The direct optical energy band gap of this sample was 2.213 eV. From TEP measurement the deposited films are of P- type semiconducting in nature.

Acknowledgement

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References

[1]. M.A.Mahdi, S. J.Kasem, J. J.Hassen, A. A. Swadi, and S.K. J.A. I-Ani, “Structural and optical properties of chemical deposition CdS thin films,” International Journal of Nanoelectronics and Materials, vol. 2, pp. 163–172, 2009.

[2]. Multiple pressure-induced transitions in HgCr2S4, Ilias Efthimiopoulos, Alexander Yaresko, Vladimir Tsurkan,, Joachim Deisenhofer, Alois Loidl, Changyong Park, Yuejian Wang, Applied Phy. Letts. 103, 201908 (2013).

[3]. S. Weber, P. Lunkenheimer, R. Fichtl, J. Hemberger, V.Tsurkan, A. Loidl, “Colossal Magnetocapacitance and Colossal Magnetoresistance in HgCr2S4, Phys. Rev. Lett. 96, 157202, 2006.

[4]. T. Kimura, T. Goto, H. Shintani, K. Ishizaka, T. Arima, and Y. Tokura, “Magnetic control of ferroelectric polarization,” Nature, vol. 426, no. 6962, pp. 55–58, 2003.

[5]. N. Hur, S. Park, P. A. Sharma, J. S. Ahn, S. Guha, and S.-W. Cheong, “Electric polarization reversal andmemory in amultiferroic material induced by magnetic fields,” Nature, vol. 429, no. 6990, pp. 392–395, 2004.

[6]. T. Lottermoser, T. Lonkai, U. Amann, D. Hohlwein, J. Ihringer, and M. Fiebig, “Magnetic phase control by an electric field,” Nature, vol. 430, no. 6999, pp. 541–544, 2004.

[7]. T.Goto,T.Kimura,G. Lawes, A. P. Ramirez, andY.Tokura, “Ferroelectricity and giant magnetocapacitance in perovskite rareearth manganites,” Physical Review Letters, vol. 92, no. 25, pp.257201–257204, 2004.

[8]. M. Jelonek, A. Winiarski, A. Chelkowski, Phys. Status Solidi A 57,K5, 1980.

[9]. P. P. Sahay, R. K. Nath, and S. Tewari, “Optical properties of thermally evaporated CdS thin films,” Crystal Research andTechnology, vol. 42, no. 3, pp. 275–280, 2007.

[10]. D. C. Cameron, W. Duncan, and W. M. Tsang, “The structural and electron transport properties of CdS grown by molecular beam epitaxy,” Thin Solid Films, vol. 58, no. 1, pp. 61–66, 1979.

[11]. G. Hodes, Chemical Solution Deposition of Semiconductor Films. Marcel Dekker, Inc, New York, 2002.

[12]. S. H. Pawar and C. H. Bhosale, “Electrochemical bath deposition technique: deposition of CdS thin films,” Bulletin of Materials Science, vol. 8, no. 3, pp. 419–422, 1986.

[13]. V. Balasubramanian, N. Suriyanarayanan, and S. Prabahar, “Thickness-dependent structural properties of chemically deposited Bi2S3 thin films,” Advances in Apllied Science Research,vol. 3, no. 4, pp. 2369–2373, 2012.

[14]. R. S. Mane, V. V. Todkar, C. D. Lokhande, S. S. Kale, and S.-H. Han, “Growth of crystalline HgCr2S4 thin films at mild reaction conditions,” Vacuum, vol. 80, no. 9, pp. 962–966, 2006.

[15]. H.B.Patil, S.V.Borse, “Optimization of Chemical Bath Deposited Mercury Chromium Sulphide Thin Films on Glass Substrate, Indian Journal of Material Science, vol. 1, 4 pages ID 694357,2013.

[16]. R S Mane, V V Todkar, C D Lokhande, Ju-Hyun Ahn and Sung-Hwan Han, “Influence of strain on the surface wettability in crystalline HgCr2S4 thin films, Nanotechnology **17** 5393–5396, 2006.

[17]. JCPDS card no. 027-0316.

[18]. V. V. Todkar, R. S. Mane, C. D. Lokhande, and S.-H. Han,“p-Type crystalline $HgCr_2S_4$

[19]. Semiconductor electrode synthesis and its photoelectrochemical studies,” Journal of Photochemistry and Photobiology A, vol. 181, no. 1, pp. 33–36, 2006.

[20]. X.Mathew, P.J.Sebastain, Solar Energy mater. Solar Cells, 59,85, 1999.

[21]. R.S. Mane, B.R. Sankapal, K.M. Gadave, and C.D. Lokhande, “Preparation of $CdCr_2S_4$ and $HgCr_2S_4$ thin films by chemical bath deposition, Materials Research Bulletin, Vol. 34, Nos. 12/13, pp. 2035–2042, 1999.

[22]. H.B.Patil, S.V.Borse, K.S.Chaudhari, “ Optical properties of $HgCr_2S_4$ thin film deposited by chemical bath deposition method, Invertis J. of Renewable energy,Vol.2,No. 2, pp. 1-5, 2012.

Preparation and Characterizations of Bi-Doped Tin Oxide Thin Film Gas Sensor

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ABSTRACT

Bi-doped thin film samples were prepared by physical vapour deposition technique. The Bi-doped tin metal was deposited on pre-cleaned standard glass substrates with above technique. The film samples were then annealed at various temperatures for 2 hrs. and were characterized for studying structural, morphological, electrical and gas sensing properties by XRD, FESEM, static gas sensing system respectively. Preparation of thin film samples, structural, surface morphological and elemental analysis are explained in this paper.

Keywords: Bi-doped tin oxide, physical vapour deposition, XRD, FESEM.

INTRODUCTION:

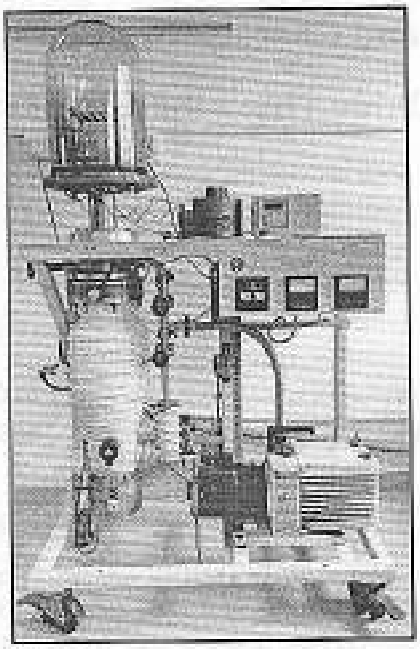
Since last few decades, among various oxides, SnO2 (tin oxide) semiconductor films have been widely employed in recognition of volatile organic compounds as stable gas sensors. They are also used in monitoring the environment, industries etc. [1], as window layer in solar cells [2], as gas sensors to sense hazardous gases like CH4, CO, NOx, CNG etc. [3-5]. SnO2 and TiO2 are promising gas sensors because [6-9] of their advantages like low cost, simple fabrication methods, and rapid response and recovery times [10].

Doping is one expected method of enhancing the conductivity and stability of the sensor by incorporating an atom or ion into host material [11, 12]. Although numerous studies have been conducted on the electronic and optical properties of different semiconductor oxides doped with metals, only a few theoretical studies exist on metal (M)-doped semiconductors oxides [13-15]. The present study aims to systematically study the effect of Bi doping concentration on the structural properties, conductivity and stability of SnO2 by combining theoretical calculations with our experiments. We have successfully fabricated Bi-doped SnO2 thin solid films by using Physical Vapour Deposition. The prepared film samples were analyzed using X-ray diffraction (XRD), FESEM, EDAX, Static gas sensing system etc.

PREPARATION OF THIN FILM SAMPLES:

Thin film samples were prepared by using Physical Vapour Deposition Technique. Pre-cleaned standard glass substrates were placed on a specially designed mask exactly above the tungsten filament containing tin wire and a lump of Bi. Appropriate amount of current was passed through the filament with the help of dimmerstat for evaporating tin and Bi. The evaporated material got deposited onto the glass substrates mounted on the mask. These samples were then heated at about 125oC for 24 hrs for maximum oxidation of the deposited material. These samples later were annealed at 300, 400 and 500oC for 2hrs. and stored in a desiccator. They were then analyzed for structural, morphological, electrical and gas sensing characterizations by XRD, FESEM and static gas sensing system respectively. Fig.1 shows the vacuum system employed for deposition purpose.

Fig.1: vacuum system

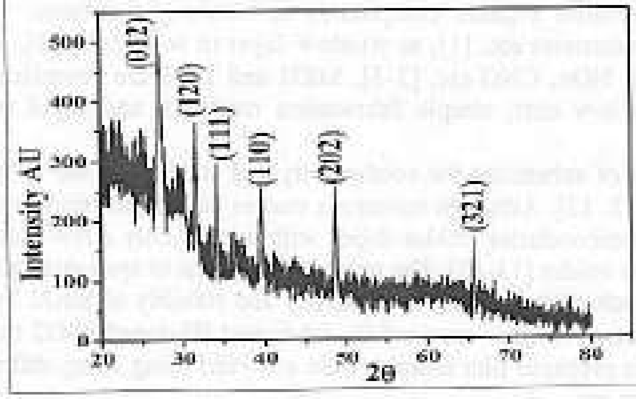


CHARACTERIZATIONS:

Structural Analysis by XRD:

Fig. 2 shows the XRD pattern of Bi-doped SnO2 thin film samples. Samples were scanned over the range of 2θ from 20-80o. The (hkl) planes (120) and (111) correspond to orthorhombic phase.

Fig. 2: XRD patterns of Bi-doped SnO2 thin film sample



The data matched with that from the JCPDS data card [20] and the planes (012) and (110) correspond to rhombohedral phase. The observed data matched with JCPDS card [21]. This data confirmed the material. The crystallite sizes calculated are systematically tabulated in the table 4.1. The structural parameters of Bi-doped SnO2 thin film samples are represented in Table 2. Crystalline nature of the films is clearly seen from the data.

Table 1: Crystallite size

Peak Position 2θ	(hkl) plane	FWHM (radians)	Crystallite size (nm)
27.16	012	0.03349	4.2588
31.63	120	0.01308	11.0148
34.15	111	0.01413	10.2654
39.61	110	0.01361	10.8308
48.70	202	0.00785	19.3885

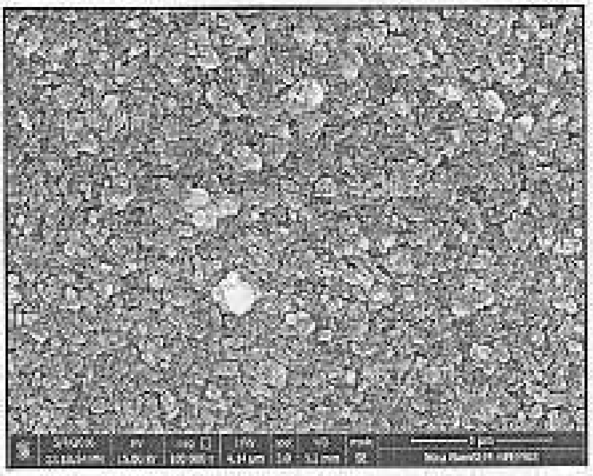
Table 2: Structural parameters of Bi-doped SnO2 thin film samples

Annealing Temp. °C	Dislocation density x 10^{16}	Crystallite Size D nm	Interplanar Distance d A°	Degree of Crystallinity DC (%)	Average Texture Coefficient	Lattice Strain g (%) x 10^{-2}
400	1.429	11.152	5.4959	92.98	0.99987	4.7936

Surface Morphology using FESEM:

The surface morphology of Bi-doped SnO2 thin film samples obtained by using FESEM are shown in Fig. 3. Average grain size for Bi-doped film samples, was observed to be 65.61 nm respectively. The compactness and agglomeration of the grains is clearly seen from the FESEM images of doped film samples. This is possibly due to annealing of the samples.

Fig.3: FESEM image of Bi-doped SnO2 thin film samples annealed at 400oC



Elemental Analysis by EDAX:

Fig. 4 shows the EDAX spectra of Bi-doped SnO2 thin film samples. Elemental composition of the film samples are summarized in Table 3.

Fig.4: EDAX spectra of Bi-doped SnO2 annealed at 400oC

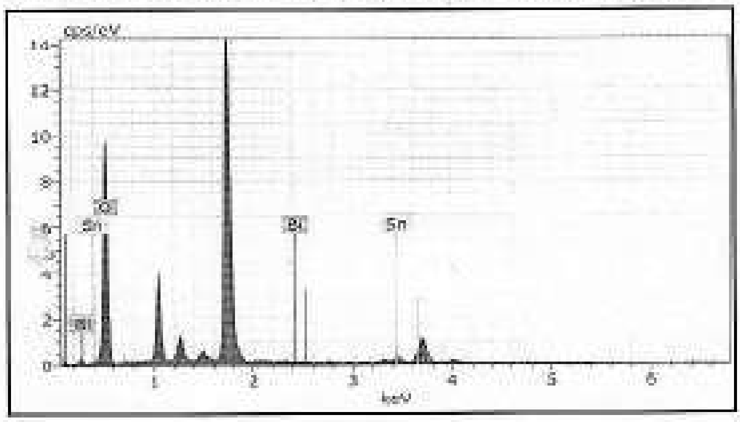


Table 3: Elemental composition of Bi-doped SnO2 thin film samples

Type of sample	Atomic Number	Element	Weight %	Atomic %
Bi-doped SnO_2	50	Sn	12.48	1.89
	8	O	87.43	98.11
	83	Bi	0.09	0.01
		Total	100.00	100.00

CONCLUSIONS:

1. The Physical Vapour Deposition method can be used to fabricate SnO2 thin film samples doped with Bismuth.
2. Once the appropriate vacuum is obtained, a large number of uniform samples can be fabricated at room temperature by this method. In addition, the samples are free from any contamination.
3. Grains formed are irregular shaped and uniformly distributed. Average grain size for Bi-doped film samples was 66.11 nm.
4. EDAX studies confirmed the nonstoichimetry of the samples.

REFERENCES:

G.W. Hunter, C.C. Liu, D. B. Makel and M. G. Hak (Ed), The MEMS Hand Book, CRC Press (2002) 1-22

A. Gotzberger and C. Helbing Sol. Energy Mater and Solar cells 62 (2000) 1

R. S. Niranjan and I. S. Mulla, Mater. Eng. B 103 (2003) 103

O. K. Varghase and L. K. Malhotra, Sensor & Actuators B 53 (1998) 19

N. S. Baik, G. Sakai, N. Muira and N. Tamajoe, Sensor & Actuators B 63 (2000) 74

Z. Wang and L. Liu: Mater. Lett. 63 (2009) 917-919

C. T. Wang and M. T. Chen: Mater. Lett. 63 (2009) 389-390

M. Hemissi, H. Amardjia-Adnani and J. C. Plenet: Current Appl. Phys. 9 (2009) 717-721

D. Zhang Y. Kim and Y. Kang: Current Appl. Phys. 6 (2006) 801 - 804

Wen Zeng, Tianmo Liu and Zhongchang Wang–Materials Transactions, vol. 51, 2 (2010) 243-245

Y. Yang, Y. Jin, H. He, Q. Wang, Y. Tu, H. Lu and Z. Ye, Dopant-Induced Shape Evolution of Colloidal Nanocrystals: The Case of Zinc Oxide, Journal of the American Chemical Society 132 (2010) 13381

D. Fattakhova-Rohlfing, T. Brezesinski, J. Rathousky, A. Feldhoff, T. Oekermann, M. Wark and B.M. Smarsly, Transparent Conducting Films of Indium Tin Oxide with 3D Mesopore Architecture, Advanced Materials 18 (2006) 2980

J. Osorio-Guillén, S. Lany and A. Zunger, Atomic Control of Conductivity versus Ferromagnetism in Wide-Gap Oxides via Selective Doping: V, Nb, Ta in Anatase TiO_2, Physical Review Letters 100 (2008) 036601

Z.Q. Li, Y.L. Yin, X.D. Liu, L.Y. Li, H. Liu and Q.G. Song, 'Electronic structure and optical properties of Sb-doped SnO_2,' Journal of Applied Physics 106 (2009) 083701

W. Dong et al. 'Theoretical calculation and experimental study on the conductivity and stability of Bi-doped SnO_2 electrode' Electrochimica Acta 132 (2014) 307–314

Preparation and Characterization of Titania Thick Film Resistors

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ABSTRACT

Titania (TiO2) thick films prepared by standard screen printing technique and fired at different temperatures in air atmosphere. The compositional, morphological and structural properties of films were analyzed by Field Emission scanning electron microscopy (FESEM), Energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD). The films were observed to be oxygen deficient, it indicates that the films are non- stoichiometry in nature. As deposited and fired films were analyzed using SEM to know its surface morphology. XRD showed the polycrystalline nature having anatase and mix anatase-rutile structure. The crystallite size changes from 25.1695 nm to 62.3517nm for strong orientation (101) with increase in firing temperature.The role of firing temperature on electrical resistivity has been studiedand showed decrease in resistance with increase in temperature.

Keywords: Thick films, FESEM, XRD, Structural properties, Electrical properties.

INTRODUCTION:

Screen printing technique was introduced in the later part of 1950's to produce compact, robust and relatively inexpensive hybrid circuit for many purposes. Later on thick film technique has attracted by the sensor field [1]. Thick films are suitable for gas or humidity sensors since the gas sensing properties are related to the material surface and the gases are always adsorbed and react with the films surface [2]. Screen printing is simple and economical method to produce thick films of various materials [3-10]. The semiconducting metal oxides such as TiO2, SnO2, ZnO, Fe2O3, and WO3 etc. offer the potential for developing portable and inexpensive gas sensing devices, which have advantages of simplicity, high sensitivity and fast response. The sensor is a device senses input signal. The working principle of these semiconductor gas sensors is based on change in conductivity when exposed to the target gases [11]. TiO2 is a widely studied transition metal oxide and behaves as n-type semiconducting oxide due to non-stoichiometry. It has been widely studied for several applications in photoelectrical and optical fields and used as gas sensor. Several deposition methods have been used to grow TiO2 films such as Spray pyrolysis, Vacuum evaporation, chemical vapor deposition, magnetron sputtering, pulsed laser deposition, sol-gel technique, screen printing technique [12]. Titanium dioxide can be synthesized in three crystalline phases: rutile, brookite and anatase [13]. TiO2 in the anatase crystalline phase is one of the most studied materials for photo catalysis properties than rutile. Among the various metal oxides that can be used in gas sensors, only those materials based on titanium oxide have been widely manufactured and utilized [14].

EXPERIMENTAL DETAILS:

Calcination, Drying and firing of Thick Film:

The glass substrates used for screen printing were cleaned initially by soap solution. Further, they were cleaned by using chronic acid to remove the finger prints and other impurities present on the substrates. Finally substrates were washed by distilled water and then clean with acetone.

Table 1: Preparation of $TiO2$ films.

1	Substrate material	Glass
2	Active Material	TiO2 (AR Grade)
3	Deposition Technique	Screen Printing
4	Types of screen	40S-Mesh No.355
5	Material Calcined time	1 hour.
6	Calcined temperature	4500c
7	Active Material to Organic vehicles ratio	70:30
8	Organic vehicles (Binders)	BCA & EC
9	Setteling time	15-20 minutes.
10	Drying under IR	45 minutes.
11	Firing Time	2 hours.
12	Peak firing temp.	3500C,4500C &5500C

Structural and morphological characterization:

The structural properties of TiO2 films were investigated using X-ray diffraction analysis from 20-800 withCuKα, λ=0.1542 nm radiation with a 0.10/step (2θ) at the rate of 2 s /step. FESEM was employed to characterize the surface morphology. The composition of TiO2 thick film samples were analyzed by an energy dispersive X ray spectrometer

The crystallite size was determined using Scherer's formula [15].

$$D= 0.9\lambda /\beta \cos\theta \quad \text{-----------------------------------} (1)$$

Electrical characterization:

The DC resistance of the film samples was measured in home-built static measurement system by using half bridge method as a function of temperature[16].

The electrical resistivity (ρ) of thick film resistor was determined by using the equation,

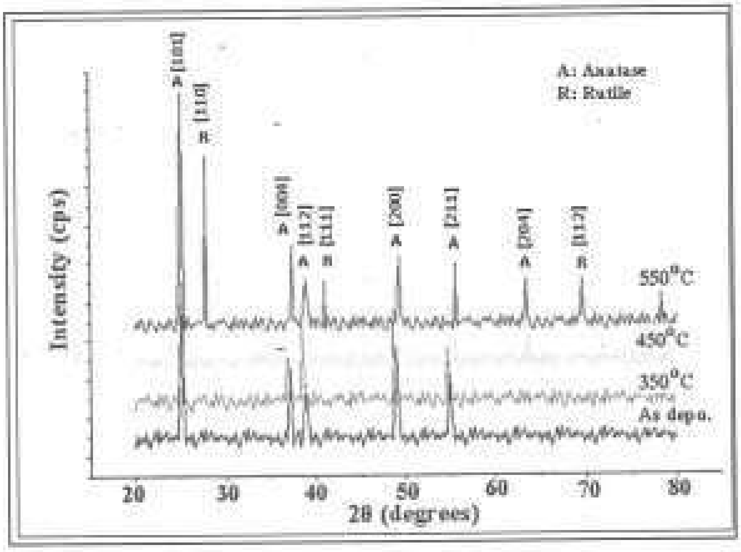
$$\rho = (R \times A) / l \quad \text{------------------------------} (2)$$

RESULTS AND DISCUSSION:

Structural Parameters:

Fig.1 shows X-ray diffraction patterns obtained for TiO2 thick films fired at 350, 450 and 5500C. In all cases, the observed peaks showed the presence of TiO2, match well with reported JCPDS data. It has been observed that the XRD peak broadening decreases with an increase of the firing temperature. The intensity of reflections increases with a rise in the firing temperature. Also XRD analysis evaluates the grain size of the thick films as function of the temperature. From this analysis all films were shown random orientation of polycrystalline nature of the material. Also for further elevated temperature surface area decreases as grain size increases hence sensitivity decreases [17]. In the field of chemical sensors, the structural stability, porosity and high surface to volume ratio are key properties for a sensing film [18].

Fig. 1: XRD pattern at different firing temperatures.



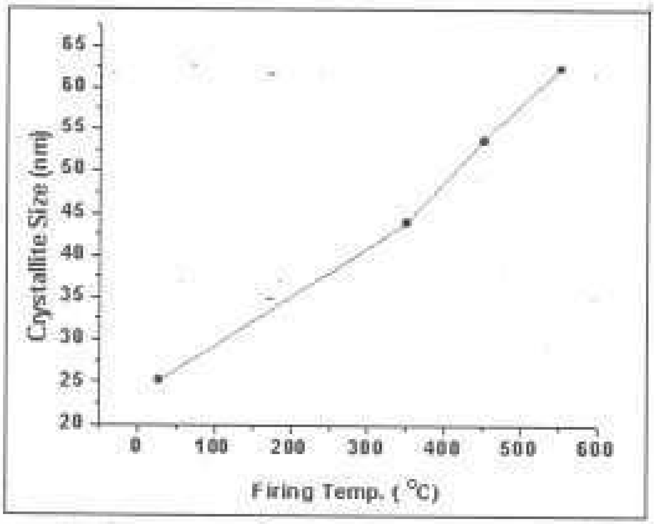
Crystallographic parameters:

The XRD pattern was used to calculate the crystallite size of TiO2films at different firing temperatures. (Scherer's formula) [19].

Table 2: Variation of structural parameters at different firing temperatures.

Firing Temp. ^{0}C	Plane (hkl)	Standard 'd' values(A^{0})	Observed 'd' values (A^{0})	Crystallite Size 'D' (nm)
550^{0}C	101 (A)	3.5126	3.5307	62.3517
	110 (R)	3.2456	3.2135	57.1990
	004 (A)	2.3775	2.3936	63.0599
	112 (A)	2.3299	2.3109	63.3269
	111 (R)	2.1870	2.1983	55.0538
	200 (A)	1.8900	1.8523	61.0578
	211 (A)	1.6643	1.6538	67.4669
	204 (A)	1.4794	1.4676	65.2318
	112 (R)	1.3466	1.3508	67.5880
450^{0}C	101 (A)	3.5126	3.5103	53.6064
	004 (A)	2.3775	2.4394	54.3445
	112 (A)	2.3299	2.3145	50.7278
	200 (A)	1.8900	1.8511	52.6053
	211(A)	1.6643	1.6384	54.1965
	204 (A)	1.4794	1.4576	60.7313
350^{0}C	101 (A)	3.5126	3.5501	43.8472
	004 (A)	2.3775	2.4161	37.7388
	112 (A)	2.3299	2.3133	46.2713
	200 (A)	1.8900	1.8501	43.6673
	211 (A)	1.6643	1.6691	46.8613
As deposited	101 (A)	3.5126	3.5476	25.1695
	004 (A)	2.3775	2.4162	18.6177
	112 (A)	2.3299	2.3140	21.0527
	200 (A)	1.8900	1.8502	26.2263
	211 (A)	1.6643	1.6688	31.4066

Fig. 2: Variation in crystallite size at different firing temperatures.



Elemental Composition:

The EDS spectra of TiO2 showed the major peaks which indicate the presence of titanium & oxygen only and no other impurity. The mass % of titanium & oxygen in all thick films fired at different temperature was not as per stoichiometry proportion and all thick films were observed to be the oxygen deficient and leads to conducting nature of TiO2 [21].

Table 3: Composition of TiO2 thick films.

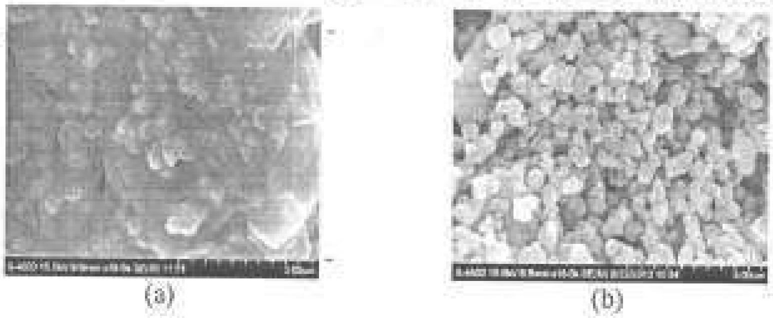
Element (Mass %)	Firing Temperature			
	As deposited	350 ^{0}C	450 ^{0}C	550 ^{0}C
Ti	67.36	78.22	79.50	83.18
O	32.64	21.78	20.50	16.82

The oxygen deficiency clearly indicates that the films are non-stoichiometry. On heating TiO2loses oxygen then titanium is excess, such oxygen deficient films would advances the adsorption of relatively large amount of oxygen species. It is very important for gas sensing applications. TiO2 thick films fired at 5500C observed the high Ti/O ratio. Therefore the optimized firing temperature 5500C selected for further studies of TiO2 thick films.

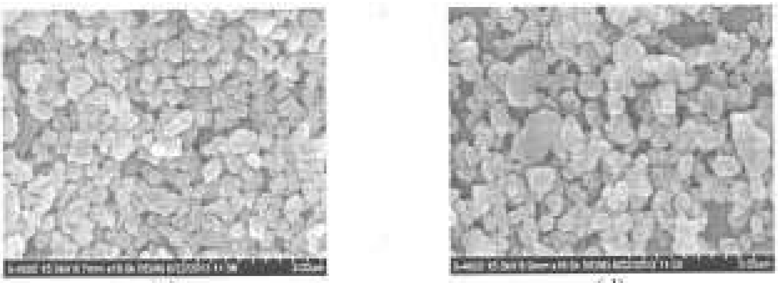
Surface Morphology Analysis:

Fig.3 (a), (b), (c) and (d) represents the FESEM images of TiO2 Thick films as deposited and fired at 350, 450 and 550 0C respectively. All the images are recorded at same magnification for comparison. The FESEM pictures clearly shown that the crystallite size increases with an increase in the firing temperature. Surface morphology has shown the particle sizes are the function of the temperature. It has been observed that an increase in the firing temperature leads to an increase in the grain & particle size which increases the mobility of atoms at the surface of the film thus decrease in surface area [20]. It can see an increase in the porosity with increase in thefiring temperature. The increase in the porous naturecan help in increasing the gas sensing performance.

Fig. 3. FESEM of TiO2 thick films fired at (a) as deposited, (b) 350 0C, (c) 450 0C and (d) 550 0C



(a) (b)

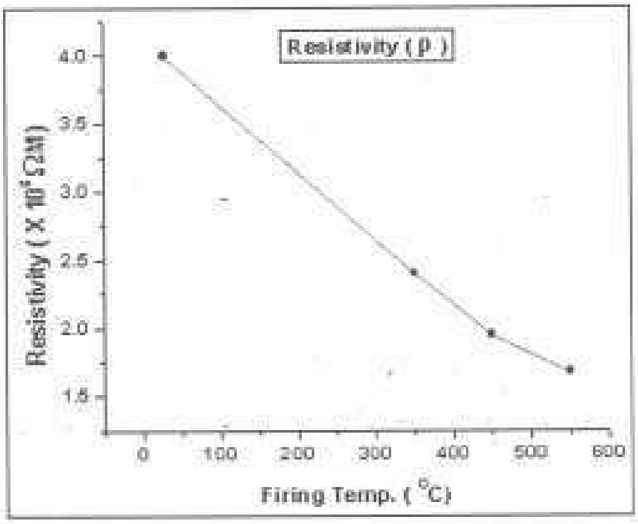

(c) (d)

Electrical Resistivity (ρ):

Table 4: Resistivity of TiO2 thick films at different firing temperatures.

FiringTemp.(0C)	As deposited	3500C	4500C	5500C
ρ x 106(Ωm)	3.998	2.400	1.945	1.674

Fig. 4: Variation ofResistivity (Ωm) withdifferent firing temperatures.



CONCLUSIONS:

Compositional and structural analysis confirmed that TiO2 thick films were non- stoichiometry, which are suitable for gas sensing applications. The films as deposited and fired at temperatures 350, 450 and 550 0C were found polycrystalline. The crystallite size increases with an increase in the firing temperature. Films fired at 550 0C were observed to have mixed anatase-rutile structure, more crystallinity, porous, oxygen deficient and good adhesion to glass substrate. An increase in temperature improved the crystallinity and thus increased the mobility of atoms at the surface of the films.In all thick films as deposited and fired at temperatures 350, 450 and 550 0C the observed d-values well matched with standard d-values. The electrical properties were found to be function of the temperature for all TiO2 thick films.The conductivity goes on increasing with increase in temperature, indicating negative temperature coefficient (NTC) of resistance. This shows the semiconducting nature of the films.

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REFERENCES:

N. JaydevDayan, S. R. Sainkar, R. N. Karekar, R. C. Aiyer, Thin Solid Films 325, 254 (1998).
K. Ram Kumar, Thick Film Deposition and Processing Short Term Course on Thin and Thick Film Hybrid

Microelectronics, Bangalore P 12.11 (1986).
B. Krishnan, V. N. Nampoori, Bull. Mater.Sci. 28, 239 (2005).
X. Q. Liu, S. W. Tao, Y. S. Shen, Sens. Actuators: B chemical 40, 161(1997).
S. G. Ansari, P. Boroojerdian, S. K. Kulkurni, S. R. Sainkar, R. N. Karekar, R. C. Aiyer, J .of Mater. Sci. 7, 267 (1996).
M. Prudenziati, B. Morten, Sens. Actuators B 10, 65 (1986).
J. Kiran, R. B. Pant, S. T. Lakshmikumar, Sens. Actuators B 113, 823 (2006).
A. T. Nimal, V. Kumar, A. K. Gupta, Indian J. of Pure and Appl. Phys. 42, 275 (2004).
L. A. Patil L., P. A. Wani, S. R. Sainkar, A. Mitra, G. J. Pathak, D. P. Amalnerkar, Mater. Chem. Phys. 55, 79 (1998).
C. A. Harper, Handbook of Thick film hybrid Microelectronics, McGraw Hill Book Co. New York, 1974.
AbhilashaShrivastava, Reshmi, Kiran Jain, Mater. *Chem. Phys.*, 105, 2007, pp. 385.
B. Joseph, K. G. Gopalchandran, P. K. Manoj, P.Koshy, V. K. Vaidyan, Bull. Mater.Sci. 22, 921 (1999).
G. A. Tompsett, G. A. Bowmaker, R. P.Cooney, J. B. Metson, K. A. Rodgers, J. M. Seakins, J. Raman Spectrosc. 26, 57 (1985).
K. Ihokura, J. Watson, The Stannic Oxide Gas Sensor: Principles and Applications, Boca Raton, FL: CRC Press, 1994.
B. D. Cullity, Elements of X-ray Diffraction, 2nd Edition, Addition Wesley, 1970, p. 102.).
L. Gao, Q. Li, Z. Song, J. Wang, Preparation of nanoscale Titania thick film and its oxygen Sensitivity*Sensors and Actuators B*, 71, 2000, pp. 179- 183.
L. Gao, Q. Li, Z. Song, J. Wang, Preparation of nanoscale Titania thick film and its oxygen sensitivity*Sensors and Actuators B*, 71, 2000, pp. 179- 183.
H. Hadouda, J. Pouzet, E. Bernede, A. Barreau, MoS2 thin film synthesis by soft sulfurization of a molybdenum, *Mat. Chem. Phys.*, 42, 291, 1995.
B. D. Cullity, Elements of X-ray Diffraction, 2nd Edition, Addition Wesley, 1970, p. 102. [20] I. S. Ahmed Frag, I. K. Battisha, M. M. El_Rafaay, *Indian Journal of Pure Appl. Phys.* 43, 446(2005).
C. G. Dighavkar, A. V. Patil, R. Y. Borse and S. J. Patil, *Optoelectronics and advanced materials-Rapid communications*, 3, 10, 1013(2009).

Rival study of strontium tartrate and calcium tartrate gel grown crystals

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ABSTRACT

In this investigation the gel grown crystals of strontium tartrate [C_4H_4 O_6Sr] and calcium tartrate [C_4H_4 O_6Ca] were grown by simple gel method by using simple single diffusion technique, The optimum conditions were established by various parameters such as pH of gel solution, gel concentration ,gel setting time, concentration of reactant etc.gel was to make by mixing sodium metasilicate [$Na_2SiO_3 9H_2O$] and supernant strontium chloride[$SrCl_2$],calcium chloride[$CaCl_2$] at pH 4.4,and transferred in glass tube of diameter 2.5 cm and 25 cm length. The mouth of test tube was covered by cotton plug and kept it for setting. After setting the gel, Then few days incorporated the supernant solution of strontium chloride[$SrCl_2$],calcium chloride[$CaCl_2$] was poured over set gel by using pipette then it was kept undisturbed. After three-four days the small nucleation growth was observed at below the interface of gel. The good quality crystals of strontium tartrate and calcium tartrate were grown. These grown crystals were characterized by XRD, SEM, chemical analysis and electrical conductivity.

Keywords: Gel grown strontium tartrate crystals, calcium tartrate crystals, XRD,SEM, Electrical conductivity.

1.INTRODUCTION

A variety of crystals required for the purpose of research and application can be grown in silica gels. The gel medium prevents turbulence and being chemically inert, it provides a three-dimensional crucible which permits the reagent to diffuse at a desirable controlled rate. Its softness and uniform nature of constraining forces that it exerts upon the growing crystals encourages orderly growth girase [1].

The growth of single crystals in gel at an ambient temperature, which are sparingly soluble in water, is a fascinating alternative to the techniques involving high temperature and expensive equipments as reported by Sangwal [2]. During last few years, successful application of gel growth technique has been demonstrated by the preparation of single crystals of alkaline earth metal iodates joshi [3] and tartrates Henisch [4]. The gel growth technique appeared quite attractive for growing crystals of such compounds on account of its unique advantages in terms of crystals produced and the simplicity of process.

In recent years, crystals growth in gel medium has attracted the attention of many investigators, such as Henisch, Dharma Prakash, Shedam, Garud [5-8].The principle relies on the slow migration of crystal constituents (ions) through silica gel so that a very slow reaction occurs with the formation of a sparingly soluble compound. When the concentration of this compound exceeds the solubility limits, crystals will be formed, the main function of the gel being to control the flow of reacting ions.

Mixed crystals growth has scarcely been studied by employing the gel technique as reported by Joshi, Dharma Prakash [9-10] and the field is in an early stage of development with many opportunities to create new species. Most of the tartrate compounds are insoluble in water and decompose before melting. Hence single crystals of such type of compounds cannot be grown by either slow evaporation or melt technique. In this situation gel method is the appropriate one for their growth. The growth of single crystals of calcium tartrate and strontium tartrate was reported by Henisch , Rahimkutty [4, 11]. Thermal studies on tartrate crystals grown by gel method were reported by many investigators, such as Henisch, Kotru [12-14]. Tartrate crystals are of considerable interest, particularly for basic studies of some of their interesting physical properties. Some crystals of this family are ferroelectric. As suggested by Abdel- Kader et al, Gon, Desai [15-17], some others are piezoelectric Yadava [18] and quite a few of them have been used for controlling laser emission Pipree [19]. As tarterates are sparingly soluble in water and decompose before melting, the gel method is found to be more promising than the high temperature crystal growth methods.

Many tartrate salts with monovalent cations; such as rubidium hydrogen tartrate Desai [20], Sodium tartrate Abdel-Kader [21] and ammonium tartrate Abdel-Kader [22] and divalent cations; such as calcium tartrate. Sahaya Shajan X [23], Cadmium tartrate Yanes [24], Manganese tartrate Lopez [25], Zinc tartrate Arora [26] and Strontium tartrate. Arora, Jain [27-28] have been studied for their dielectric and thermal properties.

In recent years, very few attempts have been made to study growth and characterization of tartrate crystals in general and strontium, calcium tartrate crystals in particular. However, there are very few reports in the literature, on the growth of these crystals by gel method. Hence, the growth of crystals of strontium, calcium tartrate by gel technique by single diffusion method is reported.

2 MATERIALS AND METHODS

Crystals of Strontium tartrate and calcium tartrate were grown by gel method by using single diffusion gel techniques. Table 1 gives details about method and chemicals used, different habits of crystals obtained their transparency etc. Monoclinic structure of strontium tartrate crystals were obtained, most of the strontium tartrate crystals are transparent, shining well isolated and opaque are showing in figure 1. Single diffusion technique is found more suitable for growth of these crystals. Crystal of calcium tartrate are orthorhombic structure, The crystals so formed are whitish, spherulitic in shape, semitransparent and well isolated. Whitish semitransparent, needle shaped crystal of calcium tartrate as shown in figure 2. Some times crystals became transparent elongated, whisker growth due to inclusion of silica in them. Reason may be the unnecessary exposure to silica gel. Various concentrations of reactants were tried. Experiments by interchanging the position of reactants were carried out. Once the optimum values of concentration of reactants were obtained. Experiments of concentration programming were also carried out. All these parameters have more or less effect on growth and habit of these crystals.

Table 1 Crystals of Strontium and Calcium tartrate

Crystals Name	Method	Chemicals used	Crystal habits	Quality
Strontium tartrate	Gel method by using single diffusion technique	Na_2SiO_3 $9H_2O$, CH_3COOH and $SrCl_2$	Dendrite, hopper, Elongated, Good	Opaque, Semitransparent, Transparent, Whitish, Good
Calcium tartrate	Gel method by using single	Na_2SiO_3 $9H_2O$,CH_3COOH	Dendrite, hopper,	Opaque, Semitransparent,

	diffusion technique	and $CaCl_2$	Elongated, Good	Transparent, Whitish, Good

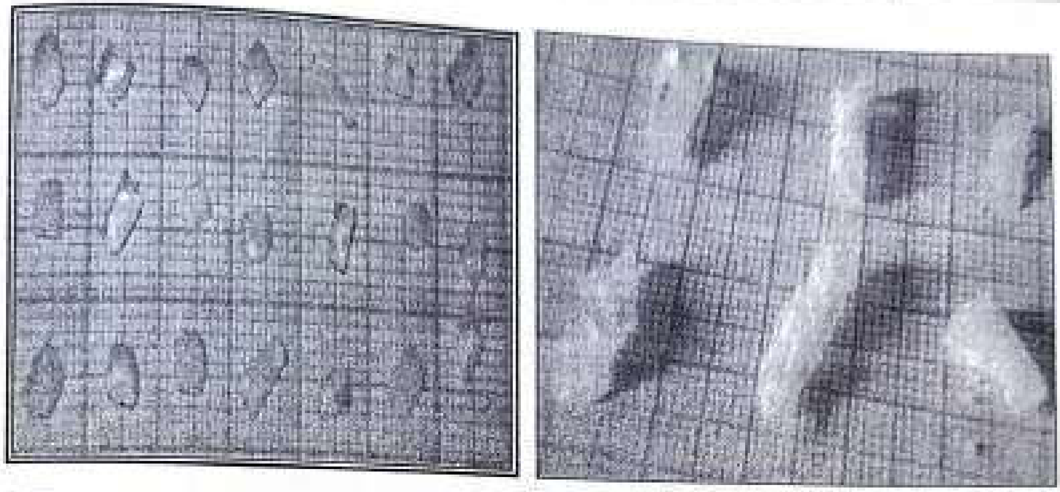


Fig.1(a) Transparent, pale yellowish crystals (b) Transparent and semitransparent, needle shaped strontium tartrate crystals.

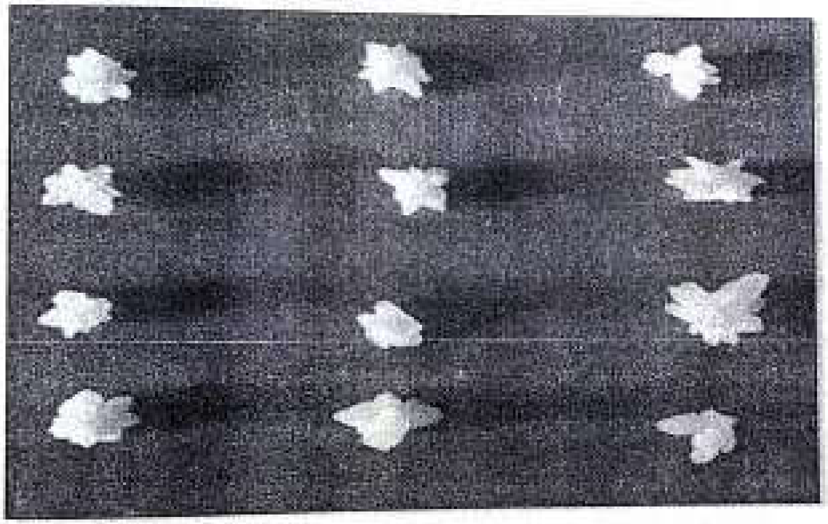


Fig.2 Transparent and semitransparent, star shaped calcium tartrate crystals

3. RESULT AND DISCUSSION

These crystals possess better habits and better transparency among the grown crystal. Better transparency of strontium tartrate may due to presence of more crystals established by varying various parameter such as gel density, pH of gel ,gel setting time, gel aging time, etc are reported in table 2.For all these two crystals, suitable value of density of sodium meta silicate solution is found 1.04gm/cc, pH 4.4,gel took 7 days to set and this gel was allowed to age 6 days. Crystal were removed from test tube after 36 days respectively. Further growth was not allowed, some times crystal became opaque or translucent due to inclusion of silica gel. Various concentrations of reactants were tired.

Experiments by interchanging the position of reactants were also carried out. Once the optimum values of concentration of reactants were obtained, experiments of concentration programming were also carried out. All these parameters have more or less effect on growth and quality of these crystals.

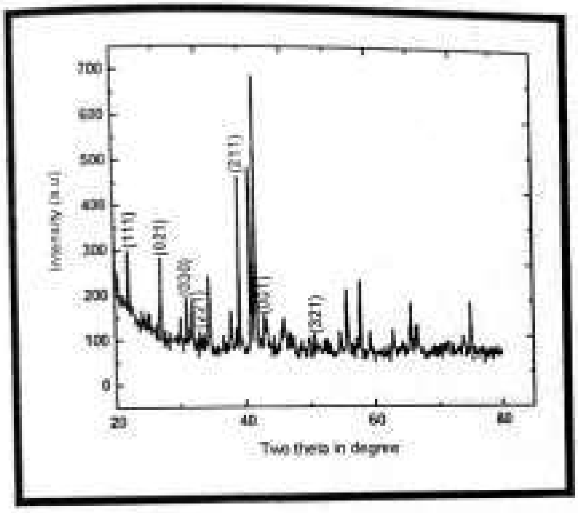
Table 2: Optimum growth condition for gel grown Strontium and Calcium tartrate crystals.

Sr.No	Parameters	Strontium tartrate	Calcium tartrate
1	Density of sodium meta silicate solution	1.04gm/cm^3	1.04gm/cm^3
2	Concentration of tartaric acid	1M	1M
3	Volume of tartaric acid	5ml	5ml
4	Volume of sodium meta silicate	16ml	18ml
5	pH of the mixture	4.4	4.4
6	Concentration	1M	1M
7	Temperature	Room temperature	Room temperature
8	Gel setting time	7days	7days
8	Gel aging time	6 days	6Hours
9	Period of growth	5 weeks	5 weeks

3.1 X-ray Diffractometry (XRD)

X-ray diffractogram is useful in the analysis of crystal structure. Cell parameters such as'd' values, unit cell volume and lattice system etc. can be evaluated using x- ray diffractogram. Materials are identified from these values in conjunction with the JCPDS powder diffraction file. X-ray diffractogram of gel grown strontium tartrate was recorded using powder rotation photograph method on "Miniflex Regaku" x-ray diffractometer at Department of Physical sciences, North Maharashtra University, Jalgaon. CuKα radiation (wavelength λ=1.54051 A^0) was used. The sample was rotated in the range (2θ), 20^0-80^0. The scanning speed was kept 10^0/min .The recorded x-ray diffractogram is shown in figure 3. XRD pattern in figure 3 shows very sharp peaks having high intensity which leads to extremely good crystalline perfection of the strontium tartrate crystals as reported by Farhana et al, Thomas et al, Jothi et al, Joshi et al, Sawant et al[29-34].

The computer program, POWD (Interactive powder diffraction data and indexing program version 23.0550) was used to calculate'd' and (hkl) values. The unit cell parameters and system calculated by the computer program are given in the table 3.These parameters satisfy the conditions for monoclinic system i.e. a≠ b≠ c and α = γ =90⁰ ≠ β.From X-ray diffraction study, it is concluded that the grown crystals of strontium tartrate have monoclinic system. The unit cell parameters and system Calculated by the computer program are shown in the table 3. These parameters fulfil the conditions for orthorhombic structure of calcium tartrate crystal i.e. a≠ b≠ c and α =β= γ =90⁰. The recorded x-ray diffractogram is shown in figure 4.



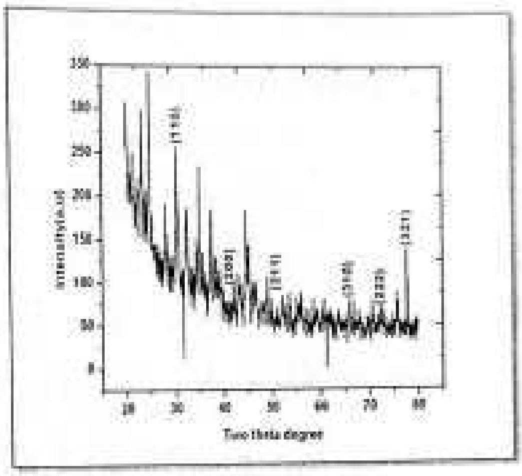


Figure 3 X-ray diffractogram of strontium tartrate. Figure 4. X-ray diffractogram of gel grown calcium Tartrate

Table 3 Calculated unit cell parameters

Sr.No	**Crystals**	**a A.U**	**b A.U**	**c A.U**	**System**
1	Strontium tartrate	7.5500A⁰	7.5500A⁰	7.5500A⁰	Monoclinic
2	Calcium tartrate	9.627A⁰.	9.627A⁰.	9.627A⁰.	Orthorhombic

3.2 SEM

In the present work powdered sample of strontium tartrate crystals was examined by using SEM technique at Department of Physics, Hanyang University, Seoul, Korea. The study of the surface of the crystal gives valuable information about its internal structure. Figure 5.1 (a) illustrate SEM photographs of crystals of strontium tartrate crystal. An enlarged SEM image is shown in Figure 5.1 (b).

It shows plate like crystal morphology. Boundaries of the plate like structure are very sharp. These crystals are grown by layer deposition. Thick and thin layers are seen in figure. The individual plates of samples are flat and the plates with the sharp edges were observed. On some plates further plate like growth was observed. The presence of small grain structures along with the plate like microstructures interlocked with each other is observed. On higher magnification plate like structure is clearly seen. The average particle size measured is to be 600nm to 1.0 μm [34-37]. The study of the surface of the crystal displays valuable information about its internal structure. Fig 5.2 (a) clarifies SEM photographs of single crystals of calcium tartrate crystal. An enlarged SEM image is shown in Fig 5.2 (b) Thick and thin layers are seen in figure. It is observed that due growth conditions small voids are created at the grain boundary. Plate like structures are stuck together to flat surface of crystallite. Miss shaped growth features are seen along with small grain size particles. Plate like crystal morphology is observed from it. These crystals are grown by layer deposition. The structure of individual plates of samples are look like flat and the plates with the sharp edges were observed. On some plates, further plate like growth was also observed.

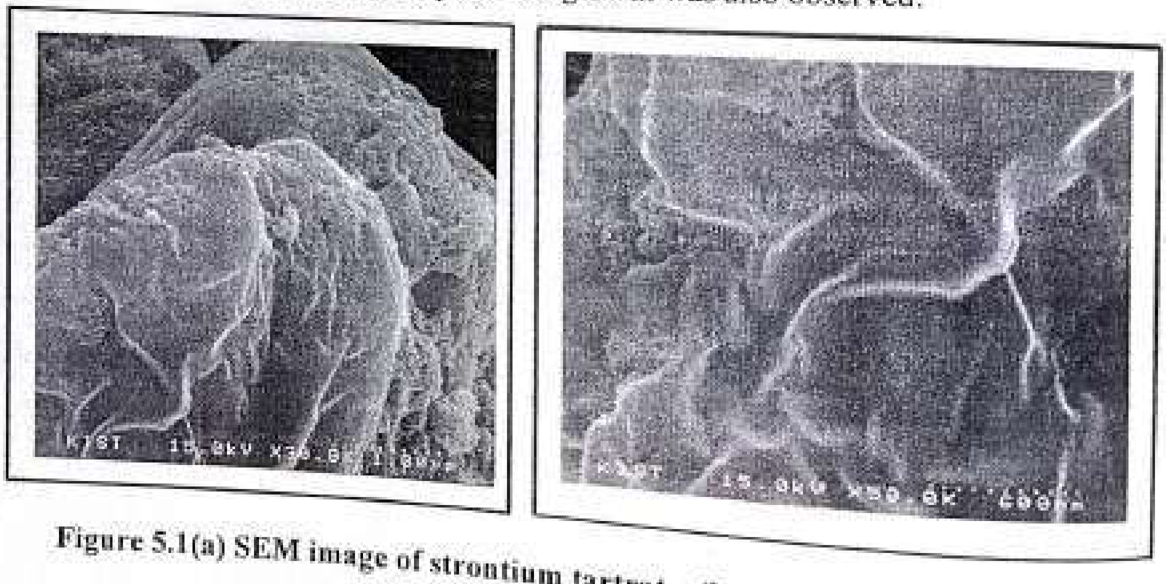


Figure 5.1(a) SEM image of strontium tartrate. (b) Magnified SEM image of strontium tartrate.

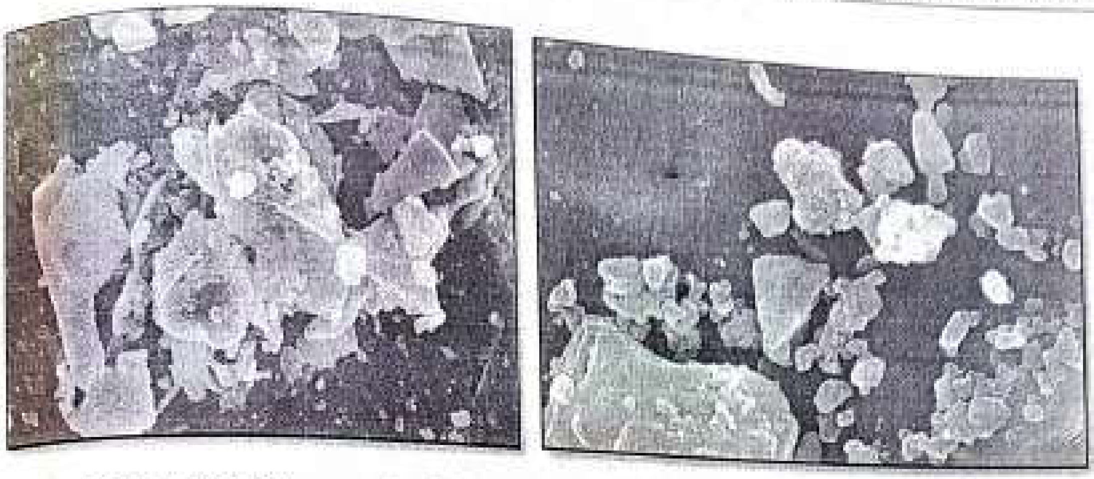


Fig 5.2 (a) SEM image of calcium tartrate crystal. (b) Magnified SEM image of calcium tartrate.

3.3 Electrical conductivity

Electrical conductivity is a measure of a material's ability to conduct an electric current. as quoted by Priya et al,Freeda et al,Ferdousi et al, Neamtu et al. [38-41].

From table 4 it is observed that, value of resistance of gel grown strontium tartrate is in mega ohm, which is a characteristics of insulating material. It can also be observed that, as voltage increases, current also increases. As temperature decreases, resistance increases and conductivity decreases. Fig 6.1 shows the graph log k v/s 1/T x10^{-4} and it re-inforces above conclusion. it is observed that, value of resistance of gel grown calcium tartrate is in mega ohm, which is a characteristics of insulating material. It can also be observed that, as voltage increases, current also increases. As temperature decreases, resistance increases and conductivity decreases.

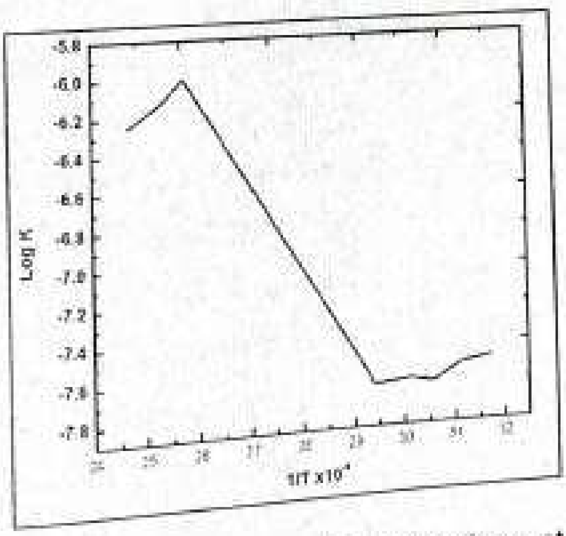


Figure 6.1 Ele. Conductivity of SrTr crystal

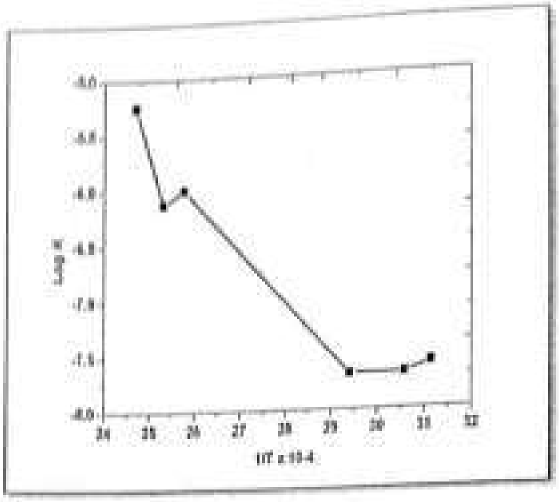


Figure 6.2 Ele. Conductivity of CaTr

4 CONCLUSIONS

1. Gel growth technique is suitable for growing crystals of Strontium and calcium tartrate.
2. Different habits of strontium and calcium tartrate crystals can be obtained by changing parameters like gel density, gel aging,pH of gel, concentration of reactants etc.
3. Unit cell parameter values nearly match with the reported ones and the structure of strontium tartrate is monoclinic while calcium tartrate is orthorhombic.
4. The SEM studies suggested different characteristics features and morphology of grown crystals.
5. The crystals possess electrical conductivity

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References

1. K. D. Girase, D. S. Bhavsar, N. D. Girase and T. K. Patil, Asian Journal of Chemical and Environnemental Research, 3, 4, 67,**(2010)**
2. K. Sangwal and A. R. Patel, *J. Crystal Growth*, 23, 282, **(1974**
3. M. S. Joshi and S. G. Trivedi, *Indian J. pure and APP. Phys.*, 21, 435,**(1983)**
4. H. K. Henisch, J. Dennis and J. I. Hanoka, *J. Phys. Chem. Solids,* 26, 493, **(1965)**
5. H. K. Henisch, *Crystal Growth in Gells, Pennsylvania State University Press, University Park, Pennsylvania,* **(1970)**
6. S. M. Dharma Prakash and P.Mohan Rao, *Bull. Mater. Sci.*, 4, 511,**(1986)**
7. M. R. Shedam and Venkateswara Rao., *Bull. Mater. Sci.*, 16, 309, **(1993)**
8. S. L. Garud and K. B. Saraf, *Bull. Mater. Sci.,* 31, 639,**(2008)**
9. M. S. Joshi., P. Mohan Rao and A. V. Antony, *Bull. Mater. Sci.*, 2, 127 **(1980)**
10. S. M. Dharma Prakash. and P. Mohan Rao, *J. Mater. Sci. Lett.*, 5, 769, (1986)
11. M. H. Rahimkutty, Rajendra Babu. and K.Shreedharan , *Bull. Mater. Sci.,* 24, 249- 252, **(2001)**
12. H. K. Henisch Crystal Growth in Gels, University Park, PA ; Pennsylvania University press **(1973)**
13. P. N. Kotru, N. K. Gupta, K. K Raina and M. L. Koul, *Bull. Mâter. Sci.,* 8, 547, **(1986)**
14. P. N. Kotru, N. K. Gupta, K. K Raina and L. B. Sarma, *Bull. Mater. Sci.,* 21, 83, **(1986)**
15. M. M. Abdel-Kader, S.FI-Kabbany , Taha M. Aboseh ly., K. K. Tahoon and A. EI-Sharkay., *J. Phys. Chem. Sol.,* 52, 655, **(1991)**
16. H. B. Gon, *J. Cryst. Growth.*, 102, 501,**(1990)**
17. C. C. Desai and A. H. Patel, *J. Mat. Sci. Lett,* 6, 1066, **(1987)**
18. V. S. Yadava and V. M. Padmanabhan, *Acta. Cryst., B* 29, 493, (1973)
19. L. V. Pipree and M. M. Kobklova, *Radio Eng. Electron Phys. (USA),* 12.33, **(1984)**
20. C. C. Desai, A. H. Patel and M. S. V. Ramana, *Ferroelectrics,* 23, 102, **(1990)**
21. Abdel-Kader M. M., FI-Kabbany and S. Taha., J. Mater. Sci. Mater. Elect.1, 201, **1991.**
22. M. M., Abdel-Kader FI-Kabbany., S. Taha., M. Aboseh ly., K. K. Tahoon and A. EI-Sharkay., *J. Phys. Chem. Sol. 52, 655.* **(1991)**
23. X. Sahaya Shajan and C. Mahadevan. *Bull. Mater. Sci.*, 4, 327. **(2004)**

24. A. C. Yanes, T. Topez, J. Stockel, J. F.Peraza, and M. E. Torres, *J. Mater. Sci. 31*, 2683,(**1996**)

25. T. Lopez, J.Stockel, J. F. Peraza and M. E. Torres, *Crys. Res. Technol*, **30, 677, 1995.**

26. S. K.Arora, V. Patel, R. G. Patel, B. Amin and Anjana Kothari., *J. Phys. Chem Solids*, 65, 965, (**2004**)

27. S. K. Arora, V. Patel, and Anjana Kothari., *Mater. Chem. Phys.* 84, 323, (**2004**)

28. A.Jain, S. Bhat, S. Pandita, M. L. Kaul and P. N Kotru., *Bull. Mater. Sci.*, 20, 1089, (**1997**)

29. Farhana khanum and Jiban Podder., *J. of Cryst. Process and technol*,1,26,(**2011**)

30. V. Thomas, Elizebeth Anit., H. Thomas, G.Jose, N. V. Unnikrishnan, Cyriac Joseph and M. A. Ittyachen, *J. Optoelectronics and Advanced Material*,7,5,2687, (**2005**)

31. L. Jothi and K. Ramamurthi, *Indian J, of Sci. and technol.* 4,6, 666, (**2011**)

32. S. J. Joshi, B. B. Parekh, K. D. Vohra and M. J. Joshi, *Bull. Mater. Sci.* 29,3, 307, (**2006**)

33. D. K. Sawant, H. M. Patil, D.S. Bhavsar , J. H. Patil and K. D. Girase, *Scholars Research Library.* 2,1 219, (**2011**)

34. Yuya Oaki and Hiroaki Imai, *Crystal Growth and Design*,3, 5,711, (**2003**)

35. Do – Hyung kim and Sang – Yun Lee, *Journal of the Korean Physical Society*, 39,2,97,(**2001**)

36. M. Ramesh and P. Sundaramoothi, *Bulg. J. Phys*, 36, 286,(**2009**)

37. S. Gopinath, R. Palanivel and R. Rajasekaran, *Int. J. Pure Appl.* Sci. Technol.1,2,**29.** 104, (**2010**)

38. D. K. Sawant, H. M. Patil and D. S.Bhavsar, *Pelagia research library*. 2, 3, 63, (**2011**)

39. M. Priya and Mahadevan., *Scholars Research Library*.,3,4, 233,(**2011**)

40. T.H. Freeda and C. Mahadevan, *Bull. Mater. Sci.*, 23,4, 335, (**2000**)

41. Ferdousi Akhtar. and Jiban Podder., **J. of Cryst. Process and Techn.**,1,18, (**2011**)

ROLE OF BUSINESS FOR DEVELOPMENT OF TRIBLES

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ABSTRACT:

It is the part of India for development in business, tribles are include in the business, The business will start in tribles region, because of lot of man power will be available in tribles region and also educated person is available. its development is sustainable, India is popular in the world if business is start in tribles region including tribles.Most tribes with significant gaming initiatives and related businesses can find themselves bombarded with myriad offers, opportunities and potential scams.

INTRODUCTION:

The late 20th century brought a new era of federal-tribal relationships and a policy of self-determination to Indian country. Indian Tribes are increasingly asserting control over their land, resources, and governance of their communities. Tribes are involved in a wide range of economic activities from tourism, gaming, energy, agriculture, forestry, manufacturing, federal contracting, and telecommunications. In many parts of the country, Tribes are becoming regional economic and political power houses. They are the largest employer in many counties. Tribal governments and tribal businesses engage in a wide range of business and financial transactions. The unique legal status of tribes is only now beginning to be used by Tribal governments to contribute to their business and economic development efforts. This century marks a new era for tribes using their sovereign status and governmental authority to achieve economic self-sufficiency and cultural preservation. There are still high levels of poverty and unemployment in Indian country and a lack of the basic infrastructure crucial to the building blocks of economic success. There are, however, increasingly more examples of tribes breaking their dependence on federal programs and creating the necessary legal infrastructure to build the foundations for successful economic development. As tribal business transactions become increasingly more sophisticated and involve non-Indian partners, investors, and lenders, there is a need to understand the basic methods for doing business in Indian country. In particular, in the energy industry, Indian tribes are shifting from being passive owners of their energy resources by evaluating ways in which they can own, develop, and produce their resources. Tribes are increasingly looking at ways to develop their resources in a manner that gives them an active ownership interest in the development of the project, often with a non-Indian business partner.

1. Why Choosing a Business Structure is Important

The choice of business structure will have long-term and far-reaching consequences for a tribal government and tribal business. The business structure you choose will have a major impact on how tribal assets are protected, how tribal sovereignty is preserved, and how potential liability is minimized. Critical decisions regarding the tax status of the business entity and whether or how sovereign immunity is waived must be made early in the decision making process. The choice of business structure may also be determined by the requirements a lender imposes as a financing condition or be determined by a business partner seeking certainty and predictability in the legal framework chosen to organize for economic development. This Handbook will help you to compare and analyze different structures and help determine which is best for you.

2. Success Factors

In the last decade, a substantial amount of research has been done to determine what impediments exist to creating long term sustainable economic development on Indian reservations and to identify the factors that have lead to significant progress on some reservations. Most tribes are committed to improving the economic welfare of its people and at the same time are concerned that this not be done in a way that diminishes their sovereignty. The Harvard Project on American Indian Economic Development (Harvard Project) has found that a key factor to achieve economic self-determination is to have institutions in place which promote self-governance and to provide a political environment in which investors will feel secure. Indian reservations have to compete with other venues to attract economic activities. To be successful, tribes must offer investors the opportunity to earn economic returns commensurate with the returns they might earn elsewhere. Investment dollars have to come from somewhere. Investor risk is raised if there is uncertainty in tax and regulatory policies that apply to on-reservation businesses or transactions. Risk is also raised if there is uncertainty regarding the enforcement of contracts or agreements. Governmental policies requiring preference hiring or policies that change frequently can also raise the risk and costs for investors or business partners. The second critical factor is the separation of tribal electoral politics from the day-to-day management of business enterprises. This relates to the direct role that tribal governments often have in development projects. Tribal governments should have a role in strategic decision-making. However, tribal governments should not make the day-to-day business decisions of tribal enterprises. Maintaining this separation can be difficult for tribal officials since enterprises and its assets belong to all tribal members. However, not insulating tribal politics from tribal businesses can create an uncertain and risky business environment for investors and business partners. Political instability, the possibility of opportunism on the part of tribal officials, and the difficulties in enforcing agreements can discourage investment. This can place tribes at a competitive disadvantage for attracting capital as well as technical and management expertise.

Key factors to consider when trying determining the best structure for a particular activity are:

Segregate politics from business--Free the tribal council from micro-managing tribal businesses while allowing the council to focus on long-term development strategies and goals. Assign responsibility to operate and manage tribal businesses to those who have business skill and knowledge.

Organizational considerations--How the entity is formed, under what law is the entity formed, and who manages the entity.

Sovereign Immunity--Tribes as governmental entities are not subject to suit unless they clearly waive immunity or Congress has waived their immunity. This raises questions regarding the ability of lenders, investors, and business partners to enforce agreements and to protect their investment. Each entity has different sovereign immunity implications that must be considered. **Liability**--Some business structures effectively shield business owners from liability for the financial obligations and debts of the business. Others do not effectively separate owner obligations from business entity obligations.

Tax considerations--Different federal income tax rules apply to different business types. State tax liability frequently depends on whether the business activity is conducted on or off an Indian reservation.

Financing--Money for a business comes in two forms: (1) debt--whereby the business borrows and then owes money to others; and (2) equity--where investors provide funding and then own part of the business. Lenders generally do not dictate choice of business entity, but equity investors may specify what business structure you can choose.

3. Overview of Structures

Tribal governments are distinct political entities in our federal system of government. They have the power of self-government and exercise sovereignty over their members and territory. Their sovereignty pre-dates the Constitution and is derived from the fact that they owned all the land that is now the United States. The U.S. Constitution acknowledges the sovereign status of Indian tribes in the Treaty Clause, in the 14th Amendment as "Indians not taxed," and in the Commerce Clause. The sovereign nature of Tribes has been recognized in the Constitution, treaties, court decisions, and the course of dealing with tribes. As sovereign Nations, Indian tribes have powers and capabilities not available to individuals. This Handbook will assist you in evaluating the different forms available for organizing economic development and to begin to take steps to achieve financial and economic independence. When developing a new tribal enterprise, an important consideration is the applicable law and regulations governing its formation and operation. In Indian country, business entities can be formed under tribal law, state law or federal law. Your choice of law and the entity that is chosen will have consequences on issues relating to tax, financing, and sovereign immunity. It will also determine how you can maximize risks and liability. An important consideration for tribes is how to preserve tribal control and to protect tribal assets while providing a business partner or lender with certainty. A tribe, because it is a sovereign nation, can form a governmental entity to perform business functions. This entity can be an instrumentality of tribal government, a political subdivision of the tribe, or an agency or division of the tribe. A tribe can also form a separate business entity formed under federal, tribal, or state law.

Below is a brief description of the main business structures.

I.Tribal Government

Many tribes conduct business through an economic development arm of the tribe. This is often referred to as in unincorporated instrumentality of the tribe. The business operation is generally overseen by the governing body of the tribe--sometimes by a business committee or a separate board, but they generally do not have a separate legal structure.

II.Section 17 Corporations

Many tribes conduct their commercial activities through federally-chartered corporations formed under Section 17 of the Indian Reorganization Act (IRA).4 To form a Section 17 Corporation, a tribe must petition the Secretary of the Interior for issuance of a corporate charter. A Section 17 corporation provides a framework by which a tribe can segregate tribal business assets and liabilities from the assets and liability of tribal governmental assets.

III.Tribally Chartered Corporations

Some tribes have adopted tribal laws that govern the formation of tribally chartered for-profit corporations. These laws authorize the formation of tribal business entities owned by the tribe. Several courts have held that sovereign immunity applies to activities of a tribally chartered corporation owned by a tribe. The issue of whether tribally charted corporations are subject to federal income taxes for income derived from on-reservation activities is up in the air. The Internal Revenue Service has this issue under consideration and has indicated that it will issue guidance, but has not yet done so.

IV. State-law Corporation

A corporation is a legal entity that is formed under the laws of the state by filing a certificate of incorporation or articles of incorporation with the jurisdiction in which it is formed. Corporations are owned by shareholders and governed by a Board of Directors elected by the shareholders. Corporations are governed by the terms and conditions contained in its articles of incorporation.

V. Limited Liability Company

The limited liability company (LLC) is a relatively new form of business entity that rose to prominence in the last ten years. Almost every state has enacted laws permitting the formation of an LLC. LLCs are formed by filing articles of organization with the state in which it is formed. It is a hybrid between a partnership and a corporation. It combines the primary advantage of a partnership--ease of formation and maintenance, and favorable taxation--with the key advantage of a corporation--limited liability protection for its owners.

4. Success Factors

When choosing a business structure, there are many things a tribe should consider regarding business issues and tribal governmental issues. One of the key factors is how to preserve tribal control while also insulating business decisions from tribal governmental decisions or tribal politics. Another critical factor for tribes is how to preserve tribal assets and limit exposure to business liabilities. Other factors are: how to effectively manage the entity, how to maximize tax benefits, how to minimize financial risks, the location of business operations--on or off the reservation, what assets will be pledged, how the business will be capitalized, which structure enables the preferred method of equity or debt financing, and the requirements of one's business partner or lender.

CONCLUSION:

1. **Adequate capitalization**. Adequately capitalize the corporation. Do not allow the corporation to be financially dependent on the parent/shareholders for working capital. 2
2. **Compliance with legal requirements for issuance of stock**. Make sure stock is issued and that you have complied with applicable legal requirements relating to issuance of a security.
3. **Maintenance of corporate records**. Maintain corporate records, including minutes of shareholders' and directors' meetings held at least annually.
4. **Maintenance of separate financial records and bank accounts**.Maintain separate financial records for each subsidiary. Keep balance sheets and profit and loss statements for each year. Maintain separate bank accounts for each subsidiary and parent.
5. **Avoidance of inter-corporate loans**. Make few loans between the parent and the subsidiary. Document all loans made and make payments in accordance with the repayment terms.
6. **No guarantees by tribe of subsidiary's debt**. The parent entity (e.g., the tribe) should not generally assure corporate creditors that it will take care of subsidiary obligations if the subsidiary is unable to do so.
7. **No assignment of contracts between tribe and subsidiary**. Make sure that contracts that are intended to bind only the subsidiary are only in the name of the subsidiary. Don't put them in the name of the parent and then assign to the subsidiary.

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REFERENCE:

1. Wright v. Colville Tribal Enterprise Corp., 111 P.3d 1244, 1250 (Wash. Ct. App. 2005).
2. Runyon v. Ass'n of Village Council Presidents, 84 P.3d 437, 440-41 (Alaska 2004). 106
3. Dixon v. Picopa Construction Co., 772 P.2d 1104, 1110 (Ariz. 1989).
4. See, e.g., Id. at 1107-08, 1109. 108 See, e.g., Id. at 1111-12;
5. Trudgeon v. Fantasy Springs Casino, 71 Cal. App. 4th 632, 642 (1999). 109

6. See, e.g., Gavle v. Little Six, Inc., 555 N.W.2d 284, 294 (Minn. 1996). 110
7. Id. at 294-95; Trudgeon, 71 Cal. App. 4th at 639-40. 111
8. Dixon, 772 P.2d at 1110-11. 112 Id. at 1108;
9. White Mountain Apache Indian Tribe v. Shelley, 480 P.2d 654, 656 (Ariz. 1971). 113
10. Dixon, 772 P.2d at 1110-11.

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Thermal and Morphological Study of Transition Metal Cobalt Oxalate Crystal Grown By Agar-Agar Gel Technique

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ABSTRACT

In this article, we have reported fabrication of various morphological of cobalt oxalate. Cobalt oxalate crystals were grown by agar-agar gel through the single diffusion technique. The tendency of cobalt oxalate crystals to spherulites growth was demonstrated. Also Liesegang ring are observed. The cobalt oxalate preparation method was played crucial role on the crystal structure and its morphology. The optimum growth conditions cobalt oxalate was achieved by controlling the parameters like, concentration of gel, concentration of reactants, aging period and reversing of reactants. The crystal structure of grown material was determined by TGA, DTA and EDAX.

Keywords: Crystal growth, cobalt oxalate, TGA, DTA and EDAX.

Introduction:

Growth of crystal ranges from a small inexpensive technique to a complex sophisticated expensive process and crystallization time ranges from minutes, hours, days and to months. The starting points are the historical works of the inventors of several important crystal growth techniques and their original aim. Crystals are used in semiconductor physics, engineering, as electro-optic devices etc., so there is an increasing demand for crystal [1-5]. For years, Natural specimens were the only source of large, well-formed crystals. The growth of crystals generally occurs by means of following sequence of process. Diffusion of the molecules of the crystallizing substance through the surrounding environment. Diffusion of these molecules over the surface of the crystal to special sites on the surface. Today almost all naturally occurring crystals of interest have been synthesized successfully in the laboratory [6-9]. It is now possible only by crystal growth techniques.

Materials and Methods

Materials used to grow the cobalt oxalate crystals are cobalt chloride, oxalic acid, and agar-agar gel. All the chemicals used for the experiment were used without any further purification. Sodium silicate glass test-tubes were used as crystallizing vessels. The test-tubes were filled with the first reactant (cobalt chloride) of desired volume and morality. The second reactant, oxalic acid having a concentration range of 0.5 to 1.5 M, was poured along the walls of the test-tube into the set-gel, and allowed to diffuse into the gel medium. The open end of the tube was closed with cotton plugs and kept undisturbed. The said procedure was carried out at room temperature. The ions of the supernatant solution reacted with ions of the first reactant via capillaries formed in gel medium. After six to seven days, nucleation kick-started at the gel-solution interface. The chemical reaction that occurred between the two reactants is given as follows:

$$CoCl_2 + H_2C_2\,O_4 \xrightarrow{\quad\quad} CoC_2O_4 + 2HCL$$

The diamond-shaped, spherulites, opaque crystals were obtained in the test-tube. The crystals were harvested by washing them carefully with acetone and collected for further characterization. Table 1 shows the optimized crystal growth parameters for the cobalt oxalate crystals.

Table 1 shows the Optimum condition of cobalt oxalate crystal

Sr.No	Condition Single Diffusion	Condition Single Diffusion
1	Percentage of gel	2.0 %
2	Concentration of cobalt chloride	1.0M
3	Concentration of oxalic acid	1.0M
4	Volume of cobalt chloride	5.0 ml
5	Volume of oxalic acid	15 ml
6	Gel setting period	34 Hours
7	Gel aging period	4 days

Liesegang rings - are a phenomenon seen in many, if not most, chemical systems undergoing a precipitation reaction under certain conditions of concentration and in the absence of convection. Rings are formed when weakly soluble salt are produced from reaction of two soluble substances, one of which is dissolved in a gel medium [10]. The phenomenon is most commonly seen as rings in a Petri dish or bands in a test tube; however, more complex patterns have been observed, such as dislocations of the ring structure in a Petri dish, helices', and Saturn rings in a test tube [11]. Despite continuous investigation since rediscovery of the rings in 1896, the mechanism for the formation of Liesegang rings is still unclear.

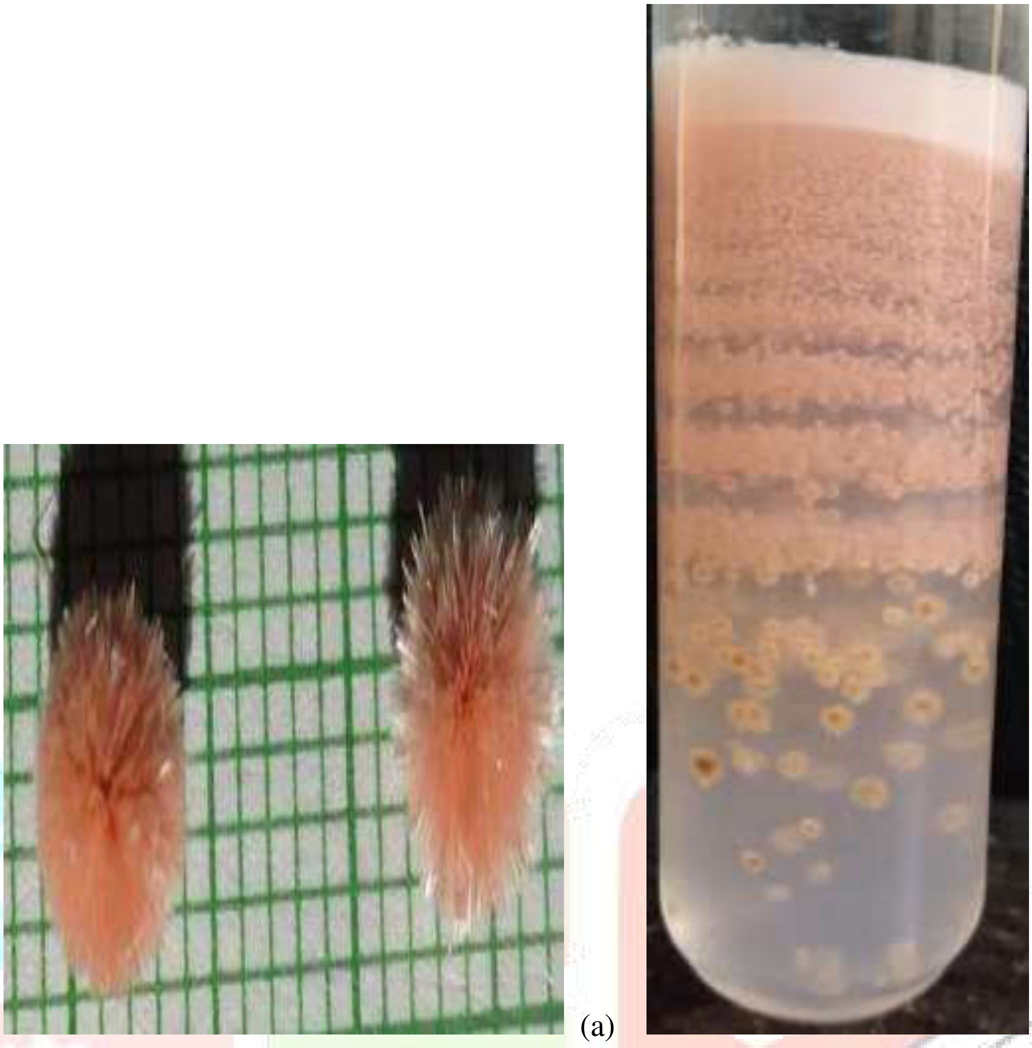
(a) (b)

Fig. 1(a) Shows the spherulites cobalt oxalate crystals (b) Shows the formation of Liesegang rings

Result and Discussion-

Thermogravimetric Analysis (TGA) of Cobalt Oxalate- The thermogram of cobalt oxalate crystal were obtained with the help of SDT Q600 V20.9 Build 20. TGA/DTA/DSC thermal analyser available at Materials Characterization Laboratory Department of Materials Science and Engineering, Yonsei University,Room No.B307,Engineering Hall 2,50 Yonsei-ro, Seodaemun-gu, Seoul 120-749, Republic of Korea. The TGA curve of cobalt oxalate agar-agar gel grown crystal is as shown in fig (2), the percentage of the weight loss in the different stages of decomposition of cobalt oxalate are presented in the table (2) . There is good agreement between the observed and calculated weight. The four stages of decomposition are described as below: In the first stage decomposition occurs in the temperature range 30^0C to 177^0C in which weight loss of 17.46% agrees very well with the calculated weight loss 17.58%. Thus it is clear that the crystals are hydrate and the weight loss calculation clearly indicate that cobalt oxalate crystals have nine water molecule as water of crystallization. It is notice that the sample losses water of hydration and becomes anhydrous at 177^0C.

In the second stage of decomposition in the temperature range 200^0C to 247^0C, the total weight loss 3.411% is seen which is due to the loss 3C and $3H_2O$ this is well agreement with calculated weight loss of 3.50%. Then an anhydrous cobalt decomposes into cobalt oxalate.

In the third stage of decomposition total weight loss 36.88% was observed in the temperature range 247^0C to 260^0C which corresponds to the loss of 2CO. This weight loss agrees very well with the calculated weight loss 37.00%. Thus cobalt oxalate further decomposes into cobalt carbonate.

Finally in the temperature range 892^0C to 930^0C, total weight loss of 2.538% was obtained. This loss is attributed to the loss of CO_2. This is in well agreement with the calculated weight loss of 2.8%. Thus the cobalt carbonate finally turns into cobalt oxide at 930^0C. Which is confirmed by residual weight up to the end of analysis 2.538%. This is in good agreement with calculated residual weight of 2.80%.[12-14]

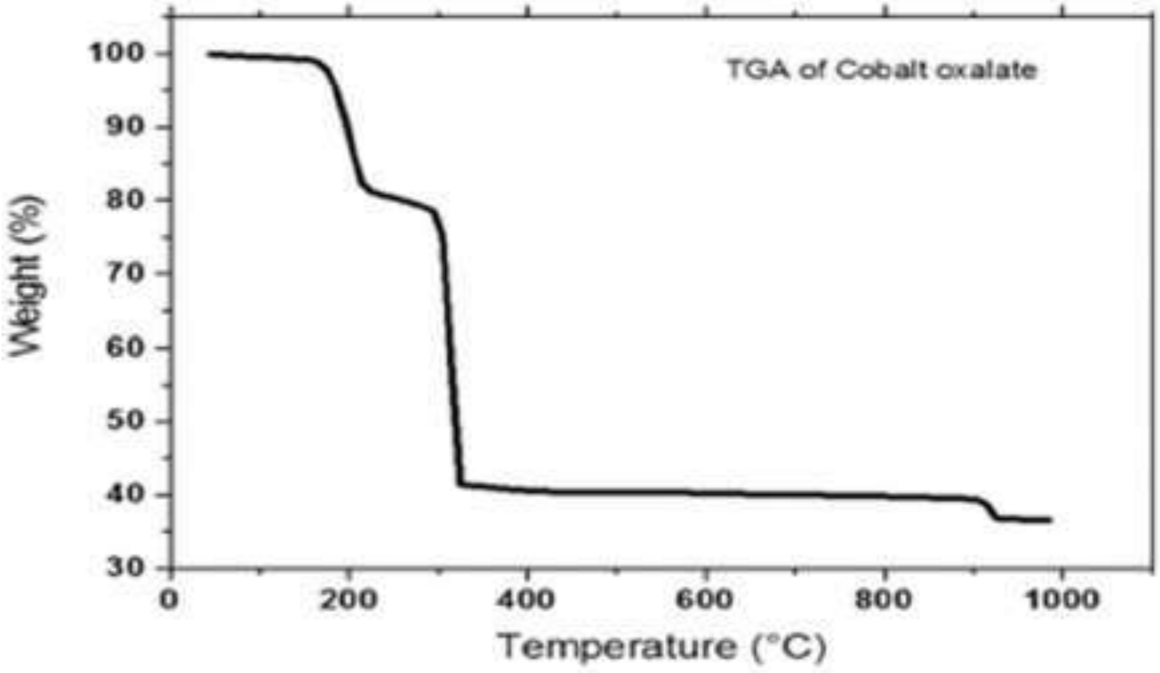

Fig.2 Shows the TGA Curve of Cobalt oxalate crystal grown by agar-agar gel technique

Table 2 Summarized data of TGA results of decomposition process of cobalt oxalate crystals

Stage	Temperature range ^{0}C	Observed Weight loss %	Calculated Weight loss %	Loss of Molecule in stage
I	30-177^{0}C	17.46%	17.58%	$9H_2O$
II	200-247^{0}C	3.41%	3.50%	3C and $3H_2O$
III	247-260^{0}C	36.88%	37.00%	2CO
IV	892-930^{0}C	2.538%	2.80%	CO_2

Differential Thermal Analysis (DTA) –

The DTA curve for cobalt oxalate agar- agar gel grown crystal is as shown in figure(3) and the DTA data collected from this curve is tabulated in the table(3). In DTA curve we observe two endothermic peak at 208.25^0C and 919^0C and one exothermic peak at 310^0C are due to decomposition of hydrated cobalt oxalate into anhydrous cobalt oxalate. In the first stage of decomposition, peak at 208.25^0C is attributed to loss of first

$4H_2O$ molecules immediately followed by another endothermic peak at 919^0C which corresponds $2H_2O$ molecules. The endothermic peaks observed in the DTA curve corresponds to the total weight loss of Nine water molecule in TGA curve [15-17].

Table 3 DTA data of Cobalt oxalate

Peaks recorded	Nature
208.25^0C	Endothermic
919^0C	Endothermic
310^0C	Exothermic

The exothermic peak at 310^0C due to the decomposition of anhydrous cobalt oxalate into cobalt oxalate. The exothermic peak attributed to the loss of 4C molecule and endothermic at 208.25^0C is attributed to the loss of 3 water molecules. The endothermic peak at 919^0C is due to the decomposition of cobalt oxalate carbonate to cobalt oxide which is attributed to the loss of $2CO_2$.

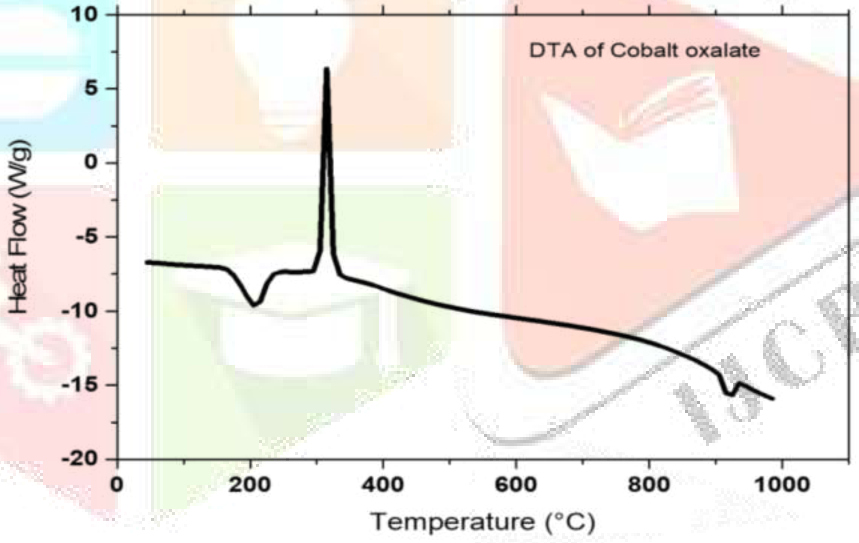

Figure 1 DTA curve for Cobalt oxalate

Energy Dispersive Analysis by X-rays (EDAX) –

The chemical composition of as grown crystals is analyzed by Energy Dispersive X-ray Analysis (EDX). Fig. 4 shows the EDX spectrum which confirms the presence of expected elements O,C and Cu.The stoichiometric composition was computed using experimental and theoretical results of EDX. Energy Dispersive analysis by X-ray (EDAX) is used for the quantitative analysis of cobalt oxalate and is also called as elemental analysis. It conclude that the (weight & atomic %) of copper (Cu) in the grown crystal measured by EDAX are very close with the values calculated from the molecular formula.[18-22].

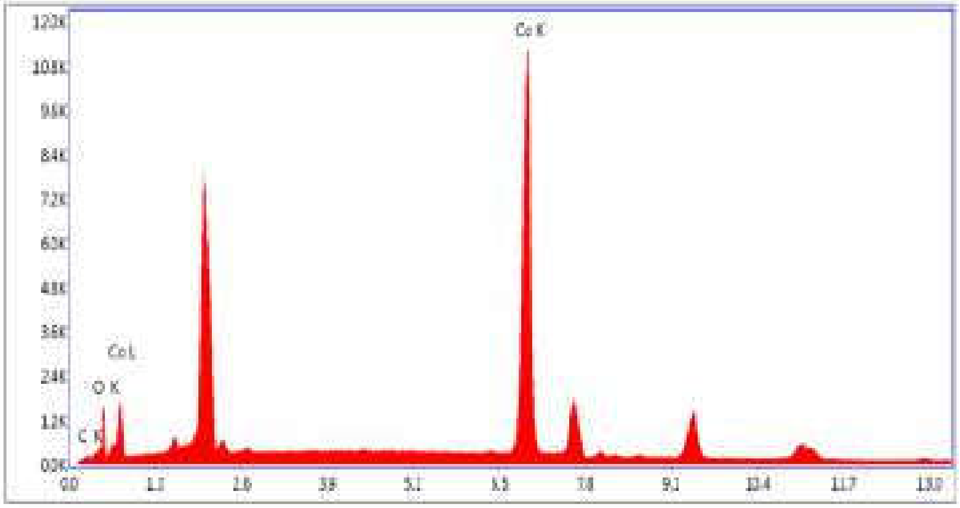

Figure 2EDAX of Cobalt oxalate

Table 4 EDAX of cobalt oxalate

Element	Weight%	Atomic%	Net.Int	Error	%	K ratio	Z	R	A	F
Ck	2.22	9.46	44.68	19.14	0.01	0.05	1.33	0.84	0.21	1.00
Ok	2.41	7.71	227.93	10.39	0.01	0.05	1.28	0.86	0.42	1.00
Cobalt	95.37	82.83	6779.47	1.88	0.97	0.80	0.98	1.01	1.0	1.03

Conclusions —

The present work reports the growth and characterization of cobalt oxalate single crystals. We have demonstrated the formation of cobalt oxalate single crystals in agar-agar gels. Cobalt oxalates exhibits star shaped, opaque and spherulites growth (flower) shape are observed. Further to obtain good quality single crystals of cobalt oxalate, both reactants –cobalt chloride and oxalic acid were interchanged. With cobalt chloride incorporated gels result only fibers. These facts have been explained by taking in account the interaction of the reactants ions with the sodium and silica ions. The effect of temperature on growth of cobalt oxalate crystals showed that there is a decrease in nucleation density at higher temperature which is due to the increases of the aqueous solubility of cobalt oxalate.

Conclusions-

Transition metal cobalt (II) oxalate crystal was grown by gel method using agar agar gel in well size and shape.Red –pink colour crystal were observed. In contrast bigger and better shape of red pink block crystal of cobalt oxalate observed, however, longer growth time was needed to grow the crystal.

Reference

1. R. N. Singh, Madhu, R. Awasthi, S. K. Tiwari, Int. J. Hydrogen energy. 34, 4693,**(2009).**

2. S. D. M. Jacques, O. Leynaud, D. Strusevich, A. M. Beale, G. Sankar, C. M. Martin,P. Barnes, Angew. Chem. Int. Ed. 45, 445 **(2006).**

3. W. X. Kuang, Y. N. Fan, Y. Chen, Langmuir, 16, 5205 **(2000).**

4. A. W. Sleight, B. L. Chamberland, Inorg. Chem. 7, 1672 **(1968).**

5. U. Kersen, L. Holappa, Appl. Phys. A: Mater. Sci. Process. 85, 431 **(2006).**

6. Ramamoorthy, R., Kanagasabai, V., Kausalya, R., Impact of celebrities' image on brand, International Journal of Pure and Applied Mathematics, V-116, I-18 Special Issue, PP-251-253, **2017**.

7. Ramamoorthy, R., Kanagasabai, V., Vignesh, M., Quality assurance in operation theatre with reference to fortis malar hospital, International Journal of Pure and Applied Mathematics, V-116, I-14 Special Issue, PP-87-93, **2017**

8. Ramya, N., Arthy, J., Honey comb graphs and its energy, International Journal of Pure and Applied Mathematics, V-116, I-18 Special Issue, PP-83-86, **2017**

9. Ramya, N., Jagadeeswari, P., Proper coloring of regular graphs, International Journal of Pure and Applied Mathematics, V-116, I-16 Special Issue, PP-531-533, **2017**.

10. Polezhaez, A.A.; Muller, S.C. (1994). "Complexity of precipitation patterns: Comparison of simulation with experiment". Chaos: An Interdisciplinary Journal of Nonlinear Science. **4** (4): 631–636. Bibcode:**1994** Chaos...4..631P. doi:10.1063/1.166040. PMID 12780140.

11. LLOYD, FRANCIS E.; MORAVEK, VLADIMIR (1930). "Further Studies in Periodic Precipitation". J. Phys. Chem. **35** (6): 1512. doi:10.1021/j150324a002.

12. P.N. Kotru,K.K.Raina and M.L. Koul, "J MatervSci Lett."6:711-14 **1987.**

13.P.N.Kotru,N.K.Gupta,K.K.Raina and I.B.Sharma, "I Mater Sci.;21:83-9,**1986.**

14.T.V.Albu, S.L.Plostinaru, and E.Segal, " J Thermal Anal.,50:425-30.**1997.**

15. K.S.Raju,Johan Varughese and M.A.Ittyachen; " Bull. Mater.Sci." 21,375. **(1998).**

16. D.K.Sawant,H.E.Patil.D.S.Bhavsar,K.D.Girase and J.H.Patil; "Journal of Thermal Analysis and Calorimetry," 107, 3. **(2012).**

17. N. S. Patil, P. A. Savale. S. K. Bachhav and S. T. Pawar ; ' Archive of physics research', Vol2(1), 39-47**, (2011).**

18. D. K. Sawant., H. M. Patil and D. S. Bhavsar., 'Pelagia research Library, DCS' Vol2(3), 63**, (2011).**

19. D. K. Sawant., H. M. Patil and D. S. Bhavsar., 'Scholars Research Library Archives of Physics Research', Vol2(2), 67**. (2011).**

20. S.J.Nandre,S.J.Shitole and R.R.Ahire; "Journal of Nano and Electronic Physics"Vol.4,4,4013. **(2012)**

21. M.Selvapandiyan, S. Sudhakar and M.Prasath; "Int. Journal of Engineering Research and Application", Vol. 7,8,(3), 65-72. **(2017).**

22. P S Rohith, N. Jagannatha and K V Pradeep Kumar. AIP Conference Proceedings **2220**, 060003 (2020); https://doi.org/10.1063/5.0001222.

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Synthesis of Cobalt Oxalate Crystal in Agar Agar Gel

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ABSTRACT

Cobalt oxalate crystals were prepared by gel method using agar-agar gel. In the present investigation, the cobalt oxalate was grown by single diffusion techniques. Applying different parameter, the effect on growth of cobalt oxalate was studied. The parameters like, concentration of gel, concentration of reactants, aging period, reversing of reactants found affecting the growth.[1] The growth was also studied by using different sizes of the test tubes. The nucleation was controlled by using such parameters and optimum conditions are obtained. Such grown crystals were found in different shape and transparency. The Surface morphology was studied by optical microscopy.

Keywords: Crystal growth, Gel method, Agar agar gel, Optical microscopy

Introduction

It has long been appreciated that advances in solid state science depends critically on the availability of defect free single crystal specimens. As a result, an enormous amount of labour and care has been lavished on the development of growth techniques. In terms of crystal size, purity and perfection, all the techniques used for the growth of single crystals from melt, vapour, and solution have their own inherent constraints. In spite of the technological advancement in condensed matter physics, crystal growing is still an extremely difficult task requiring great expertise and skill. This method is useful to grow the oxalates because they are insoluble in water and decompose before melting point. Many researchers have grown these crystals by using this technique in silica gel[2 -7] and gelatin gel, however very few researchers used the agar agar gel. The agar agar gel is not pH dependent and again makes the method simple. Khan et al in 1976 reported the growth of transition metal cobalt oxalate in silica gel.

In these context, the gel technique is found to be promising one, for getting good quality single crystals which has an advanced technological application in the fields of optics, acousto-optics, optoelectronics and electronics, etc. The crystals which cannot be satisfactorily grown from melt and vapour are grown successfully by this method A complete survey made by Henisch in this field gave a fantastic idea to the crystal growers to grow crystals using gel technique. The art and science of growing crystals in gel is historically an old phenomenon. In the early days the gel was not chosen as a medium of crystal growth, but only used to study the Liesegang ring phenomenon which is in no other way separable from the process of crystallization.

Experimental Details

Test tubes were used as crystallizing vessels, for single diffusion, the test tubes were filled by the first reactant (cobalt chloride) of desired volume and morality. Hot agar agar gel was poured in the test tubes and was kept for setting. The second reactant oxalic acid (0.5 M to 1.0M) of desired volume and morality was gently poured along the walls of test tube on the set gel and allowed to diffuse into the gel medium. The open end of tube was closed with cotton plugs and kept undisturbed at room temperature. The ions of supernatant solution reacted with ions of first reactant through capillaries formed in gel medium. After 6 to 7 day some nucleation was observed near the gel solution interface then some opaque crystal some diamond shape crystals were observed in test tube. The crystals were harvested by washing them carefully with acetone. As grown crystals were collected and observed.

In single diffusion test tubes were filled by first reactant oxalic acid, then poured hot agar agar gel in the test tube, after setting the gel then insert the cobalt chloride (0.5M to 1.0M) solution in test, after 7 to 8 day some nucleation is seen on the interface of test tube, then after few days some shiny crystal are observed.

The chemical reactions inside the gel can be expressed as-

$$CoCl_2 + H_2C_2O_4 \text{ ------------------}\rightarrow CoC_2O_4 + 2HCL$$

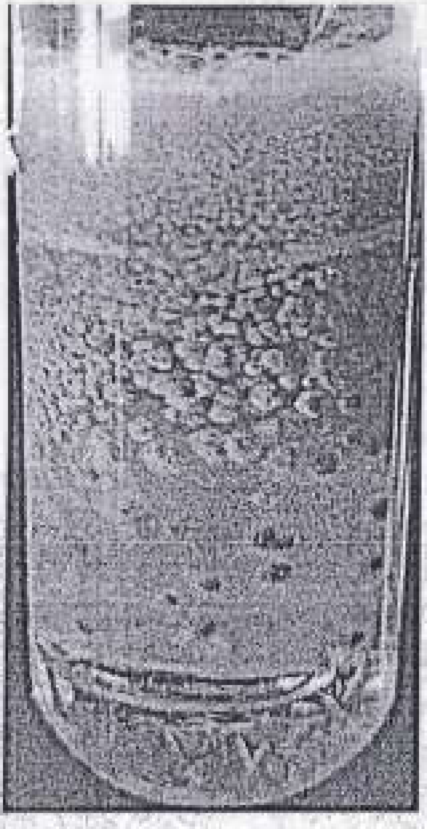
The various optimum conditions for growing crystals were found and are given in table 1.Different parameters such as concentration of reactants, gel concentration, etc have considerable effect on the growth rate. In the steady state of concentration gradient, growth rate also becomes steady which favors growth of well-developed crystals, however, very slow rate of growth along one direction results in the platy crystals. Fast growth rate in one particular direction leads formation of elongated crystals like dendrites. All types of cobalt oxalate crystals show the phenomenon of efflorescence, i.e. due to dehydration, even at room temperature, transparent crystals become opaque.

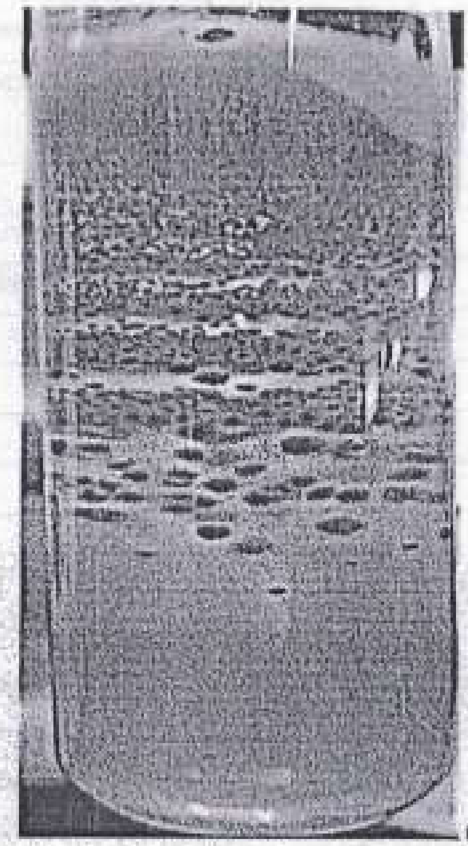
Effect of Concentration of reactants

To observe the effect of concentration of reactants on the growth of cobalt oxalate crystals, the Both reactants were prepared in the concentrations of 0.5M, 0.6, 0.7 ..., 1.0M, while the other growth parameters were kept constant, such as gel concentration (0.5%),aging period (4 days) and volume of first reactant (5 ml) and volume of second reactant (15 ml). It was found that the number of nucleation was decreased by decreasing the concentrations of both reactants such as 0.7M and 1M respectively. The same result was observed in single diffusion methods. Meanwhile it was observed that if both reactants were of same concentration (more or less) the rate of diffusion was same and nucleations were found to be 1 cm below interface. In this 1 cm region of nucleation again it was found that when the concentration was of reactants was less but in a equal proportion the crystals were widely separated. For different concentrations it was observed that, the diffusion rate was faster for higher concentration of second reactant to that of first reactant. The best result was obtained when the percentage of gel was at 0.50% and the morality of first reactant was 0.7M and concentration of second reactant was decreased up to 1M,the nucleation growth was controlled and large size cobalt oxalate crystals was obtained.

Effect of percentage of gel

To observe the effect of gel percentage, other parameters such as concentration of first and second reactants, ageing period, setting period as well as size of test tubes were keep constant. Figure 2 shows the effect on growth of cobalt oxalate crystals with variation in percentage of agar gel. It was found that for lower percentage (0.5%) of gel the growth was near the interface and like spikes which after about 34 hours covert into small particles. Such particles were large in number and their size was found very small as show in fig 2(a). When percentage of gel increased to 2.0% and 2.5% dendrite growth was observed nearly spherical in shape at its diameter is about 1cm, below the interface four layer is observed and spherical shape crystal as shown in fig 2(b) and fig 2(c). The size sphericlated and colour is light brown of growing crystals found more precise for 2.0 percentage gel as compare to 2.5 % gel. The optimum condition obtained is as shown in table 1.


(a)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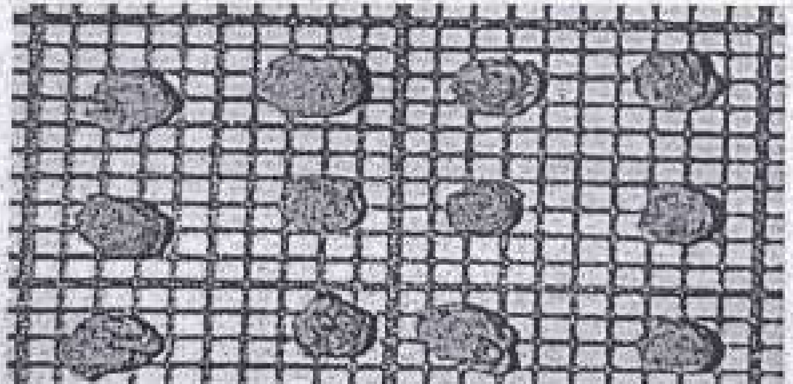
(C)

Table: 1. The optimum condition for cobalt oxalate crystals.

Sr.No	Condition Single Diffusion	Condition Single Diffusion
1	Percentage of gel	2.0 %
2	Concentration of cobalt chloride	1.0M
3	Concentration of oxalic acid	1.0M
4	Volume of cobalt chloride	5.0 ml
5	Volume of oxalic acid	15 ml
6	Gel setting period	34 Hours
7	Gel aging period	4 days

Conclusion:

Spherical, well sized and shaped cobalt oxalate crystals can be grown by the gel method using agar agar gel with single diffusion technique by applying various parameters such as change of ageing period, method of reversing reactants, change of concentration of first and second reactant alternate change,. The best result is obtained in single diffusion method for 2 % agar gel and reactants of concentration 2M.

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References

1. H. K. Henisch, Crystals in Gels & Liesegang Rings, Cambridge University Press, Cambridge, UK, 1988.
2. B. B. Parekh, M. J. Joshi, and A. D. B. Vaidya, Current Science, vol. 93, no. 3, pp. 373–378, 2007.
3. P. V. Dalal,Indian Journal of Materials Science, Volume 2013 (2013), Article ID 682950.
4. Khunur, M.Misbah; Wahyuni, Dini Tri; PoncoPranantoYuniar , Advances in Natural & Applied Sciences;2011, Vol. 5 Issue 5, p467
5. H.M.Patil, D.K. Sawant , D.S, Bhavsar, J.H. Patil and K.D.Girase, J. Th. Ana.& Calo.,Mar2012, Vol. 107 Issue 3, p1031

6. S. Pandita, R.Tickoo, K Kllamral, P. N.Kotru and N. Sahni,Bull. Mater Sci., Vol. 24, No. 5, October 2001, pp. 435–440. © Indian Academy of Sciences.435
7. A.S. Khan, T.C. Devore, and W.F. Reed (1976), Journal of Crystal Growth, 35(3): 337–339.

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Growth and Characterization of Cobalt Oxalate Crystal by Ager-Ager Gel Method

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Abstract

We have grown the cobalt oxalate crystals by adopting single diffusion technique via agar-agar gel. The tendency of cobalt oxalate crystals to form splices, twins, spherulites and dendrites was demonstrated. The growth dynamic of cobalt oxalate was studied by controlling the parameters like, concentration of gel, concentration of reactants, aging period and reversing of reactants. Physical properties of the grown crystals were analyzed by XRD, and FTIR techniques and the results are discussed.

KEYWORDS: Gel, Crystal, Gel Growth, Crystal Growth, XRD, and FTIR

Introduction

Crystals grown by the gel method has gained interest in the research community because it is cheap and easy to grow single crystals of alkaline-earth metal oxalates[1] and transition metal oxalates [2]. These materials have interesting properties like low solubility in water [3], decomposition before freezing point [4], interesting optoelectronic properties. Their role in analytical chemistry and subsequently in industries [5, 6] has created an opportunity for the researcher to investigate every scientific aspect of these materials. Therefore, efforts are being made to investigate and study the physical and chemical properties of these materials. Recently, there are reports on the growth of mixed-ligand complex formation using cadmium oxalate [7]. In the present study, we have presented the optimization of growth parameters to grow the cobalt oxalate single crystals using the agar gel method.

Materials and Methods

Materials used to grow the cobalt oxalate crystals are cobalt chloride, oxalic acid, and agar-agar gel. All the chemicals used for the experiment were used without any further purification. Sodium silicate glass test-tubes were used as crystallizing vessels. The test-tubes were filled with the first reactant (cobalt chloride) of desired volume and morality. The second reactant, oxalic acid having a concentration range of 0.5 to 1.0 M, was poured along the walls of the test-tube into the set-gel, and allowed to diffuse into the gel medium. The open end of the tube was closed with cotton plugs and kept undisturbed. The said procedure was carried out at room temperature. The ions of the supernatant solution reacted with ions of the first reactant via capillaries formed in gel medium. After six to seven days, nucleation kick-started at the gel-solution interface. The chemical reaction that occurred between the two reactants is given as follows:

$$CoCl_2 + H_2C_2\,O_4 \xrightarrow{\qquad} CoC_2O_4 + 2HCL$$

The diamond-shaped opaque crystals were obtained in the test-tube. The crystals were harvested by washing them carefully with acetone and collected for further characterization. Table 1 shows the optimized crystal growth parameters for the cobalt oxalate crystals.

Sr.No	Condition Single Diffusion	Condition Single Diffusion
1	Percentage of gel	2.0 %
2	Concentration of cobalt chloride	1.0M
3	Concentration of oxalic acid	1.0M
4	Volume of cobalt chloride	5.0 ml
5	Volume of oxalic acid	15 ml
6	Gel setting period	34 Hours
7	Gel aging period	4 days

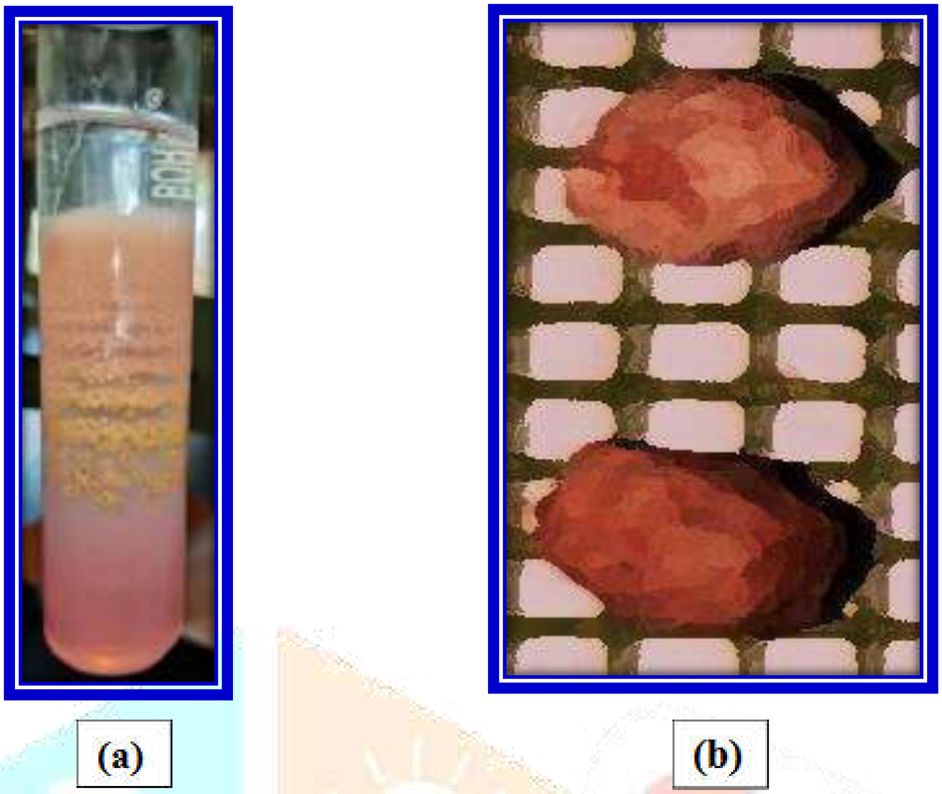

Figure 1:(a) in situo growth of Cobalt oxalate crystals in test-tube and (b) optical photograph of cobalt oxalate crystals

Result and discussion

The crystal structure analysis of the grown cobalt oxalate crystal was done via X-ray diffraction. X-ray pattern was recorded from the range of 10 to 80 degrees. The occurrence of highly resolved intense peaks at specific Bragg angles 2θ indicates the high crystallinity of the grown material and revealed monoclinic structure. The obtained crystal data has been compared with the JCPDS data and it closely matched with the reported JCPDS no. 037-0719. The unit cell parameters (‘a’ = 5.39820 Å, ‘b’ = 5.03100 Å, and ‘c’ = 5.73590Å) are close to the reported cell parameters of $CoC_2O_4.2H_2O$, indicating the monoclinic phase of cobalt oxalate crystal. Comparative data is tabulated in Table 2 for the gel-grown cobalt oxalate crystal.

Table 2. Comparison of unit cell parameters of cobalt oxalate.

Parameters	Calculated	JCPDS data
System	Monoclinic (P)	Monoclinic
a	9·67638 Å	6·4534 Å
b	6·7156 Å	7·5009 Å
c	8·6822 Å	10·940 Å

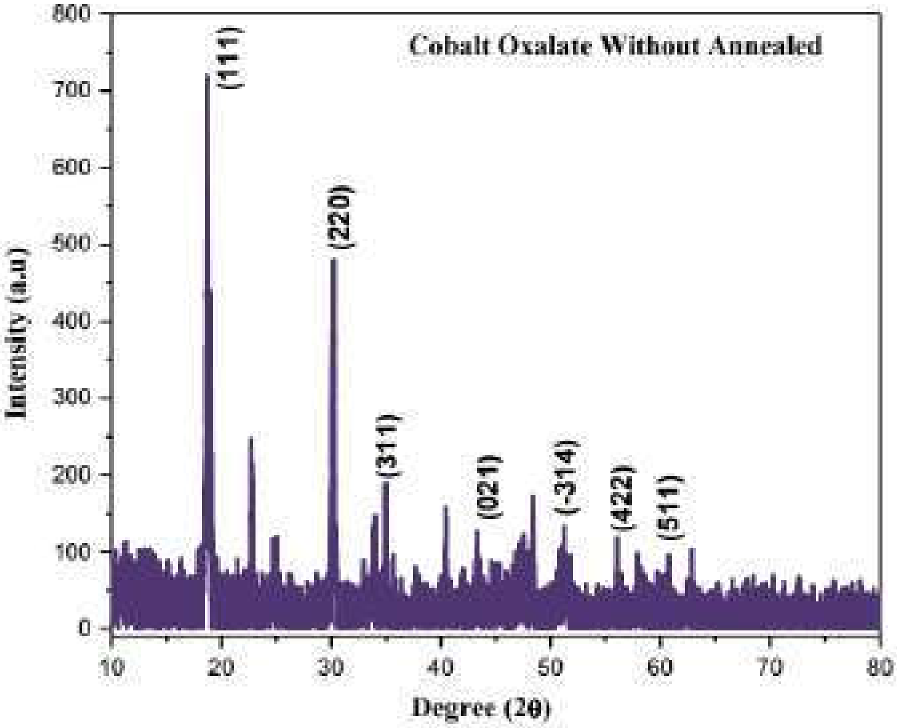

Figure 2: X-ray diffraction pattern of gel-grown cobalt oxalate crystal.

4.2 Fourier transform infrared (FTIR) Spectra

The Fourier transform infrared (FTIR) spectrum of cobalt oxalate was recorded at room temperature in the spectral range 500 – 4500cm^{-1} by KBr pellet method using SHIMADZU spectrophotometer at the department of Physics, Shivaji University Kolhapur. Figure 3 shows the FTIR spectrum of cobalt oxalate. The spectrum shows various frequencies of vibrational modes which confirm the presence of oxalate in the crystal.

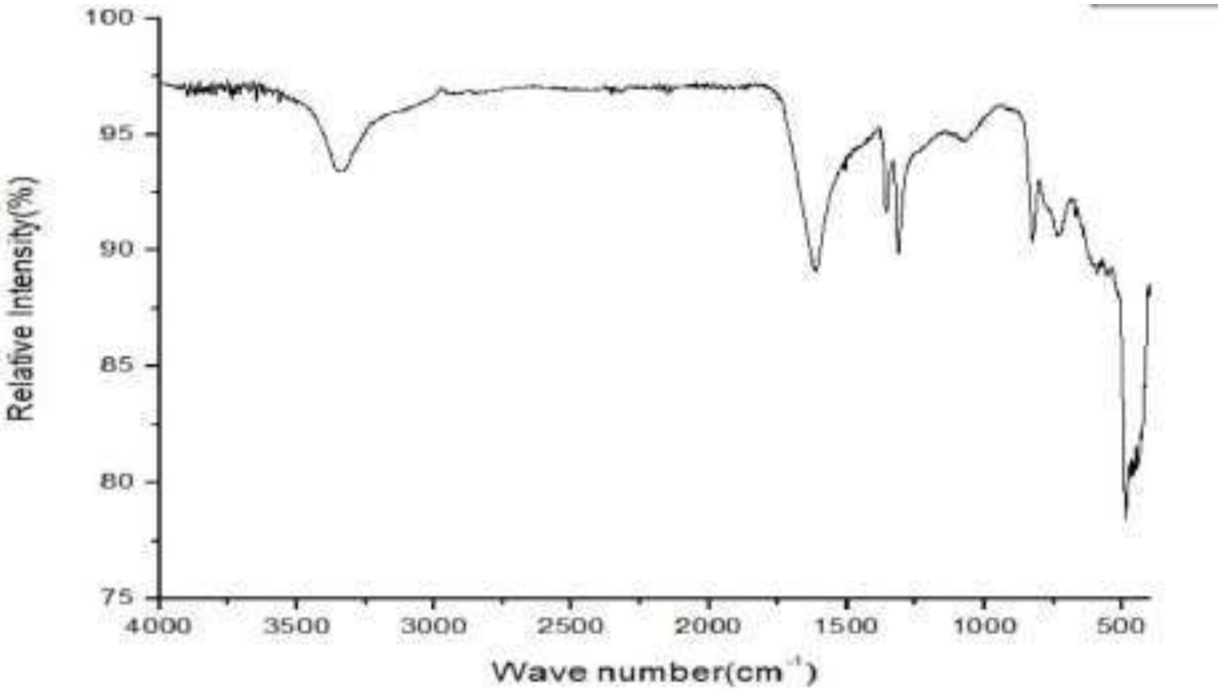

Figure 3: FTIR of Cobalt oxalate grown crystal

The sharp peak at 3300.18 $cm^{-1}$is attributed to the stretching of O−H group, indicating the presence of water of crystallization or water of hydration. However the peak at 1710. 00 cm^{-1} to 1665.00cm^{-1}correspond to α,β-unsaturated aldehydes, and ketones. The two identical sharp peaks around 1367.93 and 1327.43 cm^{-1} correspond to an asymmetric and symmetric stretch of C–H rock, respectively. Thus the FTIR spectroscopy confirmed the growth of cobalt oxalate crystals due to the presence of water of crystallization.

Conclusions

Cobalt oxalate crystals were grown by gel method using agar- agar gel in well size and shape. XRD powder diffraction patterns and analysis shows the crystalline nature of crystal with monoclinic phase. Different functional groups revealed by FTIR show the metal bond and different vibrations in the sample.

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References

[1] A. Pactor, Kristall und Technik,vol.12,no.7,pp.729–735, 1977.

[2] S.K.Arora and T.Abraham, Journal of Crystal Growth,vol.52,no.2,pp.851–857,1981.

[3] J. Dennis and H. K. Henisch, Journal of The Electrochemical Society,vol.114,no.3,pp.263–266, 1967.

[4]N.V.Prasad,G.Prasad,T.Bhimasankaram,S.V.Surya-narayana, and G. S. Kumar, Bulletin of Materials Science,vol. 19, no. 4, pp. 639–643, 1996.

[5] M. I. Diaz-Guemes, A. S. Bhatti, and D. Dollimore, Thermochimica Acta,vol.106,pp.125–132,1986.

[6] Y. Okamoto and W. Brenner,Organic Semiconductors,ReinholdPublishing, Chapman & Hall, London, UK, 1964.

[7] W. B. Schaap and D. L. McMasters, Journal of theAmerican Chemical Society, vol.83, no.23, pp.4699–4706, 1961.

[8] S.J.Nandre, S.S.Sonawane,R.R.Ahire and S.J.Shitole, Der Pharma Chemica, 2014, 6(3), PP.33-38.

[9] S.J.Nandre, S.S.Sonawane, R.R.Ahire and S.J.Shitole, Journal of Scientific Review, 2014,1(1),1-6.

[10] S.J.Nandre, S.S.Sonawane, R.R.Ahire and S.J.Shitole Renewable Research Journal, 2014, 3(1),PP. 47-52.

[11] S.J.Nandre, S.J.Shitole, and R.R.Ahire, International Journal of Chemical and Physical Sciences, 2014, 1,PP.123-130.

[10] AnilkumarKodge et al.,Int.J.ofEng.Sci.and Tech.,2011,3(8), 6381-6390. [11] Paul Bowen et al., Nanoscale, 2010, 2, 2470–2477.

[12] Ren, L et al. B. Q. Chem. Phys. Lett. 2009, 476, 78–83.

[13] R. L. Frost et al.Chinese Science Bulletin,2003, 48(17), 1844-1852.

[14] Joanne Hayley Smith, Ph.D.Thesis, University of Natal.2001. [15] E Romero et al. J.cond.-mat.mtrl –sci, 2010,

[15] S. J. Joshi, K. P. Tank, B. B. Parekh, M. J. Joshi, Cryst. Res. Technol. 45, No. 3, 303 – 310, 2010.

[16] J. J. de Yoreo and P. Vekilov, *Crystal Growth*, vol. 35, pp. 24–30, 2008.

[33] S. M. Arifuzzaman and S. Rohani, *Journal of Crystal Growth*, vol. 267, no.3-4, pp. 624–634, 2004.

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Physical and Optical Study of Cobalt Oxalate Single Crystals Grown by Agar-Agar Gel Method

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Abstract: **The cobalt oxalate single crystals were grown in agar-agar using gel method. In the present investigation, the cobalt oxalate single crystals were grown by single diffusion technique, such grown crystals were found in different size and colour. The physical and optical properties of cobalt oxalate crystals were characterized by different techniques such as SEM and UV-Vis spectroscopy and results are discussed.**

Index Terms: **Cobalt oxalate, Crystal growth, Optical properties, SEM and Single diffusion.**

I. INTRODUCTION

Single crystal growth is the rapid growing field in research because of increase in demand of single crystals for many applications there are various types of crystals which can be grown by gel method. It is simple and inexpensive technique. We have turned our attention towards the oxalates are having good application can be synthesized by gel method. Many research has grown the series of pure and mixed crystals to find out the new materials for various purpose (Bacchhav S. K. et al.,2014; Jhon M.V., et al.,2001; Gao P.,2008). There are various techniques for growing crystals like melt growth, Vapour growth, solution growth and etc. the gel technique attracted more attention towards it because of its simplicity and cost effectiveness. The crystals can be grown at ambient temperature.

Cobalt oxalate is quite interesting compound as they are having good application. The cobalt oxalate crystals have been grown by the single diffusion and double diffusion technique using silica gel and also studied as precursor of Co_4O_4 nano particles (Yuniar P.,2012). In the present work of investigation, the cobalt oxalate single crystals were synthesized using single diffusion technique at room temperature and their characterization by EDAX, Powder XR, FT-IR and TGA-DTA. The work has been already published by the author (Pawar H.et al.,2021; Pawar H.et al.,2021).The crystals were analyzed by various characterization techniques. The physical and optical properties were studies by Scanning electron microscope (SEM) and UV-Vis Spectroscopy.

II. EXPERIMENTAL

A. Crystal Growth

The growth of cobalt oxalate crystals has been carried out by single diffusion technique using gel method. The glass test tube of 25 mm diameter and 250mm length were used as crystal growth apparatus. 1% of agar gel was prepared by adding 1gm of agar powder into hot water. The solution of cobalt chloride (first reactant) and oxalic acid (second reactant) of 0.5, 1.0, 1.5 and 2.0M concentration were prepared and store in clean glassware. Cobalt chloride solution and oxalic acid solution were used as first reactant and second reactant respectively. The solution of first reactant (oxalic acid) was taken in a test tube and 2% of hot agar gel was poured along the wall. Then test tubes were kept undisturbed for setting and aging gel, after setting and aging, 1M of second reactant (cobalt chloride) solution was gently poured over set gel. The open end of test tubes was closed with cotton plug to prevent evaporation and contamination of the exposed surface by dust particles and impurities of atmosphere and were kept undisturbed. After 28 to 42 days the good quality and different morphological crystals were grown and harvest them. The figures 1 (a) with working reaction during crystal growth in test tube and (b) shows that some good quality harvested cobalt oxalate crystals.

The reaction between cobalt chloride and oxalic acid in agar – agar gel medium resulted in the growth of cobalt oxalate crystals. As grown crystals were characterized for structural, morphological, physical and optical properties. Growth of cobalt

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oxalate crystals are gained by reacting the components cobalt chloride ($CoCl_2$) and oxalic acid ($H_2C_2O_4$). The expected reaction taking place in this work is as follows

$$CoCl_2 + H_2C_2O_4 \longrightarrow CoC_2O_4 + 2HCl$$

Fig. 1 (a) working reaction during crystal growth in test tube

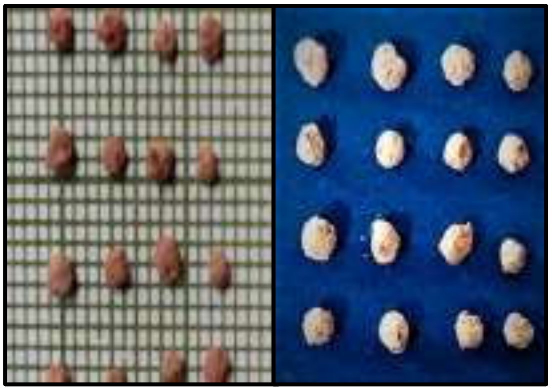


Fig. 1 (b) Harvested crystals of cobalt oxalate

III. RESULTS AND DISCUSSIONS

A. *Scanning Electron Microscopy (SEM)*

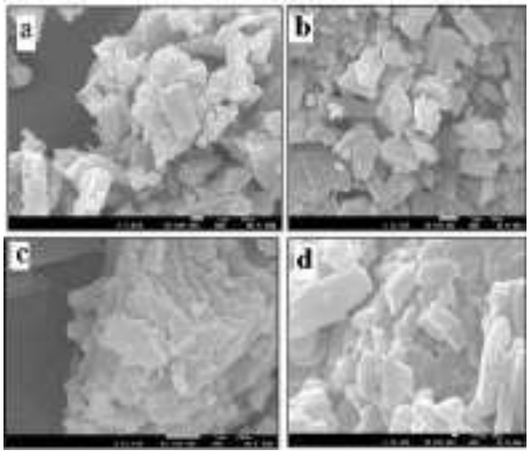


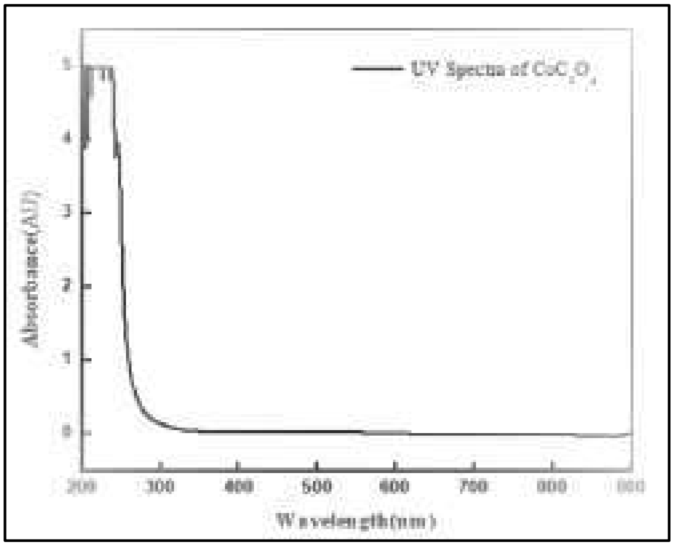
Fig. 2 (a), (b), (c) and (d) SEM images of as grown cobalt oxalate crystal

SEM images gives the information about the nature and suitability for device applications and also it is used to check the presence of imperfections. SEM analysis was carried out using JEOL, JSM 7001F scanning electron microscope. The morphology and particles size were observed by scanning electron microscopy. Fig 2(a), (b) and (c) Shows typical SEM images of the cobalt oxalate at resolution X5000, X1000, X15000 and X30000 respectively.

SEM images revealed that the growth of cobalt oxalate crystals was composed of many rectangular sheets approximately greater than 5µm in length and of the thickness more than 5µm. However, in the high magnification of samples as shown in figure 2 (c) and (d). It revealed that the rods are actually bundle of rectangular plates those are in hexagon shape, which were stacked in parallel fashion. (Usha R.et al.,2012). Figure 2 (a), (b), (c) and (d) illustrate the SEM images of same sample.

B. *UV-Vis Spectroscopy*

Absorption spectrum of cobalt oxalate crystals was obtained by a SHIMADZU UV-2450, UV- Vis spectrophotometer. Figure 5.15 shows UV-Vis absorption spectrum of cobalt oxalate crystal. The lower cutoff wavelength for CoC_2O_4 crystals was found to be 300.31 nm were shows in fig.3 form the graph the value of band gap was found 4.12 eV. The absorption coefficient is high at low wavelength and low at high wavelength. Hence it is wide transparent crystal for wide range of wavelength (300-900). The wide band gap of CoC_2O_4 crystals confirms the less absorbance in visible region (Arun K.et al., 2008; Want B.,2006; Rohit P.S..,2020). The cobalt oxalate crystal can be used for the nonlinear optoelectronic device fabricating applications. The band gap energy of Cobalt oxalate crystals is found to be 4.12 electron volt.



IV. CONCLUSION

The present work reports the growth and characterization of cobalt oxalate single crystals grown by single diffusion technique using agar-agar gel as a medium of growth. Scanning electron microscopic (SEM) analysis revealed that it consists of many rectangular sheets, those are in hexagonal shape and stacked in a parallel fashion. UV-Vis studies shows that the crystals have a wide transparency window from 300nm to 900nm enables it to good candidate for second harmonic generation.

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REFERENCES

Arun K. J. and S. Jayalekshmi, (2008), *“Optoelectronics and Advanced Materials”,* vol-2, pp701-706.

Bacchhav S. K., N. S. Patil, M. S. Kale and D. S. Bhavsar, (2014) “*Int. Journal of Engineering Research and Application”,* vol-4, pp108-112.

Gao P., Mu.Ga And Xiao, Lui-lou, (2008)“*Cryst. Res. Technology”,* vol-43, pp496.

Jhon M. V. and M. A. Ittayachen, (2001) *“Crystals Res. Technology”,* vol-36, pp141-146

Pawar H. S., S. J. Nandre, N. B. Sonawane, S. D. Chavhan, R. R. Ahire, (2021) *“International Journal of Creative Research Thaughts”,* vol-9, pp1343-1348.

Pawar H. S., S. J. Nandre, N. B. Sonawane, S. D. Chavhan and R. R. Ahire, (2021) *“International Journal of Creative Research Thoughts”,* vol-9, pp349-355

Rohit P. S., N. Jagannatha and K. V. Pradipkumar, (2020). *AIP Conference Proceeding,2020, 060003.*

Usha R. J., J. A. M. Mani, P. Sagayaraj and V. Joseph, (2012). *“Archives of Applied Science Research”,* vol-4, pp1545-1552.

Want B., F. Ahmad and P. N. Kotru, (2006) *“Cryst. Res. Technology”,* vol-41, pp-1167.

Yuniar p. et.al. (2012) *“Bulletin of chemical Reaction Eng. and Cat.”*

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Comparative Thermal Analysis Studies on Gel Grown Crystals of Li, Cu and Mixed Li-Cu tartrate

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Abstract: **The Natural as well as Gel grown crystals plays an important role in modern technology development. Gel method for the growth of crystals which are insoluble or sparingly soluble in water is the best alternative for the growth of many crystals. Crystals grown by gel method are relatively perfect compared to the other methods. In the present investigation crystals of Li- tartrate, Cu-tartrate and Mixed crystals of Li-Cu tartrate have been grown by single diffusion gel technique. The Thermal Analysis studies of these crystals are carried out in this work. The Thermal Analysis studies on these crystals.**

Index Terms: **Gel method, Thermal Analysis, Li, Cu and mixed tartrate.**

I. INTRODUCTION

It is well established that there is extensive study on tartrate-based crystal grown by gel technique, however, we have found that there are few reports on the lithium tartrate-based crystal because of its chemical properties (Henisch H.,1970; Henisch H.,1986; Sawant D., et al., 2011; Patil H., et al.,2012). Therefore, in the present study, we have investigated the growth mechanism of lithium tartrate, copper tartrate and mixed lithium-copper tartrate crystals. All the three types of crystals were grown by gel method by using single diffusion techniques, the crystal growth procedures and various different parameters affecting the growth of the crystals are discussed. The present paper contains the comparative study of all crystals under investigation regarding their growth and Thermal Analysis study. All results obtained are put at a glance in present paper.

II. GROWTH OF CRYSTALS

In The crystals of lithium tartrate, copper tartrate, and lithium-copper tartrate were grown by gel method by using single diffusion technique.

Table 1 gives details regarding method and chemicals used, different habits of crystals obtained and their transparency etc. In the present work, we obtained semitransparent, shiny and star shaped lithium tartrate crystals. The copper tartrate crystals were of diamond shaped with bluish color, while the mixed lithium-copper tartrate crystals were whitish blue in color and having a cubic shape. The adopted single diffusion gel technique proved to be beneficial because of it only we successfully obtained well-shaped and good quality crystals. All the well-defined good quality crystals were found below 2 to 3 cm in the gel interface (Krishnakumar V., et al.,2009; Sawant. D.,2012; Sonawane S.,2015; Ahmad N.,2014).

The optimum growth conditions for gel grown crystals established by varying the different parameters like pH of gel, gel setting time, gel density, room temperature etc. are reported in the Table 2 for the all these three crystals. The suitable value of gel density is found to be 1.04 gm /cm^3 and the pH value is 4 to 4.2.

III. THERMAL ANALYSIS

Thermal analysis is the measurement of how specific physical or chemical properties of a substance changes with temperature. It measures the change in weight of the substance with respect to applied temperature. In present work, thermogravimetric analysis of lithium tartrate, copper tartrate and mixed lithium-copper tartrate crystals was done. It was noticed that the pure lithium tartrate crystal was more stable at high temperature than the copper tartrate and mixed lithium-copper tartrate crystals. We observed 60 % weight loss in the temperature range of 200-212 ^{0}C for copper tartrate crystals, whereas for

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lithium tartrate crystal, weight loss is only about 28% in the same range of temperature. (Nandre S.,2013; Sawant D., et al.,2011; Yanes A., et al.,1996; Lopez T., et al.,1995). The details of weight loss with respect to temperature for all three the details of weight crystals is summarized in Table 3.1.

loss with respect to temperature for all three

Similarly, for mixed lithium-copper crystals the total loss of weight was around 68 % in the temperature range of 0-310 ^{0}C.

Table 1 Summary of lithium, copper and lithium-copper tartrate crystals grown by gel technique

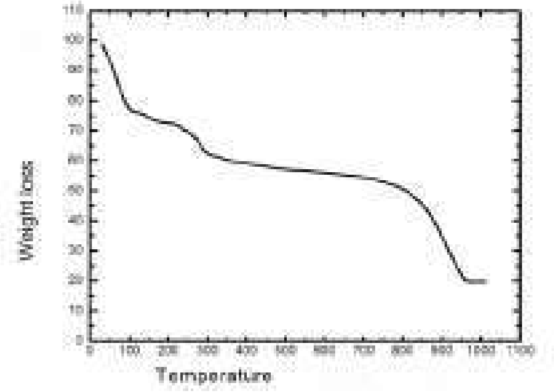
Sr.No.	Type	Method	Chemicals Used	Solvent	Quality	Size (mm)
1	Lithium Tartrate	Gel method using single diffusion techniques	Na2SiO3, C4H6O62LiCl	Methanol or Ethanol	Opaque, Transparent Good	3 x 1 x 1
2	Copper tartrate	Gel method using single diffusion techniques	Na2SiO3, C4H6O6CuCl2	Distilled water	Opaque, bluish color	2.5 x 2 x 1
3	Lithium -copper Tartrate	Gel method using single diffusion techniques	Na2SiO3, C4H6O6Cucl + 2LiCl	Methanol or Ethanol	Opaque, good	2 x 2 x 1.5

Table 2. Optimum growth conditions for gel grown tartrate crystals

Sr.No.	Parameter	Lithium tartrate	Copper tartrate	Copper – lithium tartrate
1	Concentration of tartaric acid	1M, 7ml	1 M, 7ml	1M, 5ml
2	pH of the mixture	4 to 4.2	4.2	3.8 to 4.2
3	Temperature	25 to 30^{o}C	25 to 30^{o}C	20 to 30^{o}C
4	Gel setting time	120 hours	96 hours	96 hours
5	Density of sodium metasilicate solution	1.04 gm/cm^3	1.04 gm/cm^3	1.04 gm/cm^3
6	Period of growth	4 weeks	3-4 weeks	4 weeks
7	solvent	Ethanol	Water	Ethanol or Methanol

Table.3. Kinetic data of TGA analysis for lithium tartrate, copper tartrate and lithium-copper tartrate crystals.

Compound	Steps	Temp. range ^{o}C	Observed Weight loss %	Calculated weight loss %	Loss of Molecule
Lithium tartrate	I	25-95	18	18.18	$2H_2O$
	II	95-260	10	11.90	$2H_2O$
	III	260-750	15	15.50	2CO
	IV	750-950	30	32.10	$2CO_2$
Copper tartrate	I	25-210	2.15	2.50	$5H_2O$
	II	210-240	65.80	66.15	$2H_2O$
Mixed Lithium-Copper Tartrate	I	30-100	18	19.8	$3H_2O$
	II	100-210	1.5	2.0	CO
	III	210-320	49.5	50.42	CO_2, $2H_2O$



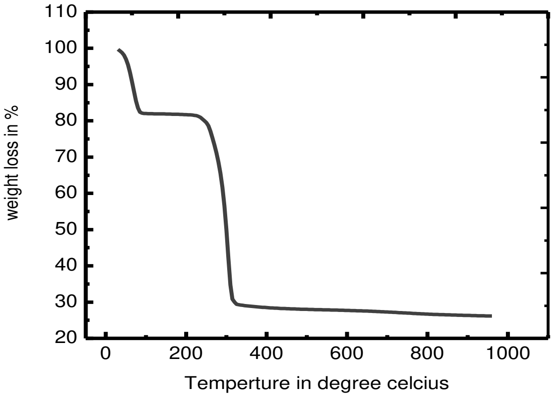


Fig. 1 TGA spectrum of lithium tartrate crystal.

Fig.2 TGA-DTA graph depicting the decomposition of lithium – copper tartrate crystal with respect to temperature

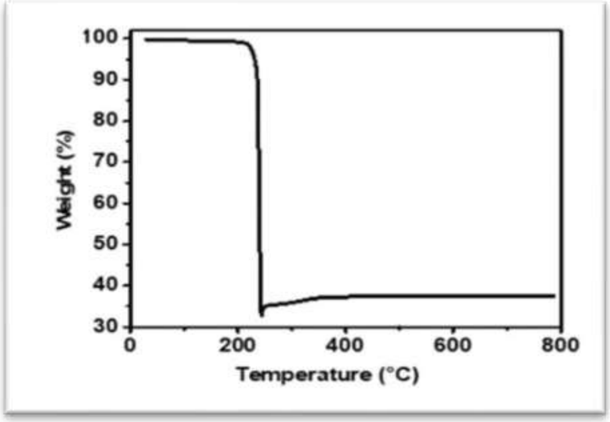


Fig. 3 TGA -DTA graph depicting the decomposition of lithium – copper tartrate crystal with respect to temperature

CONCLUSIONS

The Thermal Analysis revealed the crystallinity of the grown crystals. Thermal analysis is the measurement of how specific physical or chemical properties of a substance changes with temperature. It measures the change in weight of the substance with respect to applied temperature. In present work, thermogravimetric analysis of lithium tartrate, copper tartrate and mixed lithium-copper tartrate crystals was done.

REFERENCES

Ahmad Nazir and Kotru P.N., (2014).,Single crystal growth by gel technique and characterization of lithium hydrogen tartrate, Journal of Crystal Growth" Accepted Article 24.

Henisch H.K Patel, A.R., Venkateshwara Rao, (1982) A. Crystal growth in gel media. *Bull. Mater. Sci.* **4,** 527–548.

Henisch H.K.,(2009), Growth and Characterization Studies of SrCaMHP Single Crystal in Silica Gel Medium and Laser Induced Nucleation Reduction Strategy, *Journal of Minerals and Materials Characterization and Engineering*, 8,1.

Krishnakumar Vand Dheivanalar S. (2009), First and second-order Raman scattering of B_6O, "Journal Raman Spectroscopy". 40 ,627-631.

Lopez T, Stockel J,Peraza J.F and Torres M.E.,(1995) ,Structural Characterization of Doped Calcium Tartrate Tetrahydrate, "Crys Res.Technol" 30 (1995) 677.

Nandre S.J. Ph.D. Thesis North Maharashtra University Jalgaon (2013).

Patil H.M, Sawant D.K, Bhavsar D.S, Patil J.Hand GiraseK.D."Journalof.Therm. Anal.Calorim," 107 (2012) 1031.

Sawant D.K, Patil H.M, Bhavsar,D.S., Patil J.H and Girase K.D."Journal of Scholars Research Library"3 (2011) 404-413.

Sawant D.K, Patil H.M, Bhavsar.D.S, Patil. J.H and Girase K.D. "Scholars Research Library Archives of Physics Research",2 (2011) 67-73.

Sawant. D. K.; Ph. D. Thesis; (2012)., North Maharashtra University, Jalgaon.

Sonawane S.S. Ph.D. Thesis (2015)., J.J.T. University Rajasthan.

Yanes A.C, Topez T, Stockel J,Peraza J.F and Torres M.E. (1996) "Journal Mater Sci." 31,2683.

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GROWTH OF LITHIUM TARTRATE CRYSTAL BY HYDRO SILICA GEL METHOD

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ABSTRACT

Crystal of lithium tartrate was grown by single diffusion silica gel method at ambient temperature. The optimum conditions were established by varying various parameters such as pH of the solution, density sodium metasilicate solution, gel setting time and concentration of upper and lower reactants Solvents like i.e. ethanol and methanol were used to dissolve LiCl. Growth of lithium tartrate crystals was studied. The optimum conditions were established for the growth of good quality crystals. In the present work, white colored, star shaped and transparent crystals were obtained.

Keywords: Hydro silica gel technique, Lithium tartrate crystals.

INTRODUCTION:

The advances in the science of the solid state and material science depend upon the availability of good quality single crystals. Consequently, tremendous amount of efforts has been made on the development of crystal growth techniques, each having its own importance and potentiality with certain limitation.

The new rapidly developing branches of science and technology, such as quantum electronics, quantum and non linear optics, semiconductor instrumentation, Laser and masers etc. all involves the use of single crystals and their singular properties. So several techniques have been developed and are still being to be developed in rapid succession to synthesize better and better quality of crystals, which are rare in nature, or not yet grown in laboratory.

Crystals are the unknown pillars of modern technology. The modern technological developments depend greatly on the availability of suitable single crystals, whether it is for lasers, semiconductors, magnetic devices, optical devices, superconductors, telecommunication etc. In spite of great technological advancements in the recent years, we are still in the early stage with respect to the growth of several important crystals such as diamond, silicon carbide, gallium nitride and so on. Unless the science of growing these crystals understood precisely, it is impossible to grow them as large single crystals to be applied in modern industry. The large number of crystals is used in electronic, optical and in industries have been grown by several researchers (1-7). Hence today's demand is to grow large single crystals with high purity and symmetry.

Material and Method:

Hydro silica gel was prepared by using tartaric acid and sodium metasilicate having different pH values. The chemicals used for the growth of Lithium tartrate were of AR grade. 7ml of tartaric acid (1M) was taken in a small beaker. Sodium metasilicate solution of (1M) concentration was added drop by drop with constant stirring. The pH of solution was maintained to 4 to 4.5. The solution was then transferred in the test tube (2.5 cm diameter and 25cm length) then covered its mouth with cotton plug. It was transparent initially, after 2/3 days, it turns milky and gel converted into semisolid with little amount of water on the top of the surface.

After setting of hydro silica gel, allow the aging of the gel. Aging makes the gel harder and reduces the diameter of the capillaries present in the gel. 1M concentration of LiCl solution was prepared by dissolving LiCl in methanol and ethanol. The solution was often poured slowly with the help of pipette. The height of the supernatant component should be 60-70% of the gel height. With time, Lithium chloride diffuse in the gel & the crystals of Lithium tartrate appears in the gel. This is called "Single diffusion method". In the Present work, crystals of Lithium tartrate $(C_4H_4O_6)Li_2$.were grown by a simple gel technique using single diffusion method.

The optimum growth condition were established by varying different parameters like pH of gel solution, gel concentration, gel setting time, concentration of reactants, period of crystal growth, temperature, density of gel etc. With optimum conditions the maximum sizes of the grown crystals were increased [4]. The Lithium tartrate crystals under present investigation are shown in fig.1. The use of solvents methanol and ethanol results into the good crystals formation in gel medium (8-12).

Chemical Reaction:

The following reaction is expected to take place in the gel medium

$$2LiCl + C_4H_6O_6 \rightarrow (C_4H_4O_6)Li_2 + 2HCl$$

RESULT AND DISCUSSION:

The effects of various parameters on the growth of good quality crystals are as below.

3.1. Effect of various parameters on crystals growth- Study of kinetics of growth parameters reveals some interesting information. Effect of concentration of reactants, gel density, pH of gel, gel aging and concentration programming etc. was studied and is presented in this section with respect to the results obtained.

3.1.2 Effect of gel density- It was observed that the transparency of the gel decreases as the gel densities increases. Gels with higher densities set more rapidly than the gels with lower densities. It may be noted that well develop White colour crystals of lithium tartrate are obtained, with sodium meta silicate of density 1.04gm/cm^3.

3.1.3 Effect of concentration of reactants- As the concentration of tartaric acid is increased, more volume of sodium meta silicate was required to adjust the pH value round 4.0 to 4.2 Increased concentration of tartaric acid provides more tartrate ions to combine with lithium ions. With series of experiments the optimum conditions were obtained, Good quality crystals were grown at 1M concentration of tartaric acid.

3.1.4 Effect of concentration of supernatant- Lithium chloride dissolved in alcohol was used as supernatant with different concentration from 0.2M to1M. It was added over the set gel. It was observed that at 0.5 to 0.8M of concentration of supernatant very few nucleation's were observed with good quality white crystals.

3.1.5 Effect of pH of gel-It was observed that as the pH increased the transparency of the gel decreased. In the present work good crystals of Lithium tartrate are obtained at pH 4.0 to 4.2. The crystals growing at higher pH values were not well defined. This was due to contamination of the crystals with silica gel. It was observed that as the pH of gel increased the number of crystals decreased. As shown in table no.1

Table 1: Effect of concentration of supernatant (pH=4.4)

Test tube No.	Concentration of reactant above gel (supernatant- LiCl) M	No. of Nuclei	Observations
1	0.2	3	Crystals are not well defined. Very few nucleations, crystal size is very small.
2	0.4	6	Crystals are not well defined. Nucleation density increases, slight increase in crystal size
3	0.5	8	Star shaped, well isolated crystal
4	0.6	10	Well isolated crystals of various shapes and sizes.
5	0.8	15	Semitransparent, whitish, shining, isolated crystals; faces were well developed with bigger size crystals.
6	1	25	Transparent, whitish well isolated crystals.
7	1.2	30	Large number of crystals and are not isolated.

5. Effect of Temperature – All crystal growth experiments were carried out at room temperature. Optimum conditions are tabulated in table no.2. Fig.1 shows the grown of crystal of lithium tartrate..

Table No.2 Optimum conditions for growth of Lithium tartrate crystals.

Va Various Process Parameter	Optimum conditions
Density of sodium meta silicate solution	1.04 g/cm^3
Concentration of tartaric acid	1 M
Volume of Tartaric acid	7 ml
Concentration Lithium chloride	0.2 to 1 M
Volume of sodium meta silicate solution	18 ml
pH of the mixture	4.2
Environment Temperature	25 to 30°C
Gel setting time	120 Hours
Solvent are used	Ethanol, Methanol

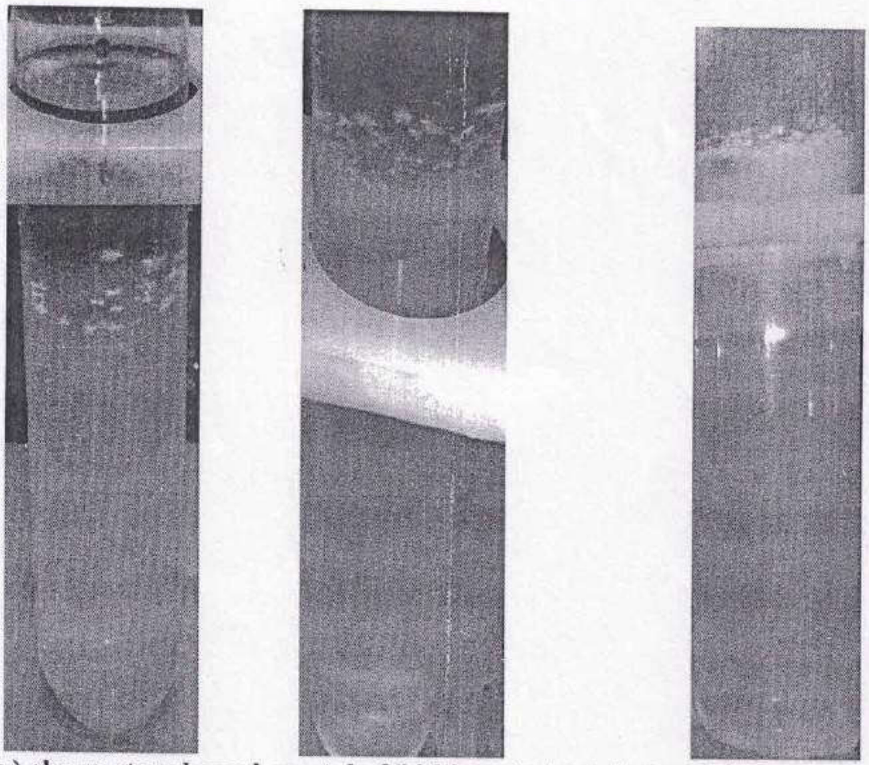

Figure 1(a, b, and c) shows star shaped crystal of Lithium tartrate in test tube

CONCLUSIONS:

1) Gel method is very simple and within the scope of the laboratory, method be utilized to synthesize crystals, if optimum conditions are established..
2) The grown Lithium tartrate crystal are white color.
3) Good size of crystals are grown.
4) The supernatant solution prepared in methanol and ethanol gives good quality crystals.

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REFERENCES:

[1] Nazir Ahmad, and P.N. Kotru. *"Journals of crystal growth" 24 November 2014.*

[2] B.Suresh Kumar and K. Rajendra babu, *Bull. Mater.Sci. Vol. 30, 4 Aug. PP. 349-355. 2007.*

[3] S. J. Shitole and K. B. Saraf, *Bull. Mater. Sci. vol. 24, no. 5,pp. 461-468.2001*

[4] V Mathivanan and M Haris *Indian Jornals of Pure and Applied Physics, Vol.51, PP.851-859. Dec* 2013

[5] D. K. Sawant., H. M. Patil and D. S. Bhavasar, *Scholars Research Library Archives of Physics research*,vol.1,no.1,pp. 8-14, 2012

[6] D. K. Sawant, H. M. Patil and D. S. Bhavasar, *Scholars Research Library Archives of Physic sresearch* vol. 2 ,no.2,pp. 67-73, 2011.

[7] S.J. Nandre, S.J. Shitole, and R.R. Ahire., Journal of Nano-and Electronic Physics. 4(4),(2012).

[8] S. L. Garud and K. B. Saraf, Bull. Mater. Sci., 32, 187,(2009).

[9] S. K. Arora, V. Patel, R. G. Patel, Amin B.and Anjana Kothari., J. Phys. Chem. Solids, 65, 965, (2004).

[10] M. H. Rahimkutty, K. R. Babu, K. S. Pillai, M. R. Sudarasana Kumar, CMK Nair.,Bull.Mater.Sci.24,249,(2001).

[11] H. B. Gon, J. Cryst. Growth., 102, 501,(1990).

[12] S. S. Sonawane, S. J. Nandre, S. J. Shitole and R. R. Ahire., Archives of Applied Science Research, 5,3,(2013)

“INFLUENCE OF FIRING TEMPERATURE ON COMPOSITIONAL AND STRUCTURAL PARAMETERS OF SCREEN PRINTED TIO$_2$ THICK FILMS”

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Abstract: TiO$_2$ thick films prepared by a standard screen printing method, the films as deposited and fired between 350, 450 and 550 ^{O}C for 2 hours in an air atmosphere. The influence of firing temperature on compositional, morphological and structural parameters such as crystallite size, texture coefficient, RMS microstrain, dislocation density and stacking fault probability have been studied. The material characterization was done using XRD, FESEM and EDS. The deposited films were polycrystalline in nature having the anatase& mix anatase- rutile structure with a preferred orientation along the (101) plane.

Keywords : TiO$_2$ films, Screen printing, Firing temperature, Structural Parameters.

INTRODUCTION:

Screen printing technique was introduced in the later part of 1950's to produce compact, robust and relatively inexpensive hybrid circuit for many purposes. Later on thick film technique has attracted by the sensor field [1]. Several deposition methods have been used to grow undoped and doped TiO$_2$ films such as Spray pyrolysis, Vacuum evaporation, chemical vapor deposition, magnetron sputtering, pulsed laser deposition, sol-gel technique, screen printing technique [2].Screen printing is simple and economical method to produce thick films of various materials [3-10]. Titanium dioxide can be synthesized in three crystalline phases: rutile, brookite and anatase. [11]. Semiconducting metal oxides (SMO) such as TiO$_2$, WO$_3$, Fe$_2$O$_3$, ZnO, SnO$_2$ etc. offer the potential for developing portable and inexpensive gas sensing devices, which have advantages of simplicity, high sensitivity and fast response. TiO$_2$ is a widely studied transition metal oxide and behaves as n-type semiconducting oxide due to non stoichiometry. The aim of the present work deals with preparation procedure of TiO$_2$ thick films by screen printing technique and studies their structural properties at different firing temperatures.

2. Experimental details:

2.1. Preparation of TiO$_2$ Thick film Sensors:

Table 1.*Preparation of* TiO$_2$ *films*

1	Substrate material	Glass
2	Active Material	TiO$_2$ (AR Grade)
3	Deposition Technique	Screen Printing
4	Types of screen	40S-Mesh No.355
5	Material Calcined time	1 hour.
6	Calcined temperature	400 ^{o}C
7	Active Material to Organic vehicles ratio	70:30
8	Organic vehicles (Binders)	BCA & EC
9	Settling time	15-20 minutes.
10	Drying under IR Lamp	45 minutes.
11	Firing Time	2 hours.
12	Peak firing temperature	350,450 & 550 ^{o}C

2.2. Structural characterization:

The crystallite size was determined using Scherrer's formula.[12]

$$D= 0.9\lambda /\beta \cos\theta \text{ ----- } (1)$$

The dislocation density was calculated using the equation:[13]

$$\rho= \sqrt{12} (e^2)^{1/2} /dD \text{ ----- } (2)$$

The stacking fault probability was calculated using the equation:[14]

$$\alpha = (2\pi^2\Delta(2\theta))/(45\sqrt{3} \tan\theta_{101}) \text{ ----- } (3)$$

The **Texture coefficient (T$_C$) was** calculated using the equation:[15]

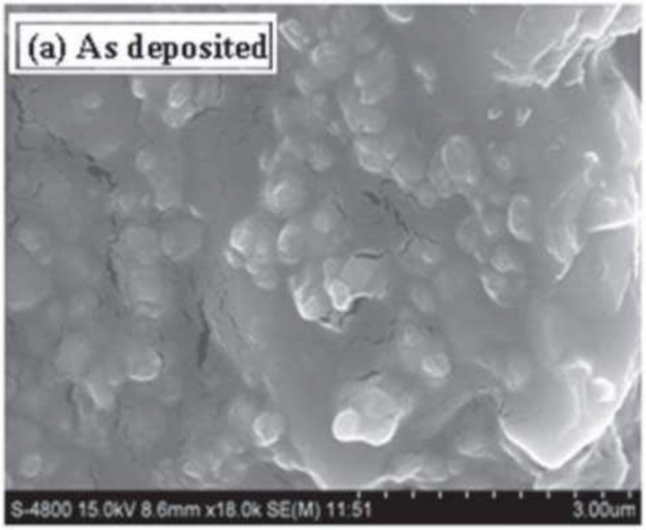
$$\mathbf{T_C =[I(hkl)/Io(hkl)]/[(1/N)\sum I(hkl)/Io(hkl)]} \text{ ----- } (4)$$

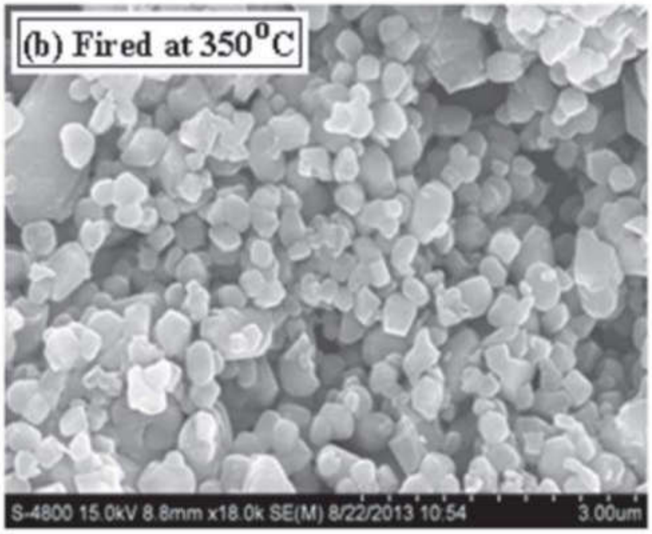
RESULTS AND DISCUSSION :

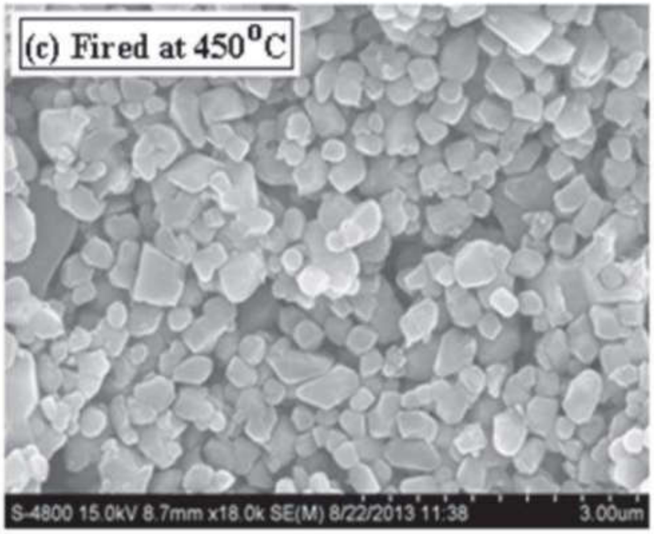
3.1. Surface Morphology Analysis:

Fig.1 (a), (b), (c) and (d) represents the SEM images of TiO$_2$ thick film samples fired at (a) as deposited, (b) 350 ^{0}C, (c) 450 ^{0}C, and (d) 550 ^{0}C respectively.

It has been observed that an increase in the firing temperature leads to an increase in the crystallite size and decrease in surface area. The loss in surface area available upon elevated heat treatment would affect the sensitivity.The particle size increases with an increase in the firing temperature hence specific surface area decreases. Normally, the smaller its grain size, specific surface area and oxygen adsorption quantity, the higher its gas sensitivity. The sensing properties of materials always benefit from the large specific surface area, which can improve the interaction between oxygen and material surface [16].







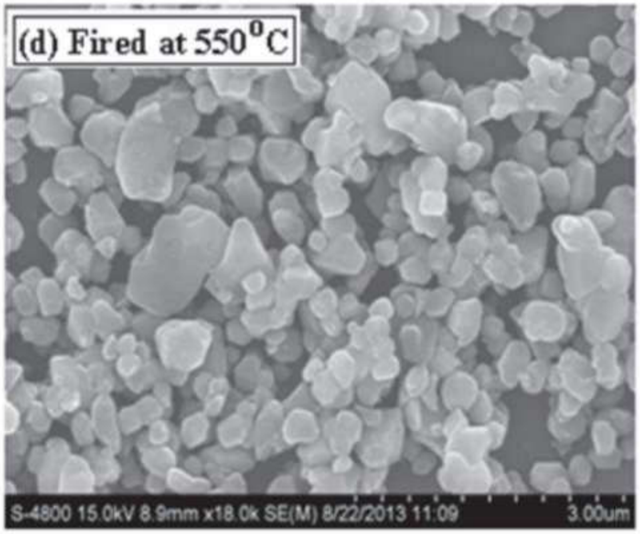


Fig. 1. SEM images of TiO_2 thick film samples fired at (a) as deposited, (b) 350 ^{0}C, (c) 450 ^{0}C and (d) 550 ^{0}C.

3.2. Elemental Composition:

Table 2 shows the composition of the films fired at different temperatures. From the analysis it was found that the TiO_2 films are non stoichiometry. The mass % of Ti and O in each sample was not as per the stoichiometric proportion and all samples were observed to be oxygen deficient. It is very important for gas sensing applications. The deficiency or excess of any type of atom in the crystal results in a distorted band structure, with a corresponding increase in conductivity. TiO_2looses oxygen on firing so that Ti is then in excess. The oxygen, of course, evolves as an electrically neutral substance so that it is associated with each excess Ti ions in the crystal, there will be two electrons that remain trapped in the solid material, thus leading to non-stoichiometricity in the solid. This leads to the formation of the n-type semiconductor [17]. The EDAX results show lot of variation Ti /O ratio with firing temperature.

Table 2. Composition of TiO_2 films.

Element (Mass %)	Firing Temperature			
	As deposited	350 ºC	450 ºC	550 ºC
Ti	67.36	78.22	79.50	83.18
O	32.64	21.78	20.50	16.82

3.3. XRD spectra analysis:

Fig.2 shows X-ray diffraction patterns obtained for TiO_2 thick films deposited on glass substrates and fired at 350, 450 and 550 ^{0}C. In all XRD spectra, the respective diffraction peaks corresponding to (101A),(004A), (112A),(200A) & (211A),crystal planes of anatase phase and (110R), (111R) & (112R)crystal planes of rutile phase were observed. Also the minor diffraction peak (204A) corresponds to anatase phase was observed in the XRD spectra of film fired at 450^{O}C and

550^{O}C.The XRD spectra showed the presence of TiO_2, match well with reported JCPDS data card No. 83-2243 (Anatase) and 83-2242 (Rutile) for confirming polycrystalline structure of the film. It has been observed that the XRD peak broadening decreases with an increase of the firing temperature. The intensity of reflections increases with a rise in the firing temperature. Also XRD analysis evaluates thegrain size of the thick films as function of the temperature. From this analysis all films were shown random orientation of polycrystalline nature of the material. The most pronounced and strongly reflected peak (101) was observed at 25.2º. Also for further temperature surface area decreases as grain size increases hence sensitivity decreases.

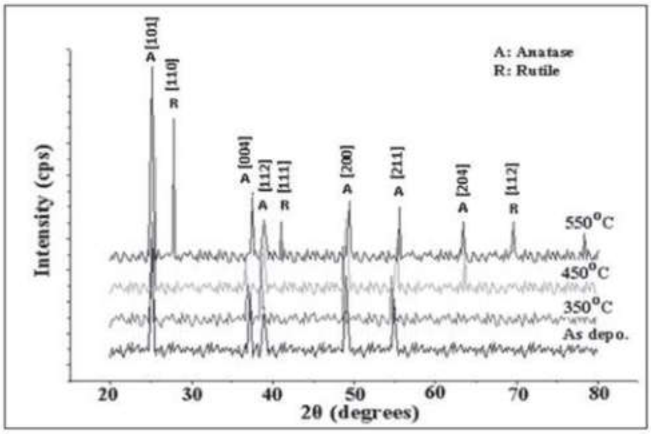


Fig. 2.XRD pattern of TiO_2 at different firing temperatures

3.4.Structural Parameters and their Analysis:

Dislocation density is defined as the length of dislocation lines per unit volume of the crystal . A dislocation is an imperfection in a crystal associated with the misregistry of the lattice in one part of the crystal with another part. The dislocation density calculated using equation-2[18] at different firing temperatures indicates a decreasing trend with firing temperature and is given in Table 3.

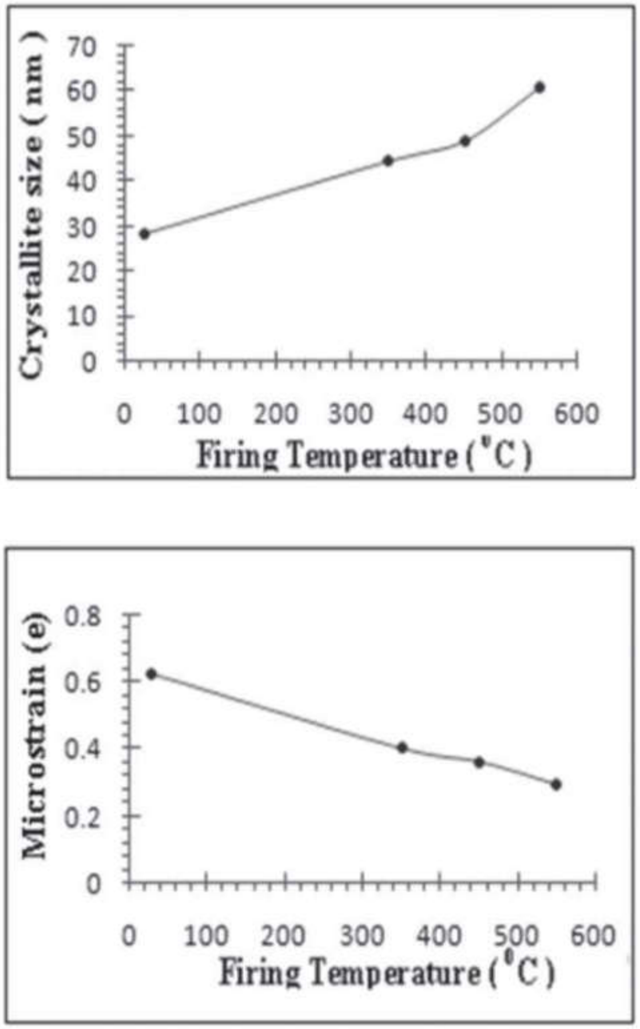
A stacking fault is a planar imperfection that arises from the stacking of one atomic plane out of sequence with another while the lattice on either side of the fault is perfect. The presence of a stacking fault gives rise to a shift in the peak positions of observed reflections with respect to the ideal JCPDS positions of the sample [19]. From the XRD patterns of films, the peak shift ($\Delta 2\theta$) for the oriented (101) plane was measured with a change in firing temperature. The stacking fault probability was calculated using equation-3 [18] at different firing temperatures is given in Table 3.

Texture Coefficient (T_C)calculated using equation-4 [20-21], it was observed that Texture Coefficient approaches less than unity. The lower values of T_C reveal that the films have poor crystallinity.

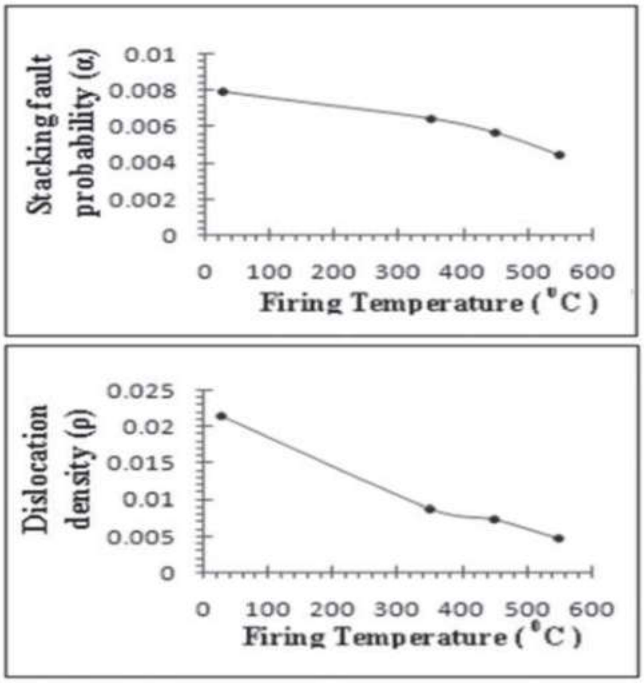
A uniform compressive or tensile strain (macrostrain) results in a peak shift of the X-ray diffraction lines.Broadening of X-ray diffraction line profiles is mainly caused by non-ideal optics of the instrument, wavelength dispersion, and microstructural imperfections in the crystals. The microstructural line broadening can be subdivided into size broadening and strain broadening. Strain broadening is caused by a varying displacement of the atoms with respect to their reference-lattice positions.

Table 3. Variation of structural parameters with firing temperatures.

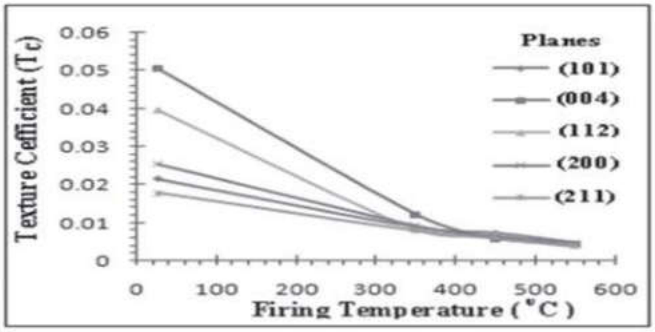
Firing Temp. ^{O}C	Structural Parameters for strong (101) orientation			
	Crystallite Size D (nm)	Microstrain (e)	Stacking fault probability (α)	Dislocation density (ρ)
As deposited	28.54429	0.628462	0.007954	0.021499
350^{O}C	44.69691	0.401631	0.006467	0.008768
450^{O}C	49.03268	0.362009	0.005703	0.007286
550^{O}C	61.18085	0.291817	0.004452	0.00468



(a) Crystallite size (D) (b) Microstrain (e)



(c) Stacking fault probability (α) (d) Dislocation density (ρ)



Texture Coefficient (T_C)
Fig. 3.Variation of Structural Parameters with firing Temperature.

CONCLUSIONS :

The thick films as deposited and fired at temperatures 350, 450 and 550°C were found polycrystalline. Films fired at 550 °C were observed mix anatase-rutile structure, more crystalline, porous, oxygen deficient and good adhesion to glass substrate. Increase in temperature improved the crystalanity and thus increased the mobility of atoms at the surface of the films. Crystallite size increased with an increase in the firing temperature, whereasmicrostrain, dislocation density and stacking fault probability decrease with an increase in the firing temperature. Compositional and structural analysis confirmed that TiO_2 thick films were non-stoichiometry, which are suitable for gas sensing applications.

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REFERENCES

[1] N. Jaydev Dayan, S. R. Sainkar, R. N. Karekar and R. C. Aiyer, *Thin Solid Films*325, 254 (1998).

[2] B. Joseph, K. G. Gopalchandran, P. K. Manoj, P. Koshy and V. K. Vaidyan, *Bull. Material Sci.*22, 921 (1999).

[3] B. Krishnan and V. N. Nampoori, *Bull.Material Sci.*28, 239 (2005).

[4] X. Q. Liu, S. W. Tao and Y. S. Shen, *Sens. Actuators : B chemical*40, 161 (1997).

[5] S. G. Ansari, P. Boroojerdian, S. K. Kulkarni, S. R. Sainkar, R. N. Karekar and R. C. Aiyer, *Journal of Material Sci.*7, 267 (1996).

[6] M. Prudenziati and B. Morten, *Sens. Actuators B,* 10, 65 (1986).

[7] J. Kiran, R. B. Pant and S. T. Lakshmikumar, *Sens. Actuators B,* 113, 823 (2006).

[8] A. T. Nimal, V. Kumar and A. K. Gupta, *Indian Journal of Pure and Appl. Phys.*42, 275(2004).

[9] L. A. Patil , P. A. Wani, S. R. Sainkar, A. Mitra, G. J. Pathak and D. P. Amalnerkar, *Material Chem. Phys.*55, 79 (1998).

[10] C. A. Harper, Handbook of Thick film hybrid Microelectronics, *McGraw Hill Book Co. New York,* (1974).

[11] G. A. Tompsett, G. A. Bowmaker, R. P.Cooney, J. B. Metson, K. A. Rodgers and J. M. Seakins, *J. Raman Spectrosc*. 26, 57 (1985).

[12] B. D. Cullity, Elements of X-ray Diffraction, 2nd Edition, *Addition Wesley*, 1970, p. 102.).

[13] M. E. Manriquez, T. Lopezand R. Gomez, *J. Molecular Catalysis A: Chemical*, 220, 2004, pp. 229 237.

[14] K. Suresh Kumar and T. Mathews, *Journal of Alloys Compounds*, 391, 2005, pp. 177-180.

[15] Jaeyun Moon, Hanshin Choi and Changhee Lee, *Journal of Ceramic Processing Research*. Vol. 1, No 1, 2000, pp. 69-73.

[16] A. Teleki, *Sensors and Actuators B*, 119, 2006, pp. 683-690.

[17] L. Gao, Q. Li, Z. Song and J. Wang, *Sensors and Actuators B*, 71, 2000, pp. 179- 183.

[18] T. Mahalingam, V. S. John, L. S. Hsu, *Journal of New Materials for Electrochemical Systems*, 10, 2007, pp. 9-14.

[19] B. E. Warren and E. P. Warekois, *ActaMetallurgica*, 3, 1955, pp. 473-479.

[20] T. Schuler and M. A. Aegerter, *Thin Solid Films*, 351, 1999, pp. 125-131.

[21] K. H. Kim and J. S. Chun, *Thin Solid Films*, 141, 1986, pp. 287-295.

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Need of Automation of Library

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Abstract :

This paper discusses what is library automation, its importance, need and benefits in the modern era. Library automation has been became an integral part of LIS education and library routine activities. It also has restricted with norms by NAAC best practices in college libraries. Basically, automation is used to reduce the the amount of staff, time devoted to repetative activities that must be done in any properly functioning library. Various library process are automated not the library as such;. a fact many lay people fail to recognize.

Keywords:

Introduction Definition Historical perspective Need Advantages Disadvantages suggestions conclusion.

Indroduction:

"Third Genration" computers using something called integrated circuits began to replace the second genration units in the late 1960s what is important about these technological developments from the library point of view, is that integrated data systems could become a reality and computers and telecommunications could be used at a cost that many organizations could afford. The equipment (Hardware) as noted earlier is available and is steadily declining in cost. What has been and contineous to be a major problem is the programme (Software) of instructions that make the cmputer useful for various functions. Most of the library functions that have been automated and are in genral use in libraries are those that are tie to physical activities. In last few years, significant progress has been made in developing artificial Intelligence (AI) computers which replicate basic human thinking and reasoning. When the AI generations of computers become commercially available there will be major changes in library automation. The main purpose of library automation is to free librarian and library staff and to allow them to contribute more meaninfully to speread knowledge and information in in teaching, learning process of educational system.

Historical perspective:

Dating from the1960s the first use of library automation was the use of computers to store bibliograhic data and to enable the circulation of stock. The project to place onto computer the stock of the U.S. library of congress resulted ultimately in the development of Machine -Readable Cataloguing. Opening up the possibility of libraries exchanging bibliographic records and encouraging co-operation between libraries. In the 1970s the library management system became the main housekeeping tool in large libraries and this trend was continued through the following two decades, leaving very few libraries without some form of system. Other fundamental developments underway in the larger computer industry market place. These were the increasing power in the performance of personal computer', the increasing predominance of non propritory software, increasing competition but just as importantly enabling increasing exchange of data over networks and the developments of internet.

Definations of Library Automation:

Automation has many definations but for our purpose, the word automation has been derived from Greek word "automose" means something, which has power of spontaneous motion or self movement. The term "automation was first introduced by D.S.Harder in 1936 who was then with General motor company in the U.S. He used the term automation to mean automatic handling of parts between prograsive production processes. few difinations as below:

1. Acording to encyclopedia of library and information science "automation is the technology concerned with design and development of process and system that minimize the necessity of human intervention to operation"(kent 1977)

2. According to Mcgraw Hill encyclopedia of science and technology automatio as a "coined word having no precise genrally accepted technical meaning but widely used to imply the concept, development or use of highly automatic machinery or control systems. (Mcgraw hill 1982)

3. According to Martin Weiks standard dictionary of computers and information processing (New york Hayden Books1969) is satisfctory Automation the entire field of investigation devoted to the design, development and application of methods, techniques for rendering a process of group of machines seg- actuating, self moving or self controlling. Automation pertains to the theory, art or technique of making a machine, a process or device more automatic.

For libraries the most common automation device is the electronic digital computer. Library processes that now being controlled by the computer include book keeping, materials ordering, cataloguing, serials control, circulation bibliograpgic data, retrieval and some aspects of inter library loan work.

Need and Objective of Library Automation. :

Without Computer, automation cannot possible. How does a computer control library process? Basically, all computers (maxis, minis, or micros-more about this later) functions in the same manner. They can convert ("read") store ("remember") do arithmetic make simple logical choices ("processing) and display ("write").

Information explosion has resulted in the production of a large amount of literature in every field of knowledge accordingly the print documents are coming to the library in huge numbers which is not possible for a library to manage the collection manually.

Now a day's no user has time to search the required and relevant information from the dense heap of information collection. They have no time to go shelve by shelve to pick up a book si it necessitated for library automation: The various factors that necessitated changing a manually operated library system an automated library system. are as follow.

- Information Explosion
- Availability of Information in various formats {Print, Non Print, graphical audio-visual etc.}
- Recording keeping activities of library can be effectively in automated environment.
- Issue return and renewal of books can be performed quickly and searching of documents through Online Public Access Catalogue {OPAC} which is a powerful searching tool of library automation.
- To improve the management of their physical and financial resources.
- Maintain bibliographical records of all the materials in a computerized form.
- Provide bibliographical details through a single enumerative access point of holdings of a library.
- Duplication of housekeeping operations.
- Provide access to information at a faster rate.
- To search, share National and International database through library networking and implement new IT process to provide high quality information.
- To facilitate wider dissemination of library information products and services.
- Enable participation in resource sharing library networks and consortia.

Requirements of Library Automation

The main steps in the process of library automation

- Preparing for automation
- System selection {Software and Hardware}
- Preparing the collection for the automated system.
- Implementing the automated system.
- Networking
- OPAC
- Staff training and user orientation.
- Evaluation
- Planning for the future.

1. Preparing for automation : Preparing for an automation system needs evaluation and planning before implementation .Statistics regarding total number of stock accession of materials, daily issue and return, time taken for routine activities, services given its effectiveness etc. were studied to find a true picture of the current status of the college library and indentifies problems facing by the students and teachers.

2. Need Assessment : Routine library activities such as circulation service involves a series of jobs such as registration of the users, issuing or charging of documents, returning oor discharging of documents, sending of reminders for over-due publications , renewal of documents reservation of documents, collection of over-due fines for documents which are returned after due date, maintenance of issue records etc. Annual stock verification and generation of monthly library statistics were not set up to the standards; an automation will make the things better. Adoption of library automation substantial reduction of time in the library house keeping process which the fourth law "Save the time of the reader strongly advocate.

Selection of System :

I) Software - Selecting the right integrated library management software package is very significant task. The strength of the automation is mainly depend on the quality of the system software. A number of software are available in the market place some software has special college library modules for the selection certain things should be remembered.

Selection Criteria, User friendliness Portability after Service cost proper documentation etc.

The success of library automation mostly depends upon the nature of the software used for the purpose. Different types of software available which are as follows

A. In-house development software or custom designed
B. Software packages developed by commercial agencies, organizations, and institutions.
C. Cooperative vendors.

Therefore selection of good library software is one of the important function of the library automation programme. List of commercial library automation software packages are given bellow.

No. Software Package	Developing Agency
1. Archives(1,2,3)	Microfax Electronic; Systems, Bombay
2. Acquas, Ascat, Ascir, Asire, Seras	Ober Information System, Calcutta
3. Basisplus & Techlibplus	Information Dimention Inc (IDI), USA (Marketed in India by NIC)
4. Catman	INSDOC, New Delhi
5. Defence Library Management System	DESIDOC, New Delhi
6. Golden Libra	Golden Age Software Technologies, Bombay
7. Granthalaya	INSDOC, New Delhi
8. Libman	Datapro Consultancy Services, Pune
9. Libra	Ivy System Ltd., New Delhi
10. Librarian	Soft-Aid, Pune
11. Library Management	Raychan Sysmatics, Bangalore
12. Library Manager	System Data Control Pvt Ltd., Bombay
13. Libris	Frontier Information Technologies Pvt. Ltd.,
14. Libsys, Micro-Libsys	Libsys Corpn., New Delhi
15. Library Manager	System Data Control Pvt Ltd., Bombay
16. Maitrayee	CMC, Calcutta (for the CALIBNET Project)
17. Slim 1.1	Algorythms, Bombay
18. Autolib	Akash Infotech Pune

Hardware:

Hardware is the next important elements of library automation programme number of products and manufacturers are available for this purpose. The hardware configuration mainly depends upon the software. There are two ypes of PCS are available in the market.

I. The branded PCs from reputed firm HP Compaq IBM etc.
II. The assembled PCs from commercial firms.

Manpower: For running any programme trained manpower are required. Hence the library professional staff should be trained properly with requisite computer knowledge for making the automation programme successful..Some sotware manufacturers are providing onsite training to the staff at the installation of software.

Finance: Finance is the blood of any system. The finance of any automation programme includes both installation and ongoing expenditures which includes maintenance, stationeries etc.

Advantages and disadvantages of library automation

Advantages of Library automation	Disadvantages of library automation
1. Easily searching of information	It is long term time consuming process
2. Time Saving	Financial expenses
3. Speedily Communication	Continuous staff training required
4. Helpful in stock verification	Security problems
5. Easily working with help of automation	Totally depends on electricity
6. Helpful in resource sharing and networking	Costly maintenance
7. It motivate to library staff	Untrained users
8. Development of library staff	

There are many inherent problems associated with library automation which can be summarized as bellow

1) Initial investment for automation programme is ver high.
2) Library staff has to undergo intensive training on automation
3) The professionals are initially psychologically traced.
4) Retrospective conversion data for big college libraries.
5) Regular update with software package.

Conclusion:

To run library automation programme in Indian libraries, we have to focus on following points

1. Economical help should be provided by central, state, local government and library authority, according to library and information policy.
2. Libraries should be conducted training programme time to time for the development of library staff.
3. Librarian should be selected appropriate hardware and software for library automation.
4. All the data or information should be secure with the help of different security tool such as use of anti-virus, firewall and taking a back-up data time to time.
5. Inverter should be used for poser.

This paper attempts to give some idea for beginners in library automation. Now a days library automation has become the buzz word in library profession and has become a bare necessity for any type of libraries. A. Automated library can offers better qualitative library and information services to their users and can maintain the library properly which manually library can't do. The record keeping activities and various report generation becomes very easy in an automated library system.

References:

1. Pandey, R (2008) NET/SLET library and information science
2. Singh M.(1988)library and information management: Theory and practice.
3. John Feather and Paul Sterges, International encyclopaedia of information and library science ed.2nd 2003
4. Faizal, S.L (2008) Report on automation of library at kendriya vidyalay pattom ,Thiruananthpuram
5. International journal of research in library science vol.1 issue1.

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Non conventional Energy Sources for Rural Development of India

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Abstract

India has a vast supply of renewable energy resources, d it has one of the largest programs in the world for deploying renewable energy products and systems. Indeed, it is the only untry in the world to have an exclusive ministry for renewable energy development, the Ministry of Non- nventional Energy Sources (MNES). Since its formation, the Ministry has launched one of the world's largest and most us programs on renewable energy. Based on various promotional efforts put in place by MNES, significant progress being made in power generation from renewable energy sources. In October 2006, MNES was renamed the Ministry New and Renewable Energy. Energy security, economic growth and environment protection are the national energy icy drivers of any country of the world. There is an urgent need for transition from petroleum based energy systems to e based on renewable resources to decrease dependence on depleting reserves of fossil fuels. Renewable energy has the ential to create many employment opportunities at all levels, especially in rural areas. Enhancing the regular use of ewable energy sources, promoting deployment, innovation nd basic research in renewable energy technologies, resolving barriers to development and commercial deployment of olar, wind, hydropower, geothermal, nuclear and biomass nologies in rural area is today's need. In this review paper, arious renewable energy resources, their potential of ducing electricity, their cost effectiveness, repeatability, fficiency, applications and limitations, transport and storage ms are focus of discussion.

y Words - Renewable energy sources, Solar, Wind, lropower, Geothermal, Nuclear.

Introduction

In recent years, India has emerged as one of the leading stinations for investors from developed countries. This action is partially due to the lower cost of manpower and od quality production. The expansion of investments has ght benefits of employment, development, and growth in e quality of life, but only to the major cities. This sector only esents a small portion of the total population. The maining population still lives in very poor conditions. India ow the eleventh largest economy in the world, fourth in ms of purchasing power. It is poised to make tremendous omic strides over the next ten years, with significant velopment already in the planning stages. This report gives verview of the renewable energies market in India. We k at the current status of renewable markets in India, the gy needs of the country, forecasts of consumption and duction, and we assess whether India can power its growth and its society with renewable resources.

Renewable energy technology has sometimes been seen as a costly luxury item by critics and affordable only in the affluent developed world. This erroneous view has persisted for many years, but 2015 was the first year when investment in non-hydro renewable, was higher in developing countries, with $156 billion invested, mainly in China, India, and Brazil. Most developing countries have abundant renewable energy resources, including solar energy, wind power, geothermal energy and biomass, as well as the ability to manufacture the relatively labor-intensive systems that harness these. By developing such energy sources developing countries can reduce their dependence on oil and natural gas, creating energy portfolios that are less vulnerable to price rises. In many circumstances, these investments can be less expensive than fossil fuel energy systems.

In isolated rural areas, electricity grid extensions are often not economical. Off grid renewable technologies provide a sustainable and cost effective alternative to the diesel generators that would be otherwise be deployed in such areas. Renewable technologies can also help to displace other unsustainable energy sources such as kerosene lamps and traditional biomass. The organization is named as Nonconventional Energy and Rural Development Society in order to promote the nonconventional energy sources like biogas plants to recover methane from animal dung night soil individual waste market waste agricultural biomass and municipal solid waste and also solar gadgets. It had mainly installed individual domestic type biogas plants for the farmers. The domestic plants mainly cater the needs of cooking and lighting demand of the family. The size of the plant ranges from 1 cum to 6 cum. The organization has organized more than 450 village level awareness camps to identify and motivate the potential beneficiaries and farmers for the installation of biogas plants. The organization had contacted the banks for getting the loan for the installation of the plants and also the Government for getting the subsidy. The organization has been recognized as Business Development Associate of Indian Renewable Energy Development Agency of Government of India for undertaking the projects on renewable energy sources particularly for biogas plants. It had installed biogas plants in the remote tribal area viz Thalingi settlement of Amaravathi Forest Range in each state to electrify the entire village. The tribal settlement has no possibility of electrification through the conventional means of electricity because it is located in the interior forest without road connectivity and transport facilities. The remote villages are to be electrified through decentralized generation using nonconventional energy sources. The technology to be used

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will depend on the size of the village and the resources available locally. A prime example of demonstration of electrification through biogas technology by the proposing organization is the Thalingi Tribal Village as first of its kind in India. The organization had installed more than 50 VermiComposting units to produce value added organic manure by making use of biodigested slurry coming out of the biogas plants. Through the promotion of VermiComposting units integrated with biogas plants the farmers were able to meet their entire fertilizer need for the organic farming. The organization has implemented a novel waste to energy and manure project. The organization is promoting Women Self Help Groups and Men Youth Groups for their empowerment and bank loan with government subsidy for the purchase of Milch animals and thereby they will be in a position to install biogas plants to meet their energy demand and the thereby selfsufficiency in fuel and fertilizer requirement. So far it had formed about 4000 Self Help Groups benefiting about 60,000 below poverty line families. On summarizing the organization experience we can conclude that the organization is having 27 years of rich experience in renewable Energy projects mainly benefiting women and farmers.

It is not an exaggeration to state that 'humanity is facing a choice between a peaceful decision on its common energy future or wars for resources in the near future. The world Population is set to grow by 0.9 percent per year on average, from an estimated 6.7 billion in 2008 to 8.5 billion in 2035, according to UNDP estimates. The situation for India is especially grim because of the deficit on even existing demand level. As such, there is a dire need for trapping and using non-conventional energy sources in India for the survival of future generations. However, it is clear that grid extension in rural areas is often not cost effective. Hence, decentralized electricity generation with non-conventional energy sources such as wind, hydro, solar, biomass, biofuels and energy from waste are best suited to the increasing demand.India has a vast supply of renewable energy resources, and it has one of the largest programs in the world for deploying renewable energy products and systems. Indeed, it used to be the only country in the world to have an exclusive ministry for renewable energy development; Ministry of New and Renewable Energy Sources (MNRE) supports the implementation of a large broad-ctrum of programs covering the entire range of new and renewable energies. These programs broadly seek to supplement conventional fossil fuel based power with renewable energy and make it available to remotest rural areas for a variety of applications like water pumping for irrigation and drinking water purposes, dying farm produce, improved chulhas and biogas plants, energy recovery from the urban, municipal and industrial wastes. In addition, they plan to exploit hydrogen energy, geothermal energy, tidal energy and biofuels for power generation and automotive application on large scale.

Discussion –

India is the fifth largest consumer of energy in the world, and will be the third largest by 2030

Why Non-Conventional Energy - In 2013-14, peak power shortage of India was around seven percent and electricity demand is expected to rise by 7.4 per cent a year during the next quarter of a century. Unfortunately, India cannot realistically expect to bridge this power deficit by increasing reliance and dependence on the fossil fuels. The reason for the same are many, ranging from socio-economic to environmental and health issues. According to Energy Statistics 2012, India imports about 75 percent of its oil which in fact comprises one- third of its total imports. Similarly, India's coal imports are likely to touch a whopping 185 million tones by 2017. Hence, the Indian government has been also making serious efforts to enhance India renewable energy production since recent past.

A major advantage of renewable energy is that it can be regenerated and is therefore sustainable as it will never run out. It has several advantages over its hydrocarbon based alternatives and provides substantial benefits for our climate, our health and our economy. Some of the important benefits of renewable energy are, little to be no global warming emissions, improved public health and environmental quality, a vast and inexhaustible energy supply, stable energy prices and a more reliable and resilient energy system. At the same time, the country is heavily dependent on fossil sources of energy for most of its demand, thus necessitating to aggressively pursue alternative energy sources such as solar, wind, biofuels, small hydro, geothermal and others. The country has an estimated renewable energy potential of around 85,000 MW from commercially exploitable sources: wind: 45,000 MW, small hydro: 15,000 MW and biomass/bioenergy: 25,000 MW. In addition, India has the potential to generate 35 MW per square km using solar photovoltaic and solar thermal energy.It has proposed an addition of 15,000 MW of Renewable Energy generation capacities during the period. Of this proposed capacity addition, wind power projects are expected to pitch in about 70 percent (10,500 MW) while Small Hydro Projects (SHP) would accounts for 9.3 percent (1,400 MW). Power plays a great role wherever man lives and works. The living standard and prosperity of a nation vary directly with the increase in the use of power. The electricity requirement of the world is increasing at an alarming rate due to industrial growth, increased and extensive use of electrical gadgets. According to world energy report, we get around 80% of our energy from conventional fossil fuels like oil (36%), natural gas (21%) and coal (23%). It is well known that the time is not so far when all these sources will be completely exhausted. Nuclear energy is a comparatively clean source of energy. However, safe handling of nuclear energy reactor is a sophisticated task and only around 7% of the world's total energy requirement is being satisfied by it today. As human needs know no bounds, today most of the nations worldwide have been passing through a phase of power deficit. The crisis is more critical among the developing nations. In India, energy demand is increasing at the rate of 9% per annum and supply is not keeping pace. Present deficit of electrical energy is 8%. The increased power demand, depleting fossil fuel resources and growing environmental pollution have led the world to think seriously for other alternative sources of energy. Basic concept of alternative energy relates to issues of sustainability, renewability and pollution reduction. In reality alternative energy means anything other than deriving energy via fossil fuel combustion. Various forms of alternative energy sources are solar, wind, biogas/biomass, tidal, geothermal, fuel cell, hydrogen energy, small hydropower etc. Solution to long-term energy problem will come only through Research and Development in the field of alternative energy sources. Many rural communities consume little electricity, and extending electricity grids to meet their energy needs may prove more costly and take longer than harnessing new and alternative sources of energy already available in these communities — wind, solar, and biomass — through Renewable Energy Technologies (RETs). The attraction of these sources lies primarily in their abundance and ready access. The RETs for exploiting these sources include biogas plants, solar lanterns, solar home lighting systems, improved cook stoves, improved kerosene lanterns, solar water pumping systems, solar water heating systems and water mills. Solar energy panels are little costly considering our average economic standard. Studies indicate that cooking with biogas highly combustible fuel comprising methane, carbon dioxide, nitrogen, hydrogen and hydrogen sulphide produced through anaerobic fermentation of organic matter) can be cheaper than cooking with any commercial fuel. Due to limited oil reserves, India has to depend on substantial imports for meeting its present and future requirement. The bulk of demand for oil is from transport sector [illegible] in order to reduce the pressure from this sector it is necessary to explore possibilities of developing substitute fuels like biomass and producer gas. Wind power has also proved to be a viable energy alternative. In India, more than 1.3 giga watts of wind energy capacity has been added over the past six years exclusively in the private sector, which either sells electricity to the electric utilities or wheels it over the utility grid for self-consumption.

Implementation of Issues

While there is no denying that nonconventional power is a boon, there are some practical implementation issues which often trouble investors. These range from physical damage to installed equipments to environmental issues. For instance, wind turbines can be hazardous to flying birds, while hydroelectric dams can create barriers for migrating fish, in addition to displacement of human habitations. Burning biomass and bio-fuels causes air pollution similar to that of burning fossil fuels, although it causes a lower greenhouse effect since the carbon placed in the atmosphere was already there before the plants were grown.

Another issue to consider is of evacuation infrastructure. Just [illegible]e conventional sources or power, significant non-conventional power generation resources are often located at large distance from the major population centers where electricity demand exists. Exploiting such resources on a large scale inevitably requires considerable investment in transmission and distribution networks as well as in the technology itself. Furthermore, power generation from renewable sources is very often intermittent in nature. Solar energy, for example can only be expected to be available during the day (50 percent of the time). Wind energy intensity varies from place to place and somewhat from season to season. Constant stream of water is often not available throughout the year for generating optimum Hydro power. This requires a substantial investment in storage capacity which adds to the overall cost of generating power. When seen in light of massive and sustained energy deficit and the grid failure which led to the world's largest power outage a couple years ago, which affected 700 million people, India needs a drastic overhaul of its energy sector. The unreliable supply of electricity, depleting natural resource and irreparable environmental degradation has become big challenges to sustainable development of the country, economically and socially.

India's tremendous energy needs cannot be met solely with conventional method of electricity generation. To overcome these problems and to meet the future energy demands, India must go towards harnessing huge potential of non-conventional source of energy. It has several advantages including decentralization of energy particularly for meeting rural energy needs, and thereby empowering rural people at the grass roots level. Like any other source, nonconventional energy has got some associated issue which needs to be resolved before aggressive deployment of electricity production from these sources can take place. The exact type and intensity of environmental impacts varies depending on the specific technology adopted, the geographic location, and other operational factors. Thus, we must stress upon research and development not only to understand the current and potential environmental issues associated with each renewable energy source but also to develop cleaner technologies. It will help achieving the national security and economic goal on the one hand and will provide enormous environmental benefits and combat climate change on the other.

Focus Area in Non Conventional Sources –

Wind Energy - India's wind power potential has been assessed at 48,500 MW. The current technical potential is estimated at about 13,000 MW, assuming 20 percent grid penetration, which would increase with the augmentation of grid capacity in potential states.India is implementing the world's largest wind resources assessment program comprising wind monitoring, wind mapping and complex terrain projects. This program covers 800 stations in 24 states with around 200 wind monitoring stations in operations at present. Windmill is an old invention and new application. For long time energy is being harnessed from wind to sail ships, grind grains and pump water. Wind power is the world's fastest growing energy resources growing at the rate of 27% per year. The sale of wind turbines in the year 2000 was to the tune of 4 billion dollars. In 2000, wind turbines produced almost 18000 megawatts of electricity worldwide and that is enough to meet the needs of 5.5 million homes. If the current growth is maintained it could produce about 10% of the world electricity needs by 2020.Wind can be used to do work. The kinetic energy of the wind can be changed into other forms of energy, either mechanical energy or electrical energy. The wind energy conversion technology functions in the following way. The wind while passing the windmill, converts its velocity with the help of windmill blades into mechanical energy and the mechanical energy is converted into electric power by means of a generator. For a wind turbine to work efficiently, wind speeds usually must be above 12 to 14 miles per hour to turn the turbines fast enough to generate electricity. The turbines usually produce about 50 to 300 kilowatts of electricity each. Once electricity is made by the turbine, the electricity from the entire wind farm is collected together and sent through a transformer. There the voltage is increased to send it long distances over high power lines. Wind power is known as 'Green Power', because of its technical and commercial viability and its environment-friendly nature. The special features of wind energy that makes it attractive are zero cost fuels, low gestation period, quicker benefits and usefulness for sustainable economic development.

The cost of power generation is estimated to be Rs. 2 to

Rs. 2.50 per KWh, depending on the site. The cost per unit of power comes down to 50 KWh, five years after the project commissioning due to the cost of fuel being nil. Thereafter, for the next 15 years, it would stay at this level, as the only recurring cost would be on the operations and maintenance of the plant. Therefore, wind harvested power is both cheaper and reliable than other conventional sources of power. Need for the use of energy through solar, wind and biomass sources in remote areas is increasing and will put the nation at the forefront of renewable power used; with the government recently proposing renewable energy standard for the nation. Outlines the renewable resources that are currently utilized in India, and the Government's Common Minimum Program to establish enough renewable energy sources to electrify all Indian villages by 2010.Under the program, an additional 4,000 MW of power from renewable sources would be added to the nation's current power generation by 2007, and the government has set a goal of elevating the share of renewable energy sources to 10% by 2012. Currently, according to the Bureau, renewable energy contributes about 5,000 MW of the nation's power needs. That is only 4.5 percent of the total installed generating capacity from all available power sources

India Wind power alone accounts for 2,483 MW, which makes the nation's wind energy program the fifth largest in the world. The features of wind energy that makes it attractive are zero fuel costs, and quicker benefits and usefulness for sustainable economic development. Gross-wind energy potential in the country is estimated at 45,000 MW, and the states with high wind power potential are Tamil Nadu, Maharashtra, Gujarat, Andhra Pradesh, Karnataka, Kerala, Rajasthan and Madhya Pradesh. The development of infrastructure facilities, will expedite the process of economic development. Energy is the most crucial input for power generation projects and this will certainly contribute to the socio-economic development of the country. Even after rapid industrialization, India is still dependent on agriculture, which is the backbone of Indian economy. To increase the agriculture production irrigation facilities, for which electricity is needed, have to be installed. Wind energy is pollution-free as wind fans have potential to reduce CO2 emissions. India is one of the few countries in the world that has made significant attempts to harness these indigenous energy sources. Rural ctrification is very essential for the social development. Energy generation by wind reduces the generation cost and will help in balancing the cost of energy.

Hydro Energy – Hydroelectricity is electrical energy generated when falling water from reservoirs or flowing water from rivers, streams or waterfalls (run of river) is channelled through water turbines. The pressure of the flowing water on the turbine blades causes the shaft to rotate and the rotating shaft drives an electrical generator which converts the motion of the shaft into electrical energy. Most commonly, water is dammed and the flow of water out of the dam to drive the turbines is controlled by the opening or closing of sluices, gates or pipes. This is commonly called penstock. Hydropower is the most advanced and mature renewable energy technology and provides some level of electricity generation in more than 160 countries worldwide. Hydro is a renewable energy source and has the advantages of low greenhouse gas emissions, low operating costs, and a high ramp rate (quick response to electricity demand), enabling it to be used for either base or peak load electricity generation, or both.Hydro power is the largest renewable energy resource being used for the generation of electricity. The 50,000 MW hydro initiatives have been already launched and are being vigorously pursued with detailed project report (DPRs) for projects of 33,000 MW capacities already under preparation. Harnessing hydro potential speedily will also facilitate economic development of states, particularly North-Eastern States, Sikkim, Uttaranchal, Himachal Pradesh and J&K, since a large proportion of our hydro power potential is located in these States. In India, hydro power projects with a station capacity of up to 25 megawatt (MW) each fall under the category of small hydro power (SHP).

Solar Energy - Solar energy is radiant light and heat from the Sun that is harnessed using a range of ever-evolving technologies such as solar heating, photovoltaic's, solar thermal energy, solar architecture ,molten salt power plant and artificial photosynthesis. It is an important source of renewable energy and its technologies are broadly characterized as either passive solar or active solar depending on how they capture and distribute solar energy or convert it into solar power. Active solar techniques include the use of photovoltaic systems, concentrated solar power and solar water heating to harness the energy. Passive solar techniques include orienting a building to the Sun, selecting materials with favorable thermal mass or light-dispersing properties, and designing spaces that naturally circulate air. India has one of the world's largest programmes in solar energy which include R&D, demonstration and utilization, testing and standardization, industrial and promotional activities. Processed raw material for solar cells, large capacity SPV modules, SPV roof tiles, inverters, charge controllers all have good market potential in India as do advanced solar water heaters, roof integrated solar air heaters, and solar concentrators for power generations (above 100 KW). Solar photovoltaic modules can convert solar energy into electricity. A large number of these modules are arranged on a panel which is called Solar panel which can either be directly connected] to the energy-using device or indirectly to batteries so that the electricity generated could be used Later when there is no sunshine. In India Solar photo-voltaic systems are being installed by Department of Non-conventional Energy Resources for lighting, running of television sets and radios, pumping water in remote area where it is difficult to carry electricity.

The Department of Tele-communications and Defense Establishments are also using solar photo-voltaic systems for their energy requirements; in our country there has been a steady rise in demand for solar photovoltaic systems. In 1991 it was about 1 M W, in 1992 it rose to 2 MW, in 1993 it was about 4.4 MW and in 1995 the demand for solar photo-voltaic systems rose to 5.6 MWs. High initial cost of solar photovoltaic modules is the main drawback of the system. However, solar photovoltaic panels require virtually nothing to run and once installed provide energy for years and years together. Therefore these systems are cheaper than other conventional sources of energy. Another major drawback of the solar photovoltaic systems is the non-availability of adequate energy, efficient hardware's required by the system. Storage batteries, inverters, lamps, motors, pumps etc. which can work efficiently on energy provided by solar photovoltaic modules are often difficult to find in the market. However, sincere efforts are being made to overcome these difficulties as should be apparent from the rise in the demand of solar energy conversion systems. We have been successful in producing silicon modules in sufficient quantity and are currently exporting them to other countries. There has also been a decline in the cost of production of solar photovoltaic modules since its manufacture was undertaken in India.

Biomass Energy - Globally, India is in the fourth position in generating power through biomass and with a huge potential, is poised to become a world leader in the utilization of biomass. Biomass power projects with an aggregate capacity of 773.3 MW through over 100 projects have been installed in the country. For the last 15 years, biomass power has become an industry attracting annual investment of over Rs. 1,000 billion, generating more than 09 billion unit of electricity per year. More than 540 million tons of crop and plantation esidues are produced every year in India portion is either wasted, or used inefficiently. Other than these, there is potential for generating approximately 2,600 MW of power from urban and municipal wastes and approximately 1,300 MW from ustrial wastes in India. A total of 48 projects with aggregate ca ty of about 69.62 MW equivalents have been installed in the country thereby utilising only 1.8 percent of the potential that exists. As well, recently GOI mandated the blending of 0 percent fuel ethanol in 90 percent gasoline. This mandate as created an approximately 3.6 billionaire demand for fuel thanol in blend mandate to the entire country. Biomass is general term used for all material originating from hotosynthesis. Biomass based energy resources are renewable and cleaner than coal, oil or fuel wood. They can also be used o minimize the pollution caused by organic wastes. All biodegradable materials when subjected to anaerobic ecomposition yield combustible gases, mostly methane (CH4) which is a major constituent of natural gas as well.

In India plenty of cow-dung and other agricultural wastes are available which may be digested an aerobically to produce bout 22,500 million cubic meters of methane (commonly called Gobar gas) and about 206 million tons of organic manure very year. Department of Non- conventional Energy Sources aunched a national gobar gas development porgramme under ch about 150,000 gobar gas plants were installed in our ou during the year 1984-85. It is estimated that these lants can save about 600,000 tons of fire wood every year nd satisfy the energy requirement of about 20 million houses Indian villages. In India attempts are also being made to lentify potential plant species which can serve as a source of quid petroleum. It is proposed to cultivate such plant species n denuded waste land and use the biomass for extraction of quid hydrocarbons. Similarly these waste lands can also be sed for the cultivation of fast growing plants. The biomass om these plants can be used to supplement our firewood stock. his biomass can also be converted into coal or coal gas to ovide a more convenient form of energy.

Other Non-Conventional Sources of Energy- Proposals utilization of ocean tidal energy, the energy of ocean waves d geothermal energy are also under consideration in India. r country has a vast coastline - about 6000 kms and a number places where we can conveniently harness energy from oceans. Similarly the hilly tracts of Himalayas and hills of Central India have a number of locations suitable for development of geothermal energy. However, the use of these forms of energy is in survey, research and planning stages only.

Conclusion

The main objective of the paper is

1) To make aware of the present energy scenario.
2) To make aware of the global energy problem and leading role of the alternative energy sources for future survival.
3) To gather, review and publicize the success stories involving alternative energy sources.
4) To encourage public organizations to adopt these sources in their premises for a reliable,safe and quality based power supply.
5) To provide a forum for experts in this field, research scholars, industrialists to share their views and innovative ideas about the topics.
6) To encourage students and invite innovative ideas from younger generation.

Keeping these objectives in view the major areas of interest of this era are: Wind energy, solar energy, Biogas / Biomass, Energy From Waste Other alternative sources of energy such as fuel cell, hydrogen energy, tidal, geothermal, energy management, etc energy sources and new technologies. The abundant availability of these sources may play a major role to help India to become a super power in years to come.

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References-

1] Shoumyo Majumdar, ¯The Current Scenario Of Developments In Renewable Energy In India inrenewable energy and energy efficiency, 2008 pp. 1-32

2] Pradeep Chaturvedi, ¯Renewable Energy in India Programmes and Case Studies, in *ISESCO*, Science and technology vision Volume 1 May 2005 (61-64)

3] S.K. Patra and P.P.Datta, ¯ Renewable sources of energy Potential and achievements , technical digest Issue – 6

4] Peter Meisen ¯ Overview of sustainable renewable energy potential in India ¯ GENI, Jan 2010.

5] G. M. Pillai, Wise ¯Indian wind energy outlook 2011 april 2011

6] Giorgio dodero, IPGSRL ¯ 2011 India energy handbook , August 2010

7] K.P. Sukumaran ¯ Bioenergy India Issue 7 , Jan -March - 2011.

8] M. S. Swaminathan research foundation ¯ Bioenergy resources status in India , Pisces, may 2011

7] www.mnes.nic.in

8] www.wisein.org

9] www.geni.org

10] Plasma Arc Gasification For Waste Management by Gp Capt (Retd) K.C. Bhasin

11] U.S. Environmental Protection Agency (2010) Municipal solid waste in the United States: 2009 Facts and Figures. Washington, DC.

12] NRG Energy Plasma Gasification – MSW

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Nucleation and Growth of Copper Tartrate Crystals in Sodium Meta- silicate gel

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Abstract

Single crystals of copper tartrate have been grown using single diffusion silica gel method. The optimum conditions are established for the growth of good quality crystals. When the crystals grown at constant temperature, it is established that the transparency and size of the grown crystals increased (Shitole and Saraf 2001; Shitole and Saraf 2002: Bhavasar and Saraf 2002 and Nandre *et al.* 2011).

Keywords:- *Gel technique and Copper tartrate Crystals.*

Introduction

The advances in the science of the solid state and material science depend upon the availability of good quality single crystals. Crystals are the unknown pillars of modern technology. The modern technological developments depend greatly on the availability of suitable single crystals, whether it is for lasers, semiconductors, magnetic devices, optical devices, superconductors, telecommunication etc. In spite of great technological advancements in the recent years, we are still in the early stage with respect to the growth of several important crystals such as diamond, silicon carbide, gallium nitride and so on. Unless the science of growing these crystals understood precisely, it is impossible to grow them as large single crystals to be applied in modern industry. The large number of crystals is used in electronic, optical and in industries. Hence today's demand is to grow large single crystals with high purity and symmetry (Nandre *et al.* 2011; Patil *et al.* 2011; Sawant *et al.* 2012 and Sawant *et al.* 2011).

Material and Method

Experimental Procedures: Gel was prepared by using tartaric acid and sodium metasilicate having different pH values. The chemicals used for the growth of copper tartrate crystals; were of

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AR grade. 7ml of tartaric acid (1M) was taken in a small beaker. Sodium metasilicate solution of (1M) concentration was added drop by drop with constant stirring. The pH of solution was maintained to 4 to 4.5. The solution was then transferred in the test tube (2.5 cm diameter and 25 cm length) then covered its mouth with cotton plug. It was transparent initially, after 2/3 days, it turns milky and gel converted into semisolid with little amount of water on the top of the surface which is called water of syneresis. Such gel can not be used for reaction as it has not set. It vibrates with the small mechanical jerks; allow the water of syneresis to evaporate completely. It may take one week & it does not vibrate with the small mechanical jerks i.e. called "Setting of gel".

After setting of gel, allow the aging of the gel. Aging makes the gel harder and reduces the diameter of the capillaries present in the gel. Take the copper chloride ($CuCl_2$) (1M) solution in a pipette & pour it slowly in the test tube. The height of the supernatant component should be 50-75% of the gel height. With time, copper chloride diffuse in the gel & the crystals of copper tartrate appears in the gel. This is called "Single diffusion method". In the Present work, crystals of copper tartrate ($CuC_4H_4O_6$).were grown by a simple gel technique using single diffusion method. The optimum growth condition was established by varying different parameters .i.e pH of gel solution, gel concentration, gel setting time, concentration of reactants, period of crystal growth, temperature, density of gel. With optimum conditions the maximum sizes of the grown crystals were increased (Nandre *et al.* 2012a; Nandre *et al.* 2012b; Nandre *et al.* 2012c; Patil *et al.* 2010a and Patil *et al.* 2010b) The copper tartrate crystals under present investigation are shown in fig.1.

Chemical Reaction -

The following reaction is expected to take place in the gel medium

$$CuCl_2 + C_4H_6O_6 \rightarrow CuC_4H_4O_6 + 2HCl$$

Result and Discussion

The various optimum conditions for growing good quality crystals were found and are given in the table 1. Different parameters such as gel density, concentration of reactants, pH of gel, impurities in the solvent, gel setting time, room temperature, etc have considerable effect on the growth rate. The effect of various parameters on the growth of copper tartrate crystals are tabulated in table 2.

1. **Effect of gel density-** It was observed that the transparency of the gel decreases as the gel densities increases .Gels with higher densities set more rapidly than the gels with lower densities. It may be noted that well develop bluish color crystals of copper tartrate are obtained, with sodium metasilicate of density 1.04gm/cm^3.
2. **Effect of concentration of reactants-** As the concentration of tartaric acid is increased more volume of sodium metasilicate was required to adjust the pH value round 4.2 to 4.5. Increased concentration of tartaric acid provides more tartrate ions to combine with copper ions. With series of experiments the optimum conditions were obtained, Good quality crystals were grown at 1M concentration of tartaric acid.
3. **Effect of concentration of supernatant-** Copper chloride is used as supernatant with different concentration from 0.2M to1.2M .It was added over the set gel. It was observed that at 0.2M of concentration of supernatant very few nucleation's were observed with very small size of the crystals and crystals were not well defined.
4. **Effect of pH of gel-**It was observed that as the pH increased the transparency of the gel decreased. In the present work good crystals of copper tartrate are obtained at pH 4.2 to 4.5. The crystals growing at higher pH values were not well defined. This was due to contamination of the crystals with silica gel. It was observed that as the pH of gel increased the number of crystals decreased.
5. **Effect of Temperature** – All Crystal growth experiments were carried out at room temperature (25 to 30^{0}c)

Table No.1: Optimum conditions for growth of copper tartrate crystals.

Various process parameter	Optimum conditions
Density of sodium meta silicate solution	1.04 g/cm^3
Concentration of tartaric acid	1 M
Volume of Tartaric acid	7 ml
Concentration Copper chloride	1 M
Volume of sodium meta silicate solution	18 ml
pH of the mixture	4.2
Room Temperature	30^{0}c
Gel setting time	96 Hours

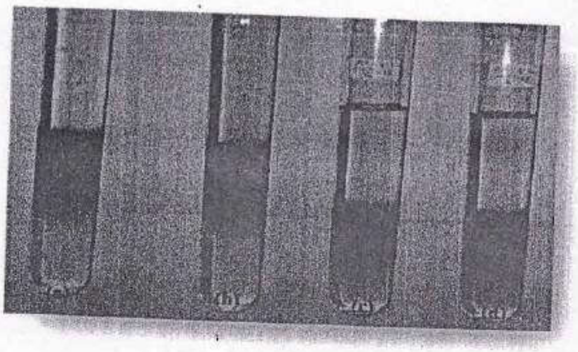

Figure 1(a, b, c and d) Shows Copper tartrate crystal inside the test tube

Table No.2 - Effect of concentration of supernatant. (pH= 4 to 4.2, Aging period = 144 hours.)

Test tube no.	Sodium Metasilicate (1.04gm/cm)^3	Tartaric acid (1M.)ml.	Concentration of supernatant	No. of Nuclei	Observation
1.	18	7	0.2	9	Very few nucleation, crystal size is very small,
2.	18	7	0.4	12	Nucleation density increases, crystal size increased slightly.
3.	18	7	0.6	15	Well shining isolated crystals. Various star shape and size are crystals are also observed.
4.	18	7	0.8	18	The crystals are developed with large size.
5.	18	7	1.0	10	Good crystals are observed, opaque, bluish colours.
6.	18	7	1.2	5	Numbers of crystals are large and are not isolated.

Conclusions

1) Copper tartrate crystal is grown by simple gel method.
2) The gel grown copper tartrate crystals are bluish color.
3) Gel method is found to be suitable for the growth of copper tartrate crystals at room temp.
4) The maximum size of grown crystals was found to be 2 to 6 mm.
5) It was found that as pH increases, nucleation centers decreases.

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References

- S. J. Shitole and K. B. Saraf, (2001). "Growth and study of some gel grown group II single crystals of iodate," *Bull. Mater. Sci.* vol. 24, no. 5,pp. 461-468.
- S. J. Shitole and K. B. Saraf, (2002). "Growth, Structural and microtopographical studies of calcium Iodate, monohydrate crystals grown by silica gel," *Cryst. Res. Technol.* vol. 37, no. 5, pp.440-445.
- D. S. Bhavasar, K. B. Saraf, (2002). "Morphology of PbI_2 Crystals Grown by Gel Method", *"Crystal Res. Technology"*;vol.37,no.1,pp. 51 – 55.
- S. J. Nandre, S. J. Shitole and R. R. Ahire, (2011). "Single Crystal Growth and Study of Strontium Iodate in Gel Method", *"Advances in applied science research"*, vol.2,no.2,PP.134-139.
- N. S. Patil, P. A. Savale, S. K. Bachhav and S. T. Pawar (2011). "Synthesis and Characterization of CdTr single crystals by gel technique", *"Archives of physics Research,"*vol.,2,no.1,pp. 39-47.
- D. K. Sawant., H. M. Patil and D. S. Bhavasar, (2012). "Nucleation and growth of barium tartrate crystals in silica", *"Scholars Research Library Archives of Physics research"*,vol.1,no.1,pp. 8-14,
- D. K. Sawant, H. M. Patil and D. S. Bhavasar, (2011). "Structural and Optical Properties of Calcium Cadmium Tartrate" *"Scholars Research Library Archives of Physics research"*,vol. 2 ,no.2,pp. 67-73,
- S. J. Nandre, S. J. Shitole and R. R. Ahire, (2012a). "Thermal and optical studies of gel grown cobalt iodate crystal", *"Scholar research Library Archives of Physics Research"*,Vol.3,no.1, pp.70-77.

- S. J. Nandre, S. J. Shitole, S. S. Sonawane and R. R. Ahire, (2012b). "Optical and Surface morphology of Zinc Tartrate Crystals","*International Journal of Basic and Applied Research*".Special Issue ,pp. 125-128
- S. J. Nandre, S. J. Shitole and R. R. Ahire, (2012c). "Structural and Optical Study of Gel Grown Crystals of Zinc Iodate", "*Journal of Scientific Review*". Vol.4,no1,pp. 203-207.
- H. M Patil, D. K Sawant, D. S. Bhavsar, J. H Patil and K. D Girase.(2010a). "Nucleation and Growth of Lanthanum Tartrate Crystals in Silica", "*Archives of Physics Research*", vol.1,no.4 pp.168-175.
- H. M. Patil, D. K. Sawant, J. H. Patil, D. S. Bhavsar, (2010b). "Sphernlitic growth oh Neodymium tartrate Crystals in silica gel." "*Journal of Scientific Review*", Vol.2,no.2, pp.108-113.

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Preparation, Characterization and Gas Sensing Performance of Pure SnO2 Thin Films Deposited using Physical Vapour Deposition Technique

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ABSTRACT

Nanocrystalline SnO_2 thin films were successfully prepared using Physical Vapour Deposition technique and were annealed at 400^oC. Structural, morphological, elemental, compositional, optical, and electrical and gas sensing properties were studied using XRD, FESEM, EDXS, UV-Vis Spectrophotometer, DC resistance measurement method respectively. Acetone, Cl_2, CO_2, Ethanol, H_2S and NH_3 sensing performance of Nanocrystalline physically vaporized SnO_2 thin films were investigated and reported in this paper. The results were systematically tabulated, interpreted and discussed.

Keywords: SnO_2 thin film, PVD technique, XRD, FESEM, gas sensor, sensitivity.

Introduction

Since last few decades there has been an increasing interest to prepare inexpensive SnO_2 thin films. Tin oxide is the most widely used metal oxide semiconductor in gas sensing because of its capability to detect combustible and hazardous gases such as methane, LPG, CNG, CO, CO_2, Cl_2, H_2S etc[1-4]. It is an n-type semiconductor of tetragonal structure with band gap energy about 3.6 eV at room temperature. It is cheap, nontoxic and has strong oxidizing power, high photochemical corrosive resistance, good electrical, optical and piezoelectric behavior. In recent years, semiconductor metal oxide films have received considerable attention because of their potential applications [5] such as photochemical and photoconductive devices in LCD, lithium-ion batteries,[6-8] a transport conductive electrode for solar cells [9,10] a gas sensing material for gas sensor devices [11], transport conducting electrodes [12] etc. The majority of the applications adopted SnO_2 as the sensing material due to its high sensitivity and stability at lower operational temperatures, in spite of its poor selectivity [13].Out of many thin film preparation techniques such as chemical vapour deposition [14], spray pyrolysis [15], sputtering [16], activated reactive evaporation [17], etc. Physical Vapour Deposition method is straight forward and simple one. Because of deposition in high vacuum and at room temperature, this technique produces contamination free uniform thin films. In the present study, we used Hind Hivac vacuum depositing unit for depositing pure tin onto the cleaned glass substrates at room temperature. The films were then heated in muffle furnace at 200^oC for 24 hrs to allow oxidation. The so formed pure SnO_2 thin films were then annealed at 300, 400 and 500^oC each for 2 hrs. Structural, morphological, electrical, optical and gas sensing characterizations of the samples were studied.

2. Experimental

2.1 Substrate Cleaning

Glass substrates were thoroughly cleaned by hot chromic acid to remove contamination. They were then rinsed with distilled water followed by acetone. Finally the substrates were dried under UV lamp at $60\text{-}80^oC$.

2.2 Preparation of nanocrystalline SnO_2 thin films

Pure SnO_2 thin films were deposited onto the glass substrates by thermal evaporation technique. The cleaned substrates were mounted onto the mask placed ~15 cm above the tungsten basket. In this method, tin was vaporized by passing appropriate current through spiral of basket using dimmerstat (0-10 A). The selection of a particular heater depends upon the form of the material to be evaporated. When the material is heated in vacuum ($\sim10^{-5}$ mbar), it undergoes sublimation and atoms get transported to the substrates where they get deposited. The samples were then placed in a muffle furnace for 24 hrs at 200^oC for allowing oxidation. Out of oxidized samples, a few samples were annealed at 400^oC for 2 hrs.

3. Results and Discussion

3.1 Electrical Characterization

3.1.1 I-V Characteristics

Simple series circuit of the sample and picoammeter with voltmeter in parallel was used to study I-V characteristics. The current versus voltage characteristics of the samples annealed at 400^{o}C were plotted. They are almost symmetrical in nature and prepared samples are ohmic in nature. The resistance values were obtained from the slope of the graphs (Fig.1).

3.1.2 Resistance versus Temperature Characteristics

The electrical properties of the samples were studied. DC resistance measurement of the films was performed by using the voltage divider consisting of a standard high resistor in series with sample and a standard voltage source. Voltage across the standard resistor was measured at different temperatures (ranging from 400^{o}C to 50^{o}C) and film resistance was calculated. The film resistance R (Ω) was plotted against temperature t (^{o}C) (Fig. 2a) and temperature coefficient of resistance (TCR) of the film material was calculated. Graph showed negative temperature coefficient of resistance and semiconducting nature of the samples.

Graph of logR versus 1/T (T being sample temperature in K) (Fig.2b) was used to evaluate activation energy in high and low temperature regions. The results are tabulated in Table1. The activation energy of tin oxide films is due to the formation of donor levels below conduction band. Earlier researchers have obtained activation energy to be 0.26 eVand 0.2 eV[18]. Some other groups reported activation energy as 0.73 eV[19].

3.2 Structural Characterization by XRD

The crystalline structure of the thin films was examined by X-Ray Diffractometer (Model-D8 Advance, Make-Bruker AXS GmbH, Berlin, Germany) using CuKα radiation having wavelength 1.5402 A^{o} within 2θ range of 20^{o} to 80^{o}. Fig.3 shows the XRD patterns of the samples annealed at 400^{o}C. All the major peaks correspond to tetragonal phase. Open peaks correspond to the substrate (glass) material. Average Crystallite size was estimated using Scherrer formula.

$$D=\frac{0.9\lambda}{\beta\cos\theta} \qquad -----(1)$$

where,**D** is crystallite size, **λ** is wavelength of radiation (1.5402 A^{o}), **β** is Full Width at Half Maxima in radians and **θ** is Bragg's angle in degrees.

Interplanar distance d was determined using Bragg's condition $2d\sin\theta = n\lambda$. Degree of crystallinity[19], grain size, interplanar distance, average texture coefficient, dislocation density, lattice strain etc. were also determined using the relations (eq.1-7) [20-22] and systematically tabulated in Table 2.

$$d=\frac{\lambda}{2\sin\theta} \qquad -----(2)$$

$$\text{Dislocation density}=\frac{1}{D^2} \qquad -----(3)$$

$$D.\,C.=\frac{I_c}{I_c+I_a} \qquad -----(4)$$

$$g=\frac{\beta}{\tan\theta} \qquad -----(5)$$

$$\text{S. A.} = \frac{6}{\rho D} \qquad ------(6)$$

$$\text{Texture Coefficient } t = \frac{I/I_0}{\frac{1}{N}\sum \frac{I}{I_0}} \qquad ------(7)$$

where I = the measured intensity, I_0= the standard intensity, N = number of diffraction peaks, Ic and Ia are respectively the intensities corresponding to crystalline and amorphous phases, ρ =density of the material in g/cc. The observed grain size from XRD patterns and FE-SEM were estimated, their values were compared.

All these structural parameters have been determined and reported in Table 2. Since the averaged texture coefficient value was 1 the formed material in thin films is confirmed to be polycrystalline in nature. The corresponding (hkl) planes for 2θ values matched with standard JCPDS data cards [23].

3.3 Surface Morphology by FESEM

The surface morphology of the films were observed using FESEM technique (Model-S4800 Type II, Make-Hitachi HiTechnologies Corporation, Tokyo, Japan).

Fig. 4 shows the FESEM micrograph images of pure SnO_2thin film samples annealed at 400^oC. The small spherical grains residing on some large, irregular shaped grains were observed from FESEM image. Micrograph shows that the grains are nano-crystalline in nature. Average grain size was estimated to be 140 nm which is much larger than 14.13 nm, the crystallite size obtained from XRD. It is found that films have uniform and smooth morphology having nanocrystalline nature with optical porosity. Optical porosity is advantageous for gas sensing. [24].

3.4 Elemental Composition: EDXS

Elemental composition of the films was determined by EDXS (Model-XFLASH5030 Detector, Make-Bruker Nano GmbH, Berlin, Germany). The EDXS spectrograph for SnO_2 thin film samples annealed at 400^oC is presented in fig. 5

Stoichiometrically expected at. % of Sn and that of O are 33.3 and 66.7 respectively. Observed at. % of Sn and O were as shown in the table above. They are much deviated from the expected values. Nevertheless, the prepared SnO_2 polycrystalline films are nonstoichiometric in nature and it is beneficial for gas sensing.

4. Optical Parameters by UV-Vis spectrophotometer

Fig.6 shows the absorbance of tin oxide thin film. Optical characterization of tin oxide films offers information about physical properties such as band gap energy, band structure and optically active defects etc. [25]. To obtain band gap, absorption coefficient was calculated from absorption data. Fig. 6 graph of (α) versus (λ).Band gap was then calculated by plotting
$(\alpha h\nu)^2$ versus ($h\nu$) using the equation
$\alpha h\nu = A(h\nu - E_g)^n$

where α is absorption coefficient, A is a constant, E_g is the optical band gap energy, $h\nu$ is the photon energy and n is constant. Value of n can be 1/2 or 2 depending upon the presence of the allowed direct and indirect transitions [25]. Fig. 7 shows graph of $(\alpha h\nu)^2$ versus ($h\nu$). Nature of the plot suggests direct interband transitions.

Band gap is determined by drawing tangent to the curve near the energy axis. The point where the line intersects the axis gives the band gap value. It is observed to be about 3.8 eV.

5. Gas Sensing Properties

5.1 Details of the Static Gas Sensing System

The static system for examining the performance of test gases is shown in fig.8. It consists of a glass chamber of known volume which encloses the sample, a Cr-Al thermocouple and electrical heater. They were connected to various ports fitted to base plate of the system. These ports enabled external electrical connections to voltmeter, temperature controller and dimmerstat. A known amount of a test gas was injected in the chamber through a gas inlet port using a micro syringe. The sample was heated by electrical heater by passing current monitored through dimmerstat. The thermocouple output was given to temperature indicator to know the sample temperature. A constant DC voltage was applied to the sample and voltage across a standard resistor was measured by digital voltmeter. The voltage was recorded corresponding to fixed temperature intervals. After every cycle of readings, the chamber was removed to expose the sample to air.

Sensitivity: Sensitivity is defined as $S = R_a/R_g$ where, R_a is the resistance of the sample in dry air and R_g is that in the presence of a test gas measured at respective temperatures. It reveals from the graphs that the gas response increases with working temperature, reaches maximum at particular temperature (operating temperature) and then decreases. It is observed that gas responses are different for different gases and vary with gas concentrations of the same gas too. It reveals that operating temperatures also vary with different gases. The observations are depicted in Table 4.

Selectivity: The selectivity or specificity of a sensor towards an analyzing gas is expressed in terms of dimension that compares the concentration of the corresponding interfering gas that produces the same sensor signal. The selectivity profile of different gases for various gas concentrations is depicted in the fig.10 below. Out of the tried test gases, ethanol showed maximum response for 2cc concentration at an operating temperature 200^{o}C.

6. Conclusions

- The pure SnO_2 thin solid films were prepared by physical vapour deposition technique in vacuum of about 10^{-5} mbar at room temperature and their various parameters were studied.
- The so prepared pure tin oxide thin films were annealed at 400^{o}C.
- The structural and morphological properties of the prepared thin films were characterized by XRD, FESEM and EDXS. The crystallite size, average texture coefficient and grain sizes were calculated along with elemental composition of the samples.
- The band gap values were obtained from the absorption spectra and found to be about 3.8eV.
- Gas responses were obtained for different test gases. Maximum response was seen for 2cc ethanol at an operating temperature 300^{o}C.
- The samples show good sensitivity but poor selectivity. All above observations infer that pure tin oxide thin solid films prove to be good sensing material.

5. Acknowledgment

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7. References

[1] J. G. Duh, J. W. Jou, B. S. Choi; J.Electrochem. Soc., 1989, 136, 27-40.

[2] A. RatnaPhani, S. Manorama, V. J. Rao; Appl. Phys. Lett., 1995, 66,34-89.

[3] D. S. Vlachos, C. A. Papadopoulos, J. N. Avarisiotis; Appl. Phys. Lett., 1996,69, 650.

[4] M. Fleischer, S. Kornely, T. Weh, J. Frank, J. Meixner;Sens. Actuators *B 2000*,69, 205.

[5] R. H. Bari, S. B. Patil, A. R. Bari-Synthesis, Characterization and Gas Sensing Performance of Sol-gel Prepared Nanocrystalline SnO_2 Thin Films, International Journal on Smart Sensing and Intelligent

Systems, 2014, 7, 2, 610-628.

[6] S. B. Deshmukh, R. H. Bari, G. E. Patil, D. D. Kajale, G. H. Jain, L. A. Patil, Preparation and Characterization of Zirconia based Thick Film Resistor as a Ammonia Gas Sensor, International Journal on Smart Sensing and Intelligent Systems, 2012, 5,3, 540-558.

[7]S. Chappel, A. Zaban, Nanoporous SnO2 Electrodes for Dye-sensitized Solar cells:Improved Cell Performance by the Synthesis of 18nm Colloids, Solar Energy Materials a Solar Cells,2002, 71, 141-152.

[8] S. Gnanam, V. Rajendram, Luminescence Properties of EG-assisted SnO2 Nanoparticles by Sol-gel Process, Digest Journal of Nanomaterials and Biostructures, 2010, 5, 699-704.

[9] Aoki A and Sasakura H J.;Appl. Phys. 1970**,**9,582.

[10] Mohammadi M, Solemani E and Mansorhaseini M Mater. Res. Bull. *2005*, 40, 1303.

[11] KeshavrajaA, Ramaswami A V and Vijayamohanan K Sensor Actuator B 1995**,**23,75.

[12] Fukano T and Motohiro T; Sol. Energy Mater. Sol. Cells 2004**,**82, 567.

[13] Hagen W,Lambrich R E and Jagois; JAdv. Solid State Phys., 1983,23**,**259.

[14]T. Okuno, T. Oshima, S. Dong Lee, S. Fujita, - Growth of SnO_2 crystalline thin films by mist chemical vapour deposition method, Physica status solidi (c), 2011 , *8, 540-542.*

[15] K. Murakami, K. Nakajima, S. Kaneko, - Initial growth of SnO_2 crystalline thin films on the glass substrate deposited by the spray pyrolysis technique, Thin Solid Films, 2007 ,515, 8632-8636.

[16] T. gui, L. Hao, J. Wang, L. Yuan, W. Jai, X. Dong-Structure and Features of SnO_2 Thin Films prepared by RF Reactive Sputtering, Chinese Optic Letters, 2010, 8, 10134-03,

[17]H. S. Randhawa, M. D. Matthews, R. F. Bunshah, SnO_2 films by activated reactive evaporation, Thin Solid Films, 1981, 83, 267-271,

[18] D. Das and R. Banerjee; Thin Solid Films, 1987, 147, 321.

[19] R. Sanjines, V.Demarne and F. Levy, Thin Solid Films, 1990, 193, 935.

[20] S. Chattopadhyay, T.C. Chaki, A.K. Bhowmick, Structural Characterization of Electron-beam Cross Linked Thermoplastic Elastomeric Films from Blends of Polyethylene and Ethylene-vinyl acetate Copolymers, J. Appl. Polym. Sci., 2001**,**81, 1936-1950.

[21] B. D. Cullity, Elements of X-ray diffraction, Addison-Wesley Publishing Co., 1956.

[22] L. E. Alexander, X-ray diffraction methods in polymer science, Wiley International, New York, 1980.

[23] JCPDS data card of SnO_2 (01-072-1012 and 00-006-0395).

[24] Patil P S, Kawa R K, Sadale S B and Chigare P S Thin Films, 2003, 34437.

[25] G.E.Patil, D.D. Kajale,S.D.Shinde, R.H. Bari, D. N. Chavan, V.B. Gaikwad, G. H. Jain, Sensors and Transducers Journal, Vol.9, Special Issue, Dec. 2010**,** 96-108.

(Tables & Figures)

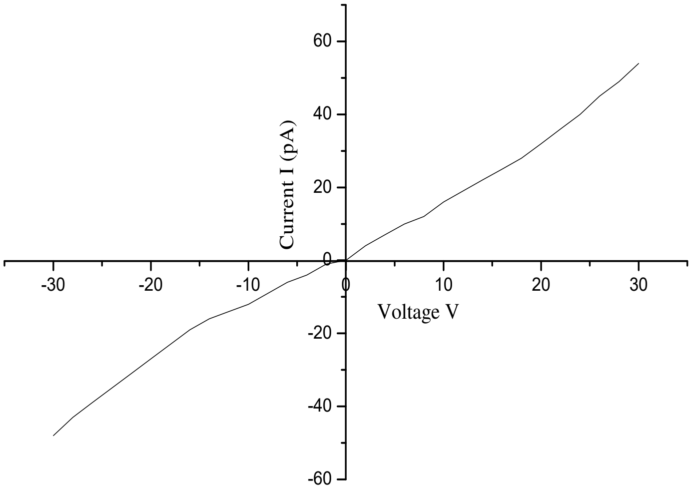

Fig. 1 I-V characteristics of SnO_2 thin films

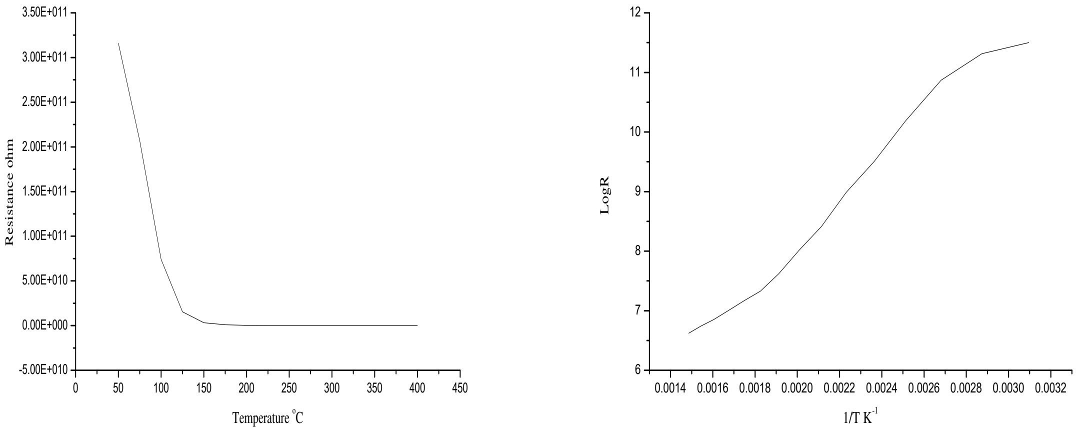

Fig. 2 Electrical Properties.

Graph of (a) Resistance R versus temperature (°C) (b) logR versus 1/T (K^{-1})

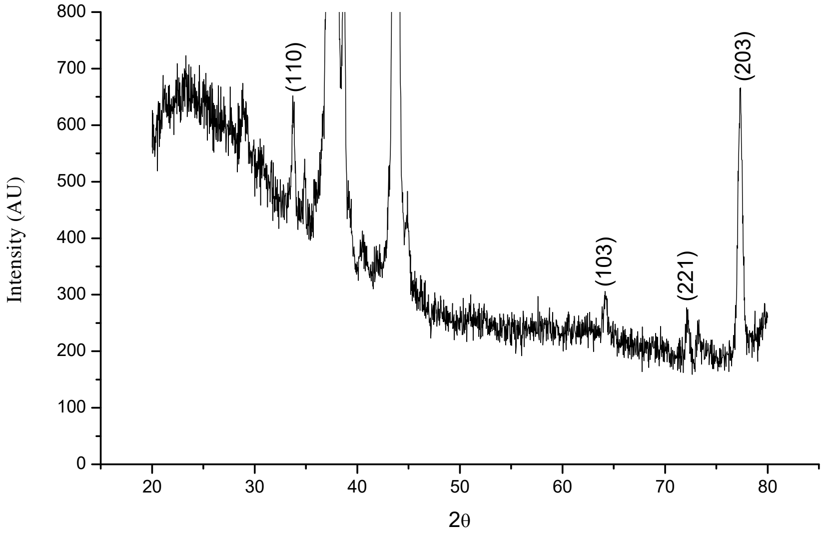

Fig. 3 XRD patterns of samples annealed at 400°C

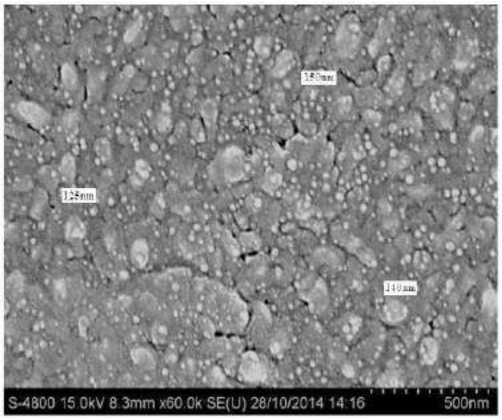

Fig. 4: FESEM micrographs of samples annealed at 400^{o}C

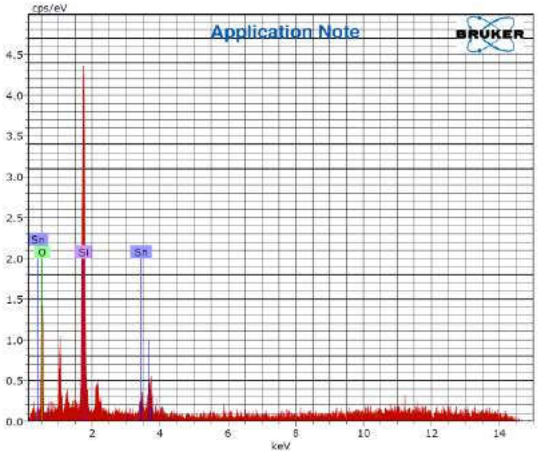

Fig. 5 Elemental analysis of samples annealed at 400^{o}C

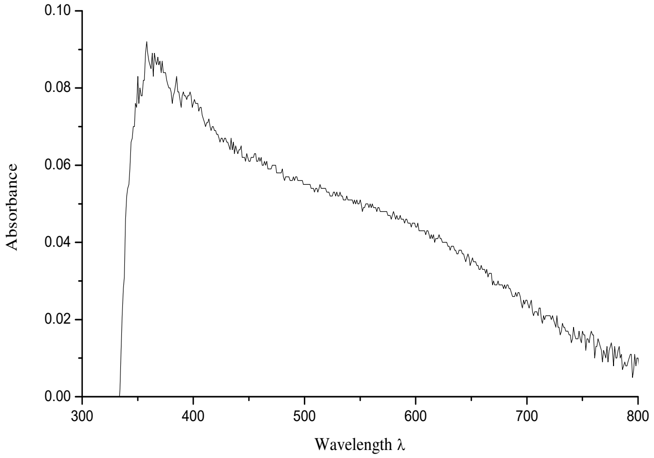

Fig. 6 Plot of absorbance versus wavelength

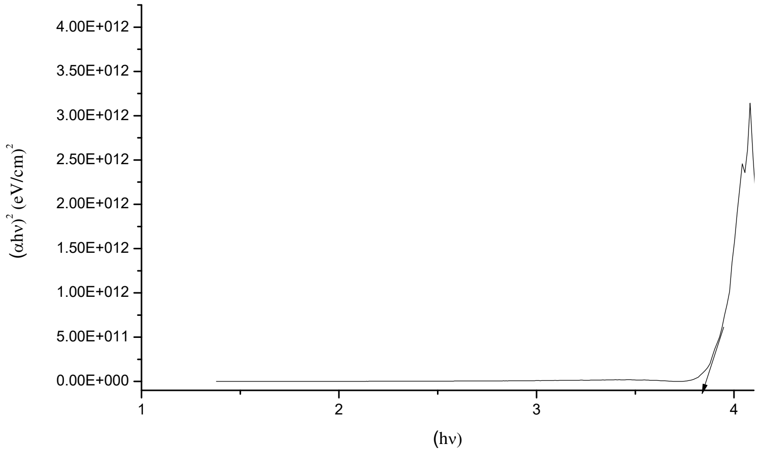

Fig. 7 graph of $(\alpha h\nu)^2$ versus (hν)

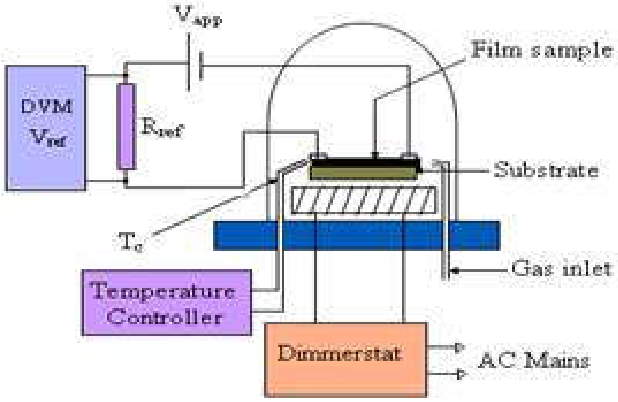

Fig.8 Static Gas Sensing System

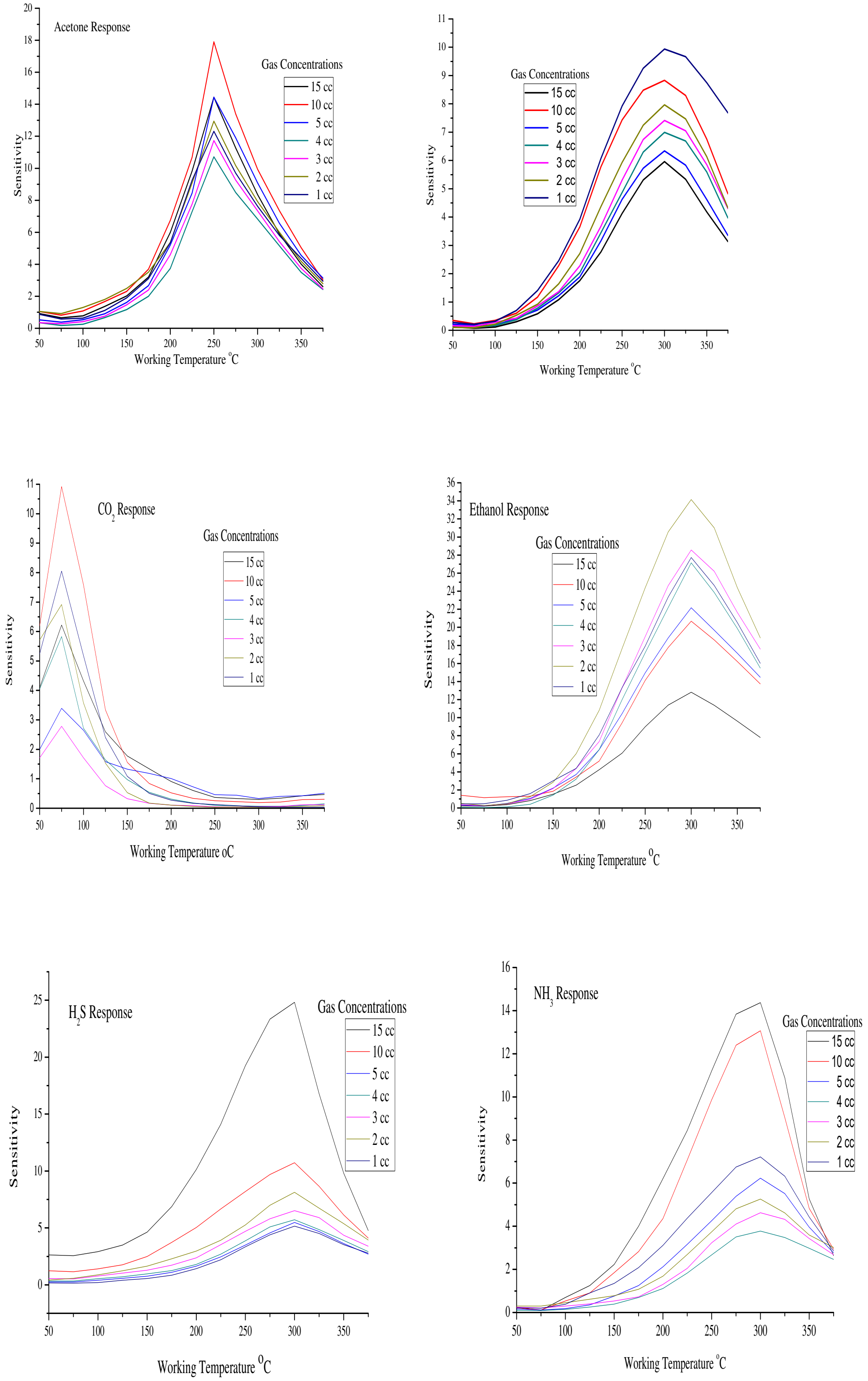

Fig. 9 SnO_2thin film Sensitivity for various target gases

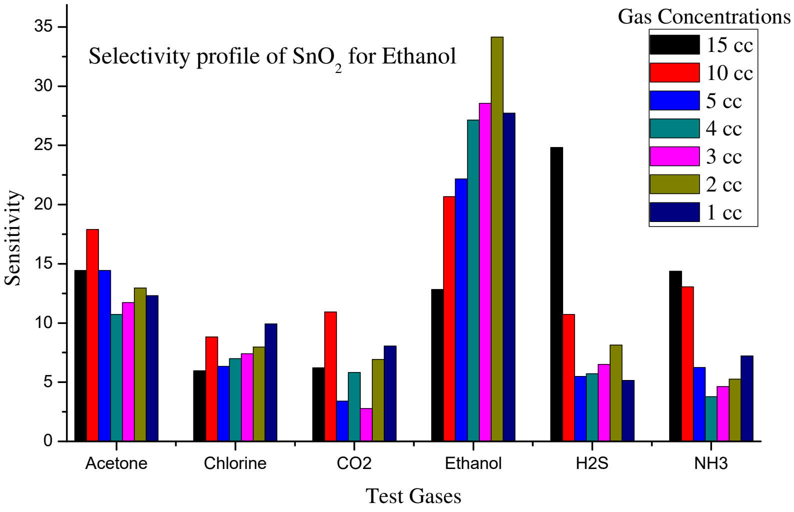

Fig.10 The selectivity profile of SnO_2 for ethanol

Table1

Annealing temperature °C	Resistance MΩ	TCR /°C	Activation Energy eV	
			HTR	LTR
400	6.373	-0.0019	0.411	0.850

Table 2

Annealing Temp. °C	h,k,l	2θ	Dislocation density $x10^{15}/m^2$	Crystallite Sizefrom XRD nm	Grain Size (FESEM) (nm)	Average Texture Coefficient	Lattice Strain g(%)	Interplanar Distance d A°	DC (%)
400	102	44.39	0.0050	14.13	145	1.00	0.874	2.038	70.60

Table 3

Elements	Annealing temp. 400°C	
	Mass %	At. Wt.%
O	49.10	64.73
Si	45.75	34.36
Sn	5.14	0.91
Total	100.00	100.00

Table 4

Gas	Gas Concentrations							Operating Temp °C
	15 cc	**10 cc**	**5 cc**	**4 cc**	**3 cc**	**2 cc**	**1 cc**	
Acetone	14.4362	**17.9020**	14.4362	10.7155	11.7303	12.9479	12.3101	250
Chlorine	5.9602	8.8318	6.3404	6.9904	7.4134	7.9641	**9.9377**	300
CO_2	6.2199	**10.9213**	3.39194	5.8282	2.783	6.9162	8.0478	75
Ethanol	12.8197	20.6769	22.1651	27.1342	28.5608	**34.1464**	27.7286	300
H_2S	**24.816**	10.7240	5.4777	5.7108	6.5156	8.1343	5.1554	300
NH_3	**14.3698**	13.0648	6.2278	3.78	4.6281	5.2595	7.2143	300

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Structural and optical properties of $Cd_xCr_{2-x}S_4$ thin films grown by CBD method for solar cell applications

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Abstract

We report the structural and Optical properties of crystalline Cadmium Chromium sulfide (x= 0.6) thin films was deposited on glass substrate using the chemical bath deposition method. The prepared thin films were characterized by X-ray diffraction analysis; scanning electron microscopy. From UV spectroscopy, the value of fundamental absorption edge from the intercept lies between 1.5528 - 3.7083 eV and the corresponding α *values were* 6.869×10^5 *to* $1o.4129 \times 10^5$ cm^{-1}*. The direct optical energy band gap of this sample was 2.2735 eV lying in the range of semi-conducting materials, suitable for solar cell applications.*

Key words : CBD, XRD, SEM, absorption coefficient, direct optical band gap.

1. Introduction

Cadmium Chromium sulfide ($CdCr_2S_4$) is a chalcogenide metal sulfide semiconductor of the II-VI group compound semiconductors. The technological interests in polycrystalline based devices are mainly caused by their low production cost[1]. The uses of thin film polycrystalline semiconductors have attracted much interest in an expanding variety of application in various magneto-optical and optoelectronic devices[2]. Many techniques have been reported in the deposition of thin films such as evaporation, sputtering, spray pyrolysis; molecular beam epitaxy and photo-chemical deposition. In these deposition methods there are some problems in each of them[3-4]. Among all, chemical bath deposition (CBD) is simple and low cost technique and is suitable for a large area deposition[5]. Ferromagnetic chalcogenite $CdCr_2S_4$ have outstanding properties such as giant magneto-resistance, magnetocapacitive, red shift of the optical absorption edge and giant Faraday rotation, providing for design of devices with various applications[6-8]. Thin films of diluted magnetic semiconductors attract many researchers due to their wide range of applications in various fields. The films of $CdCr_2S_4$ are usually crystallized in cubic structure with lattice constants 10.2 Å[9]. As the trade of fabricating smaller devices continued toward nanoscale technology, new effects related to the small size were realized in producing novel devices, magneto- optical and optoelectronics[10, 11].

In the present study, the chemical bath process is performed by slow release of S^{2-} and controlled free Cd^{2+} and Cr^{2+} react to form $CdCr_2S_4$ nuclei on glass substrate and in the bath solution in form of precipitation. The properties of the deposited thin films basically depend on the deposition parameters such as deposition temperature, complexing agent, thiourea, deposition time, pH value, composition of materials and film thickness. Finally, we report the deposition of $CdCr_2S_4$ thin films and the investigation of the different deposition parameters to obtain uniform film having expected thickness.

2. Materials and Methods

In the present investigation, thin films of $Cd_x Cr_{2-x}S_4$ (X=0.6) were grown on glass substrate by chemical bath deposition technique. All AR grade (MERCK) chemicals were used for growth of $Cd_xCr_{2-x}S_4$ thin films. For deposition of $Cd_xCr_{2-x}S_4$ solutions of $CdCl_2$, CrO_3 and NH_2-CS-NH_2 were prepared separately of concentration 0.1 M using double distilled water as solvent and were mixed in stoichiometric proportion. EDTA was used as complexing agent. pH of the reaction mixture was adjusted by adding ammonia. The deposition carried out in borosil glass pot of capacity 100ml is used to put chemical reactant in the form of solution is serve as chemical reaction bath. This chemical reaction bath is put inside constant temperature oil bath. The chemical reactant in form of solution is stirred by magnetic stirrer. Well clean glass microslides are dip vertically in the chemical reaction bath by supporting to glass pot of reaction bath. The stirring speed of magnetic stirrer is so adjusted that the solution can stirr slowly during the deposition process. After deposition of $CdCr_2S_4$ thin films, the substrate were taken out and washed with double distilled water and dried in air and finally, preserved in an air tight container. The thickness of deposited thin films was measured by the weight difference technique. The structural properties of the films were analyzed with using Bruker AXS D8 Advanced model X-ray diffractometer (CuK_α radiation; $\lambda = 0.15405$ nm) and grain size was determined from a Scherrer formula. The film surface morphology was investigated using scanning electron microscopy (FE-SEM HITACHI S4800 II). The optical absorption studies were carried out using UV-VIS spectrophotometer (UV-VIS 2400 SHIMADZU) in the 200-800 nm wavelength range.

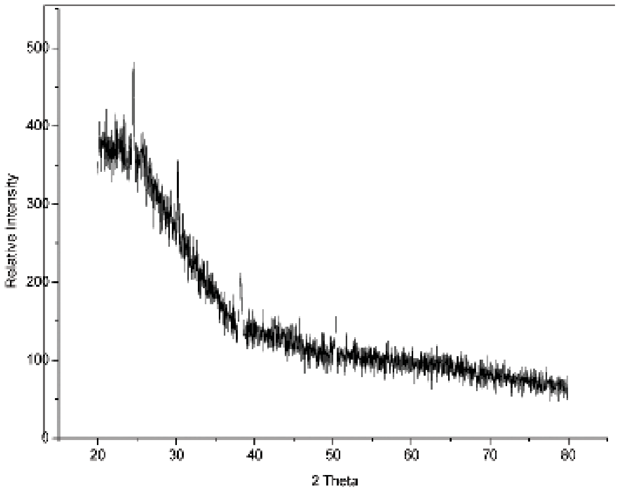

Fig. 1. XRD of $Cd_xCr_{2-x}S_4$ (X= 0.6)

3. Results and Discussions

X-ray diffraction studies were carried out at room temperature as shown in figure (1). The observed peaks are matching well with reported JCPD'S data card. The XRD pattern shows that the deposited films are polycrystalline having cubic structure[11,12,13] with noticeable growth along the (2 2 0) plane (JCPDS card no. 03-065-7117). In addition the other small peaks *viz.*, (2 2 2), (3 3 1). Table 1. represents the observed and reported XRD data.

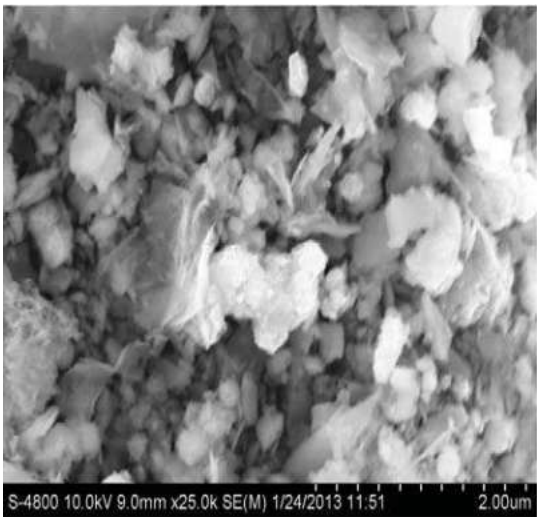

Fig. 2. SEM image of $Cd_xCr_{2-x}S_4$ thin film

Table 1.

Planes (h k l)	2 Theta (degree)		d-spacing values d (°A)	
	JCPDS data card	Experiment	JCPDS	Experiment
2 2 0	24.559	24.560	3.62180	3.62179
2 2 2	30.198	30.200	2.95719	2.95575
3 3 1	38.268	38.267	2.35013	2.35108

Figure 2 shows SEM image of $Cd_xCr_{2-x}S_4$ thin film. The particles covered over the surface of substrate are randomly oriented and elongated in different directions with some voids. The grain size measured from SEM images (24-41 nm) was almost same as that of estimated by XRD studies. But, these grain sizes are little bit more than that in XRD observations. This may be due to two or more grains fusing together to form the cluster type of structure.

4. Optical Properties

The optical absorption spectra were obtained in the 355 nm - 735 nm wavelength range by employing a Shimadzu 2450 UV-Visible model of the spectrophotometer. Figure 3 shows the optical absorbance spectra versus wavelength range nm of the film deposited in this work. The fundamental absorption edge is one of the most important features of the absorption spectrum of a semiconductor. The increased absorption near the edge is caused by the transition of electron from the valance band to conduction band. Figure 4 shows the plot of absorption coefficient α against photon energy. The value of fundamental absorption edge from the intercept lies at 1.5599 - 3.6674 eV and the corresponding absorption coefficient values were 5.624×10^5 to 9.097×10^5 cm^{-1} supporting direct transition of the material[10]. The higher value of absorption coefficient in the UV region makes the material useful in forming p-n junction, solar cells with other suitable thin film materials for photo-voltaic applications[14].

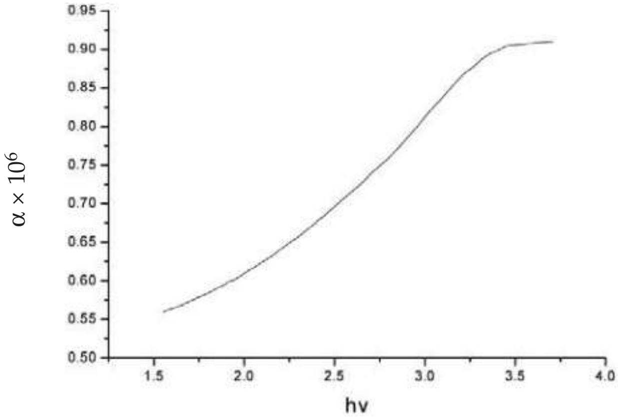

Fig. 3. $\alpha \times 10^6$ Vs hγ

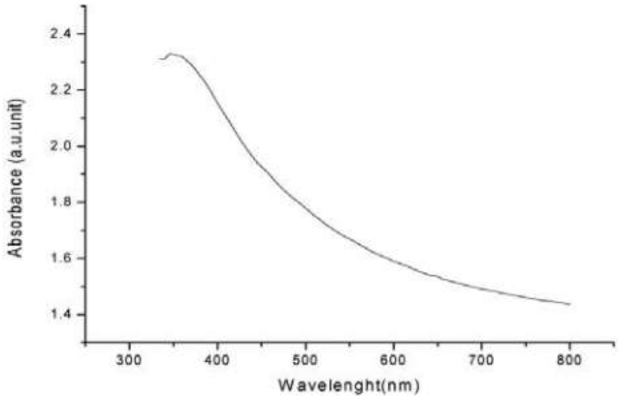

Fig. 4. Absorbance (α) V s Wavelength (λ)

The optical band gap of these films has been calculated using the relation (Tauc 1974).

$$\alpha h\nu = A(h\nu - Eg)^n$$

Where, hv is the photon energy, α is the absorption coefficient, *Eg* the band gap, *n* = 2 for indirect band gap material. Figure 5 shows $(\alpha h\nu)^2 \times 10^{12}$ verses photon energy (hv) for $Cd_xCr_{2-x}S_4$ thin film, optical band gap was obtained by extrapolating these curve. The direct optical energy band gap of this sample was 2.2735 eV. The reported values in literature are 2.23-2.61 eV[10, 11, 15]. The decrease in band gap energy with increase in film thickness is commonly observed phenomenon in semiconducting thin film[10, 16].

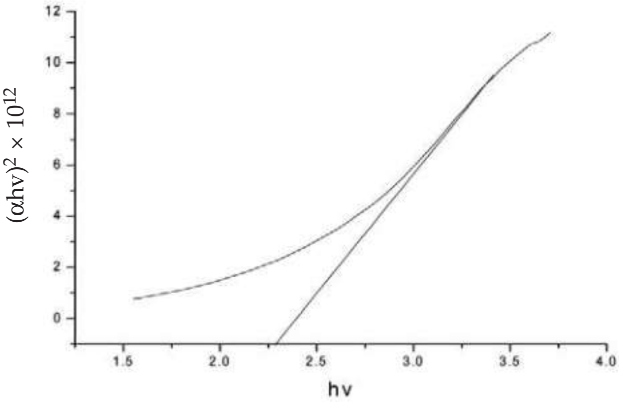

Fig. 5. $(\alpha h\nu)^2 \times 10^{12}$ Vs hγ

5. Conclusions

1. The film was deposited successfully by CBD.
2. XRD analysis confirms that the deposited film was polycrystalline in nature.

3. From SEM, the particles are distributed uniformly over the surface of the film with some voids.
4. The direct optical energy band gap of this sample was 2.2735 eV.

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References

[1] **M.A. Mahdi, S.J. Kasem, J.J. Hassen, A.A. Swadi** and **S.K.J.A.I-Ani**, *Int. J. Nanoelectronics and materials* **2**, (2009) 163-172.

[2] **S.S. Kale** and **C.D. Lokhande**, *Mater. Chem. Phys.* **62**, (200) 103.

[3] **P.P. Sahay, R.K. Nath** and **S. Tewari**, *Crys. Res. Technol.*, **42**, (2007) 275-283.

[4] **D.C. Cameron, W. Duncan** and **W.M. Tsang**, *Thin Solid Films*, **58**, (1979) 69-76.

[5] **S.M. Mahdavi, A. Irajizad, A. Azariari** and **R.M. Tilaki**, *Scientia Iranica*, **15**(3), (2008) 360-365.

[6] **L. Golik, S.M. Grigorovitch, M.I. Elinson, Z.E. Kunkova** and **V.M. Ukrainskyi**, in: Proceeding of the Third International Conference on Thin Films, Basic Prpblems, Applications and Trends, Budapest, Hungary, **7**, (1975) 17.

[7] **J. Hemberger, P. Lunkenheimer, R. Fichtl, H.A. Krug von Nidda, V. Tsurkan** and **A. Loidl**, *Nature (London)*, **434, 364** (2005).

[8] **C.P. Sun, C.C. Lin, J.L. Her, C.J. Ho, S. Taran, H. Berger, B.K. Chaudhuri** and **H.D. Yang**, *Phys. Rev.* **B 79**, (2009) 214116.

[9] **R.S. Mane, V.V. Todkar, C.D. Lokhande**, **Ju-Hyun Ahn** and **Sung-Hwan Han**, Nanotechnology, **17**, (2006) 5393-5396.

[10] **V.V. Todkar, R.S. Mane, C.D. Lokhande, Habib M. Pathan, Oh-Shim Joo** and **Hoeil Chung**, *J. of Phys. and Chem. of Solids*, **69**, (2008) 1802-1807.

[11] **A.M. Salem** and **ME El-Chazzawi**, *Semicond. Sci Technol*, **19**, (2004) 236-241.

[12] **D.C. Cameron, W. Duncan** and **W.M. Tsang**, *Thin Solid Films*, **58**, (1979) 69-76.

[13] **B.D. Cullity**, Elements X-ray Diffraction, Addison-Wesley, (1967) 1-80.

[14] **H.B. Patil, K.S. Chaudhari** and **S.V. Borse**, *Arch. of Sci. Res.*, **3**(5), (2011) 465-470.

[15] **Akman, H. Karacha** and **M. zdemir**, *Balkan Phy. Letts.*, **16**, (2009) 161037.

[16] **T. Mahalingam, S. Thanikaikarasan, V. Dhanasekaran, Mariappan, P. Jayamurugan, S. Velumani** and **Jin-Koo Rheec**; *Material Sci. and Engi.* **B 174**, (2010) 249-252.

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An overview of arsenic removal technologies in India

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Abstract

In the context of prevalence of high concentrations of arsenic in tubewell water, a wide range technology has been tried for the removal of arsenic from drinking water. The most common technologies utilized the conventional processes of oxidation, co-precipitation and adsorption onto coagulated flocs, adsorption onto sorptive media, ion exchange and membrane techniques for arsenic removal. The conventional technologies have been scaled down to meet the requirements of households and communities and suit the rural environment. Some technologies utilized indigenous materials for arsenic removal. This paper presents a short review of the technologies used for arsenic removal in Bangladesh and India.

Key words : Arsenic removal, drinking water, membrane techniques

1. Introduction

Groundwater is available in shallow aquifers in adequate quantity in the flood plains for development tubewell based water supply for scattered rural population. Bangladesh and West Bengal in India achieved remarkable successesby providing drinking water at low-cost to the rural population through sinking of shallow tubewells in flood plain aquifers. Unfortunately arsenic contamination of shallow tubewell water in excess of acceptable limit has become a major public health problem in both the countries. Thousands of people have already shown the symptoms of arsenic poisoning and several millions are at risk of arsenic contamination from drinking tubewell water. Arsenic toxicity has no known effective medicine for treatment, but drinking of arsenic free water can help the arsenic affected people to get rid of the symptoms of arsenic toxicity. Hence, provision of arsenic free water is urgently needed to mitigate arsenic toxicity and protection of health and wellbeing of rural people living in acute arsenic problem areas of Bangladesh and India. The alternative options available for water supply in the arsenic affected areas include arsenic avoidance and treatment of arsenic contaminated ground water. Treatment of surface waters by low-cost methods, rain water harvesting and water from deep aquifers would be potential sources of water supply to avoid arsenic ingestion through shallow tubewell water. The use of alternative sources will require a major technological shift in water supply. Treatment of arsenic contaminated well water is an alternative option to make use of a huge number of tubewells likely to be declared abandoned for yielding water with high arsenic content.

There are several methods available for removal of arsenic from water in large conventional treatment plants. The most commonly used technologies include oxidation, co-precipitation and adsorption onto coagulated flocs, lime treatment, adsorption onto sorptive media, ion exchange resin and membrane techniques (Cheng *et al.*, 1994; Hering *et al.*, 1996, 1997; Kartinen and Martin, 1995; Shen, 1973; Joshi and Chaudhuri, 1996). A detailed review of arsenic removal technologies is presented by Sorg and Logsdon (1978). Jackel (1994) has documented several advances in arsenic removal technologies. In view of the lowering the drinking water standards by USEPA, a review of arsenic removal technologies was made to consider the economic factors involved in implementing lower drinking water standards for arsenic (Chen *et al.,* 1999). Many of the arsenic removal technologies have been discussed in details in AWWA reference book (Pontius, 1990). A comprehensive review of low-cost, well-water treatment technologies for arsenic removal with the list of companies and organizations involved in arsenic removal technologies has been compiled by Murcott (2000) with contact detail.

Some of these technologies can be reduced in scale and conveniently be applied at household and community levels for the removal of arsenic from contaminated tubewell water. During the last 2-3 years many small scale arsenic removal technologies have been developed, field tested and used under action research programs in Bangladesh and India. A short review of these technologies is intended to update the technological development in arsenic removal, understand the problems, prospects and limitations of different treatment processes and delineate the areas of further improvement for successful implementation and adaptation of technologies to rural conditions.

2. Oxidation

Arsenic is present in groundwater in As (III) and As (V) forms in different proportions. Most treatment methods are effective in removing arsenic in pentavalent form and hence include an oxidation step as preteatment to convert arsenite to arsenate. Arsenite can be oxidized by oxygen, ozone, free chlorine, hypochlorite, permanganate, hydrogen peroxide and fulton's reagent but Atmospheric oxygen, hypochloride and permanganate are commonly used for oxidation in developing countries:

$$H_3AsO_3 + ½O_2 = H_2AsO_4^- + 2H^+ \quad (1)$$

$$H_3AsO_3 + HClO = HAsO_4\_\_ + Cl^- + 3H^+ \quad (2)$$

$$3H_3AsO_3 + 2KMnO_4 = 3HAsO_4 + 2MnO_2 + 2K + 4H + H_2O \quad (3)$$

Air oxidation of arsenic is very slow and can take weeks for oxidation (Pierce and Moore, 1982) but chemicals like chlorine and permanganate can rapidly oxidize arsenite to arsenate under wide range of conditions.

2.1 *Passive Sedimentation*

Passive sedimentation received considerable attention because of rural people's habit of drinking stored water from pitchers. Oxidation of water during collection and subsequent storage in houses may cause a reduction in arsenic concentration in stored water (Bashi Pani). Experiments conducted in Bangladesh showed zero to high reduction in arsenic content by passive sedimentation. Arsenic reduction by plain sedimentation appears to be dependent on water quality particularly the presence of precipitating iron in water. Ahmed *et al.* (2000) showed that more than 50% reduction in arsenic content is possible by sedimentation of tubewell water containing 380-480 mg/L of alkalinity as $CaCO_3$ and 8-12 mg/L of iron but cannot be relied to reduce arsenic to desired level. Most studies showed a reduction of zero to 25% of the initial concentration of arsenic in groundwater. In rapid assessment of technologies passive sedimentation failed to reduce arsenic tothedesiredlevelof50µg/Linanywell (BAMWSP, DFID, Water Aid, 2001).

2.2 *In-situ Oxidation*

In-situ oxidation of arsenic and iron in the aquifer has been tried under DPHE- Danida Arsenic Mitigation Pilot Project. The aerated tubewell water is stored in a tank and released back into the aquifers through the tubewell by opening a valve in a pipe connecting the water tank to the tubewell pipe under the pump head. The dissolved oxygen in water oxidizes arsenite to less mobile arsenate and also the ferrous iron in the aquifer to ferric iron, resulting a reduction in arsenic content in tubewell water. The possible reactions of arsenate to ferric hydroxide are shown in Equations 7 to 8. Experimental results show that arsenic in thetubewell water following *in-situ* oxidation is reduced to about half due to underground precipitation and adsorption on ferric iron.

2.3 *Solar Oxidation*

SORAS is a simple method of solar oxidation of arsenic in transparent bottles to reduce arsenic content of drinking water (Wegelin *et al.,* 2000). Ultraviolet radiation can catalyze the process of oxidation of arsenite in presence of other oxidants like oxygen (Young, 1996). Experiments in Bangladesh show that the process on average can reduce arsenic content of water to about one-third.

3. Co-precipitation and Adsorption Processes

Water treatment with coagulants such as aluminium alum, $Al_2(SO_4)_3.18H_2O$, ferric chloride , $FeCl_3$ and ferric sulfate $Fe_2(SO_4)_3.7H_2O$ are effective in removing arsenic from water. Ferric salts have been found to be more effective in removing arsenic than alum on a weight basis and effective over a wider range of pH. In both cases pentavalent arsenic can be more effectively removed than trivalentarsenic.

In the coagulation-flocculation process aluminium sulfate, or ferric chloride, or ferric sulfate is added and dissolved in water under efficient stirring for one to few minutes. Aluminium or ferric hydroxide micro-flocs are formed rapidly. The water is then gently stirred for few minutes for agglomeration of micro-flocs into larger easily settable flocs. During this flocculation process all kinds of micro- particles and negatively charged ions are attached to the flocs by electrostatic attachment. Arsenic is also adsorbed onto coagualtedflocs. As trivalent arsenic occurs in non-ionized form, it is not subject to significant removal. Oxidation of As(III) to As(V) is thus required as a pretreatment for efficient removal. This can be achieved by addition of bleaching powder (chlorine) or potassium permanganate as shown in Equations 2 and 3. The possible chemical equations of alum coagulation are as follows:

Alum dissolution

$$Al_2(SO_4)_3.18H_2O = 2Al^{+++} + 3SO_4 + 18H_2O \tag{4}$$

Aluminium precipitation (acidic)

$$2Al^{+++} + 6H_2O = 2Al(OH)_3 + 6H^+ \tag{5}$$

Co-precipitation (Non-stoichiometric, non-defined product):

$$H_2AsO_4 + Al(OH)_3 = \text{Al-As (complex)} + \text{Other Products} \tag{6}$$

Arsenic adsorbed on aluminiun hydroxide focs as Al-As complex is removed by sedimentation. Filtration may be required to ensure complete removal of all flocs. Similar reactions take place in case of ferric chloride and ferric sulfate with the formation of Fe-As complex as end product which is removed by the process of sedimentation and filtration.

The possible reactions of arsenate with hydrous iron oxide are shown below where [$\equiv FeOH°$] represents oxide surface site (Mok and Wai, 1994; Hering *et al.*, 1996).

$$Fe(OH)_3\ (s) + H_3AsO_4 \rightarrow FeAsO_4.2H_2O + H_2O \tag{7}$$

$$\equiv FeOH° + AsO_4^{3-} + 3H \rightarrow \equiv FeH_2 + AsO_4 + H_2O \tag{8}$$

$$\equiv FeOH° + AsO_4 + 2H^{3-} \rightarrow \equiv FeHAsO_4 + H_2O \tag{9}$$

Immobilization of arsenic by hydrous iron oxide, as shown in Eqs. 7 to 9, requires oxidation of arsenic species into As(V) form for higher efficiency. Arsenic removal is dependent on pH. In alum coagulation, the removal is most effective in the pH range 7.2-7.5 and in iron coagulation, efficient removal is achieved in a wider pH range usually between 6.0 and 8.5 (Ahmed and Raham, 2000).

3.1 *Bucket Treatment Unit*

The Bucket Treatment Unit (BTU), developed by DPHE-Danida Project is based on the principles of coagulation, co-precipitation and adsorption processes. It consists of two buckets, each 20 liter capacity, placed one above the other. Chemicals are mixed manually with arsenic contaminated water in the upper red bucket by vigorous stirring with a wooden stick for 30 to 60 seconds and then flocculated by gentle stirring for about 90 second. The mixed water is then allowed to settle for 1-2 hours. The water from the top red bucket is then allowed to flow into the lower green bucket via plastic pipe and a sand filter installed in the lower bucket. The flow is initiated by opening a valve fitted slightly above the bottom of the red bucket to avoid inflow of settled sludge in the upper bucket. The lower green bucket is practically at reated water container.

The DPHE-Danida project in Bangladesh distributed several thousands BTU units in rural areas of Bangladesh. These units are based on chemical doses of 200 mg/L aluminum sulfate and 2 mg/L of potassium permanganate supplied in crushed powder form. The units were reported to have very good performance in arsenic removal in both field and laboratory conditions (Sarkar et al., 2000 and Kohnhorst and Paul, 2000). Extensive study of DPHE-Danida BTU under BAMWSP, DFID, Water Aid (2001) rapid assessment program showed mixed results. In many cases, the units under rural operating conditions fails to remove arsenic to the desired level of 0.05 mg/L in Bangladesh. Poor mixing and variable water quality particularly pH of groundwater in different locations of Bangladesh appeared to be the cause of poor performance in rapid assessment.

Bangladesh University of Engineering and Technology (BUET) modified the BTU and obtained better results by using 100 mg/L of ferric chloride and 1.4 mg/L of potassium permanganate in modified BTU units. The arsenic contents of treated water were mostly below 20 ppb and never exceeded 37 ppb while arsenic concentrations of tubewell water varied between 375 to 640 ppb. The BTU is a promising technology for arsenic removal at household level at low cost. It can be built by locally available materials and is effective in removing arsenicifoperated properly.

3.2 *Stevens Institute Technology*

This technology also uses two buckets, one to mix chemicals (reported to be iron sulphate and calcium hypochloride) supplied in packets and the other to separate flocs by the processes of sedimentation and filtration. The second bucket has a second inner bucket with slits on the sides as shown in Figure 1 to help sedimentation and keeping the filter sand bed in place. The chemicals form visible large flocs on mixing by stirring with stick. Rapid assessment showed that the technology was effective in reducing arsenic levels to less than 0.05 mg/L in case of 80 to 95% of the samples tested (BAMWSP, DFID, Water Aid, 2001). The sand bed used for filtration is quickly clogged by flocs and requires washing atleast twice aweek.

3.3 *BCSIR Filter Unit*

Bangladesh Council of Scientific and Industrial Research (BCSIR) has developed an arsenic removal system, which uses the process of coagulation/co-precipitation with an iron based chemical followed by sand filtration. The unit did not take part in a comprehensive evaluation process.

3.4 *Fill and Draw Units*

It is a community type treatment unit designed and installed under DPHE-Danida Arsenic Mitigation Pilot Project. It is 600 L capacity (effective) tank with slightly tapered bottom for collection and withdraw of settled sludge. The tank is fitted with a manually operated mixer with flat-blade impellers. The tank is filled with arsenic contaminated water and required

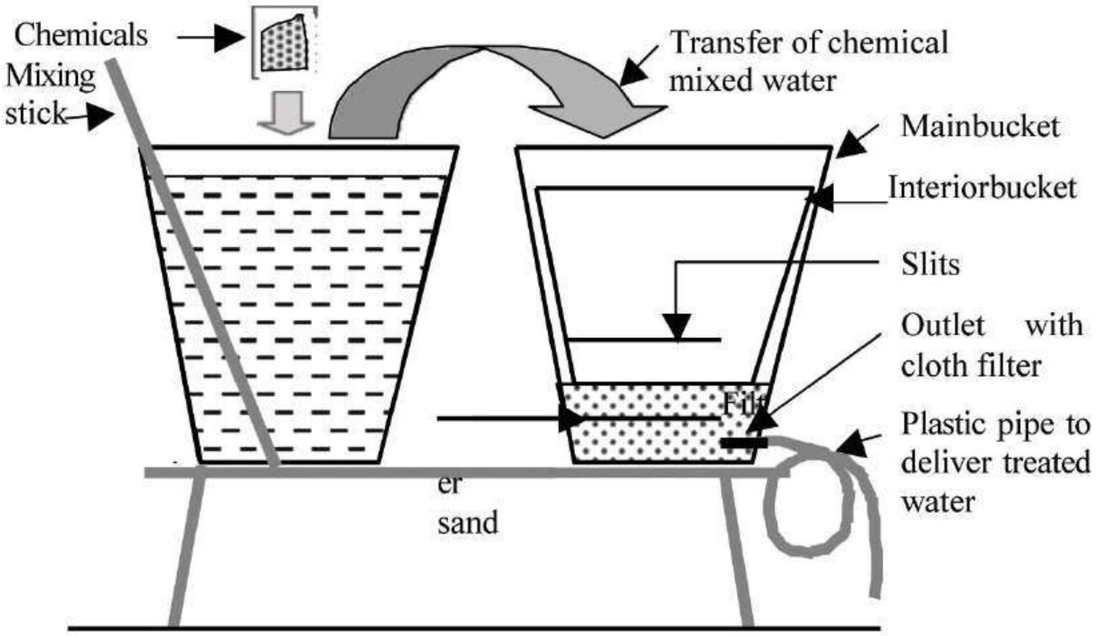

Fig. 1.

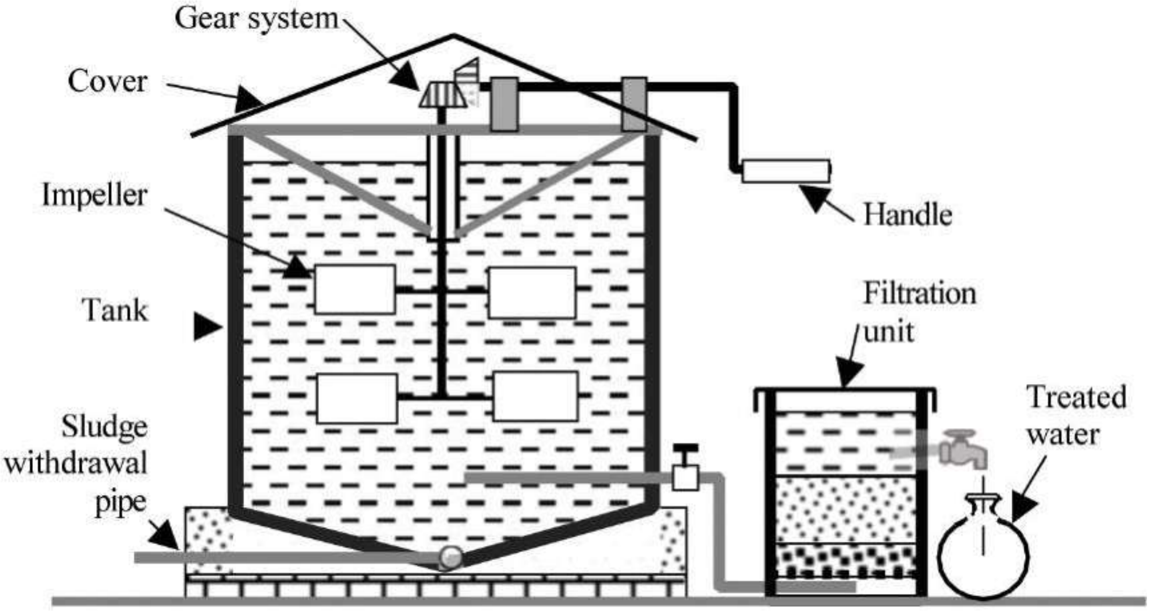

Fig. 2. DPHE-Danida Fill and Draw arsenic removal unit

quantity of oxidant and coagulant are added to the water. The water is then mixed for 30 seconds by rotating the mixing device at the rate of 60 rpm and left overnight for sedimentation. The water takes some times to become completely still which helps flocculation. The floc formation is caused by the hydraulic gradient of the rotating water in the tank. The settled water is then drawn through a pipe fitted at a level, few inches above the bottom of the tank and passed through a sand bed and finally collected through a tap for drinking purpose as shown in Figure 2. The mixing and flocculation processes in this unit are better controlled to effect higher removal of arsenic. The experimental units installed by DPHE-Danida project are serving the clusters off a milies and educational institutions.

3.5 *Arsenic Removal Unit Attached to Tubewell*

The principles of arsenic removal by alum coagulation, sedimentation and filtration have been employed in a compact unit for water treatment in the village level in West Bengal, India. The arsenic

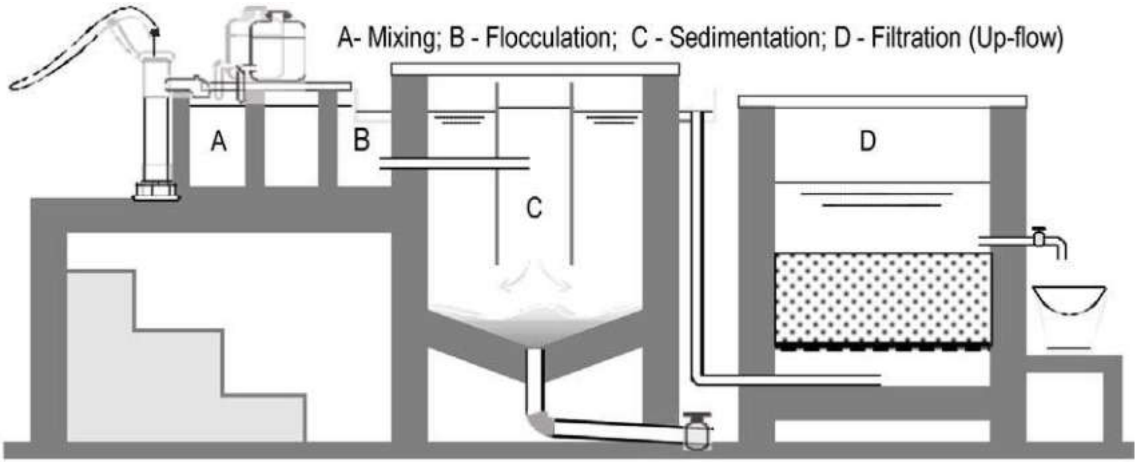

Fig. 3. Arsenic removal plants attached to tubewell (designed and constructed in India)

removal plant attached to hand tubewell as shown in Figure 3 has been found effective in removing 90 percent arsenic from tubewell water having initial arsenic concentration of 300 g/L. The treatment process involves addition of sodium hypochloride (Cl_2), and aluminum alum in diluted form, mixing, flocculation, sedimentation and up flow filtration in a compact unit.

3.6 *Naturally Occurring Iron*

The use of naturally occurring iron precipitates in ground water in Bangladesh is a promising method of removing arsenic by adsorption. It has been found that hand tubewell water in 65% of the area in Bangladesh contains iron in excess of 2 mg/L and in many acute iron problem areas, the concentration of dissolved iron is higher than 15 mg/L. Although no good correlation between concentrations of iron and arsenic has been derived, iron and arsenic have been found to co-exist in ground water. Most of the tubewell water samples satisfying Bangladesh Drinking Water Standard for Iron (1 mg/L) also satisfy the standard for Arsenic (50 μg/L). Only about 50% of the samples having iron content 1 - 5 mg/L satisfy the standard for arsenic while 75% of the samples having iron content > 5 mg/L are unsafe for having high concentration of arsenic.

The iron precipitates [$Fe(OH)_3$] formed by oxidation of dissolved iron [$Fe(OH)_2$] present in groundwater, as discussed above, have the affinity for the adsorption of arsenic. Only aeration and sedimentation of tubewell water rich in dissolved iron has been found to remove arsenic. The Iron Removal Plants (IRPs) in Bangladesh constructed on the principles of aeration, sedimentation and filtration in a small units have been found to remove arsenic without any added chemicals. The conventional community type IRPs, depending on the operating principles, more or less work as Arsenic Removal Plants (ARPs) as well. A study suggests that As(III) is oxidized to As (V) in the IRPs to facilitate higher efficiency in arsenic removal in IRPs constructed in Noakhali (Dahi and Liang, 1998). The Fe-As removal relationship with good correlation in some operating IRPs has been plotted in Figure 4. Results shows that most IRPs can lower arsenic content of tubewell water to half to one-fifth of the original concentrations. The efficiency of these community type Fe-As removal plants can be increased by increasing the contact time between arsenic species and iron flocs. Community participation in operation and maintenance in the local level is absolutely essential for effective use of these plants.

Some medium scale Fe-As removal plants of capacities 2000-3000 m^3/d have been constructed for water supplies in district towns based on the same principle. The treatment processes involved in these plants include aeration, sedimentation and rapid

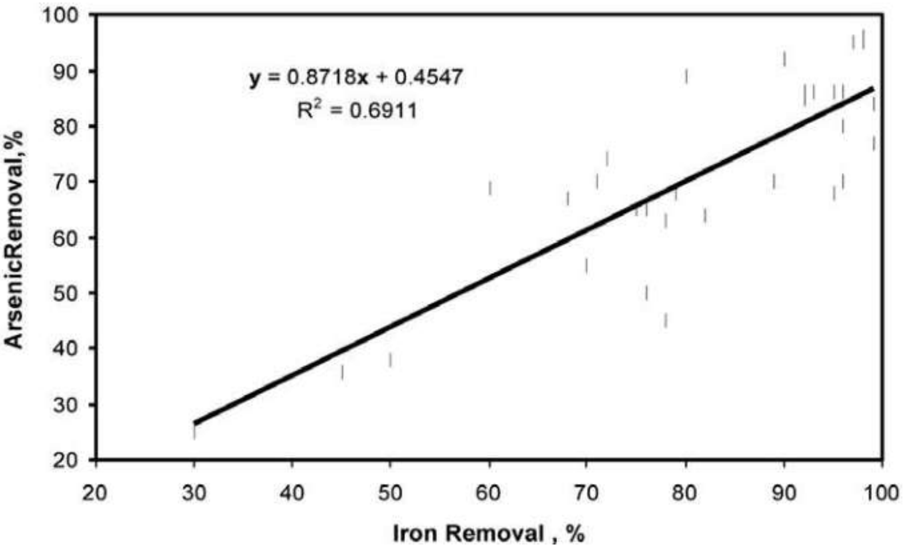

Fig. 4. Correlation between Fe and As Removal in Treatment Plants

sand filtration with provision for addition of chemical, if required.

These plants are working well except that treated water requirement for washing the filter beds is very high. Operations of small and medium size IRP-cum-ARPs in Bangladesh suggest that arsenic removal by co-precipitation and adsorption on natural iron flocs has good potential.

3.7 *Chemical Packages*

In Bangladesh, different types of chemical packages have been distributed in the form of tea bags, small packets and powder or tablet form for the removal of arsenic from drinking water. The principals involved in arsenic removal by these chemicals involve oxidation, sorption and co-precipitation. Application methodology and efficiency of any of these chemicals have not been fully optimized by long experimentation. Quality assurance and dose control in rural condition are extremely difficult. The residuals of added chemicals in water after treatment can do equal harm. The use of unknown chemicals and patented process without adequate information should be totally discouraged.

4. Sorptive Filtration Media

Several sorptive media have been reported to remove arsenic from water. These are activated alumina, activated carbon, iron and manganese coated sand, kaolinite clay, hydrated ferric oxide, activated bauxite, titanium oxide, siliciumoxide and many natural and synthetic media. The efficiency of all some sorptive media depend on the use of oxidizing agent as aids to sorption of arsenic. Saturation of media by different contaminants and components of water takes place at different times of operation depending on the specific sorption affinity of the medium to the given component. Saturation means that the efficiency in removing the desired impurities becomes zero.

4.1 *Activated Alumia*

Activated alumia, Al_2O_3, having good sorptive surface is an effective medium for arsenic removal. When water passes through a packed column of activated alumina, the impurities including arsenic present in water are adsorbed on the surfaces of activated alumina grains. Eventually the column becomes saturated, first at its upstream zone and later the saturated zone moves downstream towards the bottom end and finally the column get totally saturated.

Regeneration of saturated alumina is carried out by exposing the medium to 4% caustic soda, NaOH, either in batch or by flow through the column resulting in a high arsenic contaminated caustic waste water. The residual caustic soda is then washed out and the medium is neutralized with a 2% solution of sulfuric acid rinse. During the process about 5-10% alumina is lost and the capacity of the regenerated medium is reduced by 30-40%. The activated alumina needs replacement after 3-4 regeneration. Like coagulation process, pre-chlorination improves the column capacity dramatically. Some of the activated alumina based sorptive media used in Bangladesh include :

- BUET Activated Alumina
- Alcan Enhanced Activated Alumina
- ARU of Project Earth Industries Inc., USA
- Apyron Arsenic Treatment Unit

The BUET and Alcan activated alumina have been extensively tested in field condition in different areas of Bangladesh under rapid assessment and found very effective in arsenic removal (BAMWSP, DFID, Water Aid, 2001). The Arsenic Removal Units (ARUs) of Project Earth Industries Inc. (USA) used hybrid aluminas and composite metal oxides as adsorption media and were able to treat 200-500 Bed Volume(BV) of water containing 550 g/L of arsenic and 14 mg/L of iron (Ahmed et al. , 2000). The Apyron Technologies Inc. (ATI) also uses inorganic granular metal oxide based media that can selectively remove As(III) and As(V) from water. The Aqua-BindTM arsenic media used by ATI consist of non-hazardous aluminium oxide and manganese oxide for cost-effective removal of arsenic. The proponents claimed that the units installed in India and Bangladesh consistently reduced arsenic to less than 10µg/L.

4.2 *Granular Ferric Hydroxide*

M/S Pal Trockner (P) Ltd, India and Sidko Limited, Bangladesh installed several Granular Ferric

Hydroxide based arrsenic removal units in India and Bangladesh. The Granular Ferric Hydroxide (AdsorpAs®) is arsenic selective adsorbent developed by Technical University, Berlin, Germany. The unit requires iron removal as pre-treatment to avoid clogging of filter bed. The proponents of the unit claims to have very high arsenic removal capacity and produces non-toxic spent granular ferric hydroxide.

4.3 *Read-F Arsenic Removal Unit*

Read-F is an adsorbent produced and promoted by Shin Nihon Salt Co. Ltd, Japan for arsenic removal in Bangladesh. Read-F displays high selectivity for arsenic ions under a broad range of conditions and effectively adsorbs both arsenite and arsenate without the need for pretreatment. The Read-F is Ethylene-vinyl alcohol copolymer (EVOH)-borne hydrous cerium oxide in which hydrous cerium oxide ($Coe_2 \cdot n\ H_2O$), is the adsorbent. The material contains no organic solvent or other volatile substance and is not classified as hazardous material. Laboratory test at BUET and field testing of the materials at 4 sites under the supervision of BAMWSP showed that the adsorbent is highly efficient in removing arsenic from groundwater (SNSCL, 2000).

4.4 *Iron Coated Sand*

BUET has constructed and tested iron coated sand based small scale unit for the removal of arsenic from groundwater. Iron coated sand has been prepared following a procedure similar to that adopted by Joshi and Choudhuri (1996). The iron content of the iron coated sand was found to be 25 mg/g of sand. Raw water having 300 µg/L of arsenic when filtered through iron coated sand becomes essentially arsenic-free. It was found that 350 bed volumes could be treated satisfying the Bangladesh drinking water standard of 50 ppb. The saturated medium is regenerated by passing 0.2N sodium hydroxide through the column or soaking the sand in 0.2N sodium hydroxide followed by washing with distilled water. No significant change in bed volume (BV) in arsenic removal was found after 5 regeneration cycles. It was interesting to note that iron coated sand is equally effective in removing both As (III) and As (V). Iron coated brick dust has also been developed in Bangladesh for arsenic removal from drinking water.

4.5 *Indigenous Filters*

There are several filters available in Bangladesh that use indigenous material as arsenic adsorbent. Red soil rich in oxidized iron, clay minerals, ironore, iron scrap or fillings and processed cellulose materials are known to have capacity for arsenic adsorption. Some of the filters manufactured using these materials include:

- Sono3-KolshiFilter
- Granet Home-madeFilter
- Chari Filter
- Adarsha Filter
- Shafi Filter
- Bijoypur Clay/Processed Cellulose filter

The Sono3-Kolshi filter uses zero valent iron fillings and coarse sand in the top Kolshi, wood coke and fine sand in the middle Kolshi while the bottom Kolshi is the collector of the filtered water (Khan *et al.,* 2000). Earlier Nikolaidis and Lackovic (1998) showed that 97 % arsenic can be removed by adsorption on a mixture of zero valent iron fillings and sand and recommended that arsenic species could have been removed through formation of co-precipitates, mixed precipitates and by adsorption onto the ferric hydroxide solids. The Sono 3- Kolshi unit has been found to be very effective in removing arsenic but the media habour growth of microorganism (BAMWSP, DFID and Water Aid, 2000). The one-time use unit becomes quickly clogged, if groundwater contains excessive iron.

The Garnet home-made filter contains relatively inert materials like brick chips and sand as filtering media. No chemical is added to the system. Air oxidation and adsorption on iron-rich brick chips and flocs of naturally present iron in groundwater could be the reason for arsenic removal from groundwater. The unit produced inadequate quantity of water and did not show reliable results in different areas of Bangladesh and under different operating conditions. The Chari filter also uses brick chips and inert aggregates in different Charis as filter media. The effectiveness of this filter in arsenic removal is not known.

The Shafi and Adarsh filters use clay material as filter media in the form of candle. The Shafi filter was reported to have good arsenic removal capacity but suffered from clogging of filter media. The Adarsha filter participated in the rapid assessment program but failed to meet the technical criterion of reducing arsenic to acceptable level (BAMWSP, DFID and Water Aid, 2000). Bijoypurclay and treated cellulose were also found to adsorb arsenic from water (Khair, 2000).

4.6 *Cartridge Filters*

Filter units with cartridges filled with soptive media or ion-exchange resins are readily available in the market. These unit remove arsenic like any other dissolved ions present in water. These units are not suitable for water having high impurities and iron in water. Presence of ions having higher affinity than arsenic can quickly saturate the media requiring regeneration or replacement. Two household filters were tested at BUET laboratories, These are:

- Chiyoda Arsenic Removal Unit, Japan
- Coolmart Water Purifier, Korea.

The Chiyoda Arsenic Removal Unit could treat 800 BV meeting the WHO guideline value of 10 µg/L and 1300 BV meeting the Bangladesh Standard of 50 µg/L when the feed water arsenic concentration was 300 µg/L. The Coolmart Water Purifier could treat only 20 L of water with a effluent arsenic content of 25 µg/L (Ahmed *et al.*, 2000). The initial and operation costs of these units are high and beyond the reach of the rural people.

5. Ion Exchange

The process is similar to that of activated alumina, just the medium is a synthetic resin of more well defined ion exchange capacity. The process is normally used for removal of specific undesirable cation or anion from water. As the resin becomes exhausted, it needs to be regenerated. The arsenic exchange and regeneration equations with common salt solution as regeneration agent are as follows:

Arsenic exchange

$$2\mathbf{R}\text{-Cl} + HAsO_4^- = R_2HAsO_4 + 2Cl^- \qquad (10)$$

Regeneration

$$\mathbf{R}_2HAsO_4 + 2N^+ + 2Cl^- = 2R\text{-Cl} + HAsO_4 + 2Na \qquad (11)$$

Where **R** stands for ion exchange resin.

The arsenic removal capacity is dependent on sulfate and nitrate contents of raw water as sulfate and nitrate are exchanged before arsenic. The ion exchange process is less dependent on pH of water. The efficiency of ion exchange process is radically improved by pre-oxidation of As (III) to As (V) but the excess of oxidant often needs to be removed before the ion exchange in order to avoid the damage of sensitive resins. Development of ion specific resin for exclusive removal of arsenic can make the process very attractive.

Tetrahedron ion exchange resin filter tested under rapid assessment program in Bangladesh (BAMWSP, DFID and Water Aid, 2000) showed promising results in arsenic removal. The system needs pre-oxidation of arsenite by sodium hypochloride. The residual chlorine helps to minimize bacterial growth in the media. The saturated resin requires regeneration by recirculating NaCl solution. The liquid wastes rich in salt and arsenic produced during regeneration require special treatment. Some other ion exchange resins were demonstrated in Bangladesh but sufficient field test results are not available on the performance of thoseresins.

6. Membrane Techniques

Membrane techniques like reverse osmosis, nanofiltration and electrodialysis are capable of removing allkinds of dissolved solids including arsenic from water. In this process water is allowed to pass through special filter media which physically retain the impurities present in water. The water, for treatment by membrane techniques, shall be free from suspended solids and the arsenic in water shall be in pentavalent form. Most membranes, however, cannot withstand oxidizing agent.

6.1 *MRT-1000 and Reid System Ltd.*

Jago Corporation Limited promoted a household reverse osmosis water dispenser MRT-1000 manufactured by B & T Science Co. Limited, Taiwan. This system was tested at BUET and showed a arsenic (III) removal efficiency more than 80%. A wider spectrum reverse osmosis system named Reid System Limited was also promoted in Bangladesh. Experimental results showed that the system could effectively reduce arsenic content along with other impurities in water. The capital and operational costs of the reverse osmosis system would be relatively high.

6.2 *Low-pressure Nanofiltration and Reverse Osmosis*

Oh *et al.* (2000) applied reverse osmosis and nanofiltration membrane processes for the treatment of arsenic contaminated water applying low pressure by bicycle pump. A nanofiltration membrane process coupled with a bicycle pump could be operated under condition of low recovery and low pressure range from 0.2 to 0.7 MPa. Arsenite was found to have lower rejection than arsenate in ionized forms and hence water containing higher arsenite requires pre-oxidation for reduction of total arsenic acceptable level. In tubewell water in Bangladesh the average ratio of arsenite to total arsenic was found to be 0.25. However, the reverse osmosis process coupled with a bicycle pump system operating at 4 Mpa can be used for arsenic removal because of its high arsenite rejection. The study concluded that low-pressure nanofiltration with pre-oxidation or reverse osmosis with a bicycle pump device could be used for the treatment of arsenic contaminated ground water in rural are as (Oh *et al.*, 2000).

7. Discussions

A remarkable technological development in arsenic removal from rural water supply based on conventional arsenic removal processes has been taken place during last 2-3 years. A comparison of different arsenic removal processes is shown in Table 1.

All the technologies described in this paper have

Table 1. A comparison of main arsenic removal technologies.

Technologies	Advantages	Disadvantages
Oxidation/Precipitation		
• Air Oxidation • Chemical oxidation	• Relatively simple, low-cost but slowprocess • Relatively simple and rapidprocess • Oxidizes other impurities and kills microbes	• The processes remove only a part of arsenic
Coagulation Coprecipitation :		
• Alum Coagulation • Iron Coagulation	• Relatively low capital cost, • Relatively simple operation • Common Chemicals available	• Produces toxic sludges • Low removal of As(III) • Pre-oxidation may be required
Sorption Techniques		
• Actvated Alumina • Iron Coated Sand • Ion Exchange Resin • Other Sorbents	• Relatively well known and commercially available • Well defined technique • Plenty possibilities and scope ofdevelopment	• Produces toxic solid waste • Replacement/regeneratio n required • High tech operation and maintenance • Relatively high cost
Membrane Techniques		
• Nano filtration • Reverse osmosis • Electrodialysis	• Well defined and high removal efficiency • No toxic solid wastes produced • Capable of removal of other contaminants	• Very high capital and running cost • High tech operation and maintenance • Toxic wastewater produced

their merits and demerits and are being refined to make suitable in rural condition. The modifications based on the pilot-scale implementation of the technologies are in progress with the objectives to:

- Improve effectiveness in arsenic removal
- Reduce the capital and operation cost of the systems
- Make the technology user friendly
- overcome maintenance problems
- resolve sludge and arsenic concentrates management problems.

Arsenic removal technologies have to compete with other technologies in which cost appears to a major determinant in the selection of a treatment option by the users. The rural people habituated in drinking tubewell water may find arsenic removal from tubewell water as a suitable option for water supply. Inmany arsenic affected areas, arsenic removal may be the only option in the absence of an alternative safe source of water supply.

A rapid assessment of 9 household level arsenic removal technologies has been completed recently (BAMWSP, DFID and Water Aid, 2000). On the basis of this study the Technical Advisory Group (TAG) of Bangladesh Arsenic Mitigation Water Supply Project (BAWSP) has recently recommended the following household arsenic removal technologies for experimental use in arsenic affected areas:

- Alcan Enhanced Activated Alumia
- BUET Activated Alumina
- Sono3-KolshiMethod
- Stevens Institute Technology

The widely used DPHE/Danida two buckets system and Tetrahedron ion exchange resin filters will be reviewed when more information on performance of the systems and its revised version are available. Few more technologies in addition to technologies described in this paper are available for arsenic removal at household and community levels. These technologies need evaluation in respect of effectiveness sin arsenic removal and community acceptance.

8. Conclusion

The technologies found effective and safe for arsenic removal from tubewell water need promotion for wider implementation in the acute arsenic problem areas to avoid ingestion of excessive arsenic through tubewell water. The arsenic removal technologies are expected to improve further through adaptation in rural environment.

References

[1] **Ahmed M.F** and **Rahaman M. M.**, *Water Supply and Sanitation - Low Income Urban Communities*, International Training Network (ITN) Centre, BUET, 2000.

[2] **Ahmed. F., Jalil M.A., Ali M.A., Hossain M.D.** and **Badruzzaman A.B.M.,** An overview of arsenic removal technologies in BUET, In *Bangladesh Environment*-2000, M.F.Ahmed (Ed.), Bangladesh Poribesh Andolon, 177-188.

[3] **BAMWSP DFID** and **WaterAid Bangladesh**, *Rapid Assessment of Household Level Arsenic Removal Technologies*, Phase-! and Phase-II, Final Report, WS Atkins International Limited, 2001.

[4] **Chen H.W., Frey M.M., Clifford D., McNeill L.S.** and **Edwards M.**, Arsenic treatment considerations, *Journal of American Water Works Association*, **91**(3), (1999) 74-85.

[5] **Cheng C.R., Liang S., Wang H.C.** and **Beuhler M. D.**, "Enhanced coagulation for arsenic removal", *J. American Water Works Association*, **86**(9), (1994) 79-90.

[6] **Dahi E.** and **Liang Q.**, "Arsenic Removal in Hand Pump Connected Iron Removal Plants in Noakhali, Bangladesh " presented at *International Conference on Arsenic Pollution of Ground Water in Bangladesh : Causes, Effect and Remedies,* Dhaka, (1998).

[7] **Hering J.G., Chen P.Y., Wilkie J.A., Elimelech M.** and **Liang S.**, Arsenic removal by ferric chloride, *J. American Water Works Association*, **88**(4), (1996) 155-167.

[8] **Hering J.G., Chen P., Wilkie J.A.** and **Elimelech M.,** Arsenic removalfrom drinking water during coagulation, *J. Env. Eng., ASCE*, **123**(8), (1997) 800- 807.

[9] **Jekel M.R.**, Removal of arsenic in drinking

water treatment. In J.O. Nriagu (Ed.) *Arsenic in the Environment, Part 1: Cycling and Characterization*, John Wiley & Sons, Inc., New York, (1994).

[10] **Joshi A.** and **Chaudhury M.**, Removal of arsenic from groundwater by iron-oxide-coated sand, *ASCE Journal of Environmental Engineering,* **122**(8), (1996) 769-771.

[11] **Kartinen E.O.** and **Martin C.J.**, an overview of arsenic removal processes, *J. Desalination*, **103**, (1995) 79-88.

[12] **Khair A.**, Factors responsible for the presence of arsenic in groundwater: Bangladesh context, In *Bangladesh Environment*-2000, M.F.Ahmed (Ed.), Bangladesh Poribesh Andolon,: (2000) 198-209.

[13] **Khan A.H., Rasul S.B., Munir A.K.M. Alauddin M., Habibuddowlah M.** and **Hussam A.**, On two simple arsenic removal methods for groundwater of Bangladesh, In *Bangladesh Environment-2000*, M.F.Ahmed (Ed.), Bangladesh Poribesh Andolon: (2000) 151-173.

[14] **Kohnhorst A.** and **Paul P.**, Testing simple arsenic removal methods, In *Water, Sanitation and Hygiee: Challenges of the Millennium,* Preprints of the 26 WEDC Conference, Dhaka, and Bangladesh, (2000) 177-181.

[15] **Mok W.M.** and **Wai C.M.**, Mobilization of arsenic in Contaminated River Water in Arsenic in the Environment (J.O. Nriagu Ed.), John Wiley & Sons Inc, (1994).

[16] **Murcott S.**, A comprehensive review of low-cost, well-water treatment technologies for arsenic removal, (2000) http://phys4.harvard.edu/~wilson,/murcott2.

[17] .html.

[18] **Nikolaidis N.P.** and **Lackovic J.**, "Arsenic Remediation Technology- AsRT", presented at *International Conference on Arsenic Pollution of Ground Water in Bangladesh: Causes, Effect and Remedies,* (1998).

[19] **Oh J.I., Yamamoto K., K., Kitawaki H., Nakao S., Sugawara T.** and **Rahaman**.

[20] **M.M.** and **Rahaman M.H.**, Application of low-pressure nanofiltration coupled with a bicycle pump for the treatment of arsenic-contaminated ground water, Desalination, **132**, (2000) 307-314.

[21] **Oh, J.I., K., Urase T., Kitawaki H., Rahaman M.M., Rahaman M.H.** and **Yamamoto, K.**, Modelling of arsenic rejection considering affinity and steric hindrance effect in nonofiltration membranes, *Water Science and Technology,* **42**(3-4), 173-180.

[22] **Pierce M.L.** and **Moore C.B.**, Adsorption of Arsenite and Arsenate on amorphous iron hydroxide, *Water Resources,* **16**, (1982) 1247-1253.

[23] **Pontius F.W.** (Ed.), Water Quality Treatment: a handbook of community water supplies, *American Water Works Association,* McGraw-Hill, New York, (1990).

[24] **Sorg T.J.** and **Logsdon G.S.**, Treatment technology to meet the interim primary drinking water regulations for inorganics: Part 2, *Journal of the American Water Works Association,* **70**(7), (1974) 379-393).

[25] **Shen Y.S.**, Study of arsenic removal from drinking water", *J. American Water Works Association,* **65**(8), (1973) 543-548.

[26] **Shin Nihon Salt Co. Ltd.**, Report on Performance of Read-F Arsenic Removal Unit (ARU), (2000).

[27] **Sarkar A.**, **Thogersen Choudhury, Rahaman Akhter** and **Choudhury**, Bucket Treatment unit for arsenic removal, In *Water, Sanitation and Hygiene: Challenges of the Millennium,* Preprints of the 26 WEDC Conference, Dhaka, Bangladesh., (2000) 308-310.

[28] **Wegelin M., Gechter D., Hug S., Mahmud A.** and **Motaleb A.**, (2000). SORAS-a simple arsenic removal process (http://phys4.harvard.edu/wilson/mitigation/SORAS_Paper.html).

[29] **Young E.**, Cleaning up arsenic and old waste, *New Scientist*, (1996).

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A review of solar powered generation by photovoltaic technology

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Abstract

In the global environmental concern the various forms of solar energy like solar heat, solar photovoltaic, solar thermal electricity, and the solar fuel the rising demand for energy offer a clean, environmental-friendly, very promising and generous energy resource to mankind. In this there is a brief discussion of early research and a description hot photovoltaic cells convert sunlight to electricity.Solar powered is the conversion of sunlight rays into electricity using semiconducting material that exhibit the photovoltaic effect or indirectly using concentrated solar power. The research has been happen for the development of an affordable, in exhaustive and clean solar powered energy for the long term benefits. It is one of the finest ways to hardness the solar power energy. This paper reviews the progress and initiation of solar power generation research and development.

Key words : Solar energy, solar photovoltaic technology, Renewable energy, MPPT.

1. Introduction

Photovoltaic (PV) is the field of technology and research associated to the application of solar cells for energy by changing sun energy (sunlight, containing sun ultra violet radiation) directly into electricity.Solar cells, also called photovoltaic (PV) cells by scientists, directly convert sunlight into electricity. This process of PV gets the name of converting light (photons) to electricity (voltage), which is known as PV effect and it was discovered in 1954, when scientists at bell telephone discovered that silicon (an element found in sand) created an electric charge when exposed to sunlight. Soon solar cells were bringing used to power space satellites and smaller items like calculators and watches. Photovoltaic devices are sharp and simple in design requiring very little maintenance and their largest advantage being they give the output construction as stand-alone systems from microwatts to megawatts. Due to the rising demand for clean sources of energy, the manufacture of solar cells and photovoltaic arrays has extended dramatically in recent years. Every two yearsPhotovoltaic production has been expanding, increasing by an average of 48% each year since 2002, making it the world's fastest-growing energy technology. At the end of 2008, the growing global PV installations reached 15,200 Megawatts. Roughly 90% of this generating capacity contains of grid tied electrical systems. Such installations may be ground-mounted or made into the roof or walls of a building, known as Building Unified Photovoltaic or BIPV for short.

Hence the power sources to be used such as, solar home systems, pumping, remote buildings, communications, satellites and space vehicles, converse osmosis plants, and for even megawatt scale power plants. With such a huge array of applications, the demand for photovoltaic is growing every year. A typical photovoltaic system employs solar panels, each containing a number of solar cells, which generate electricity power. The first step is the photoelectric effect monitored by an electrochemical process where crystallized atoms, ionized in a series, create an electric current[1]. PV installations may be ground-mounted, rooftop mounted or wall mounted. They may be mounted in a permanent direction to maximize production and value or they may be mounted on trackers that follow the sun across the sky. Solar PV causes no pollution[2]. The direct transformation of sunlight to electricity occurs without any affecting parts. Photovoltaic systems have been used for fifty years in specified application, standalone and grid-connection PV systems have been in usage for more than twenty years[3]. They were first mass-produced in 2000, when German environmentalist and the Euro solar organization got government finance for a ten thousand roof program[4]. On the other hand, grid-connection PV system have the major difficulty that the power output is dependent on direct sunlight, so about 10-25% is lost if a tracking system is not used, since the cell be indirectly facing the sun at all times[5]. Power output is also harmfully affected by weather conditions such as the amount of dust and water vapour in the air or the amount of cloud cover[6, 7]. The potential of PV/T collectors has been predictable since 1970 and has received increased care in the past decade. Compared to using dispersed solar technologies for heat and electricity and the production are to be form the same collector surface is often considered more cost operative[8], requires less space and shows significantly lower balance-of-system expenses. The potential of PV/T collectors is large, as many potential users have immediate requirements for heat and electricity. Net metering and financial reasons, like preferential feed-in tariffs for solar generated electricity; have supported solar PV installations in many countries including Australia, Germany, Israel, Japan, and the United States.

2. Concepts and benefits

2.1 *Concept and feasibility studies*

In 1839 the first time discovered the photovoltaic effect by Becquerel[9]. Now, after some time in 1877, the photovoltaic effect in solid selenium was observed by Adams and Day[10]. The first photovoltaic cell developed in 1883, and its effect was less than 1%[10]. Due on in 1904 paper on photovoltaic effect was published by Einstein[10]. In 1927 various different type of photovoltaic cell was developed by using copper and semiconductor copper oxide, but the effect of this device is less than 1%[9]. On 1941 the silicon photovoltaic cells developed by Ohl[11]. In 1960 the photovoltaic power generation technology, the space program continued to demand to improved. Scientist requiredgetting as much electrical power as likely from photovoltaic collector, and cost existed secondary importance[12]. On earlier the conventional energy sources reduction rapidly, environmental concern, and high energy demand to investigate the PV technology, many governments decided to investigate the PV technology for large scale energy application, both standalone and grid connected (without storage) configuration. The latter has been widely investigated and they form the reference model because it performs as the most feasible technology and economical solution. Right from the start, the development has had a dynamic and articulate characteristic and has been managed both in R& D and demonstration field with particular emphasis on technology feasibility ad cost efficacy. The industrial has always looked at the actual dimension of the unaided intermediate market as a reference to increase the PV market continuously[13]. Production of cost has been reduced in recent years for more wide range use through production and technological advance, and is usual to fall in future.

2.2 *Benefits and application*

Solar energy is one of the most available forms of energy on the Earth's surface, besides; it is very promising and generous. As kind of renewable energy, solar energy is paid more and more attention in the world. Out of all renewable energy resources, solar energy is one of the most feasible alternative and sustainable energy resources in the world. Solar power system derives clean, pure energy from the sun direct use of heat resulting from the absorption of solar radiation. Solar photovoltaic system and solar power system is one of renewable energy system, both the system uses PV modules to convert sunlight into electricity through a simple solid-state device, lack of moving parts, ability to function unattended for long period low maintenance cost, long effective life, high reliability, and quick response in output to input radiation changes, high power handling capabilities from micro to kilowatt and even megawatt, which is more important for space application than terrestrial (may be favorable for some terrestrial application), amenable to onsite installation, decentralized/dispersed power;

therefore the power distribution problem by wires might could be eliminated where the power is required by the use of solar cells at the site[14]. The electricity generated can be stores or use directly, fed back into grid line or combined with one or more other electricity generator or more renewable energy sources. Solar PV system is very reliable and clean sources of electricity and its range of application is suit and wide, such as residential, industry, agriculture, livestock, *etc*. The major factor that limits the use of various applications of solar energy is that, it is cyclic time-dependent energy source. So, solar systems require energy storage to provide energy during the darkness period[15]. In energy storage technologies Inclusive research and advancement proposals benefits for solar in energy application. There is considerable work being done on fuel cell technology, which should offer a very low-price and more efficient mechanism for storing energy. Solar systems, which when not connected to grid, store energy in conventional lead acid battery. Similarly, hydrogen offers considerable potential as a major power source, and examinations are being done to use solar to produce hydrogen asa power source[16].

This Solar system can be classified into two categories; those are thermal system which convert solar energy to thermal energy and photovoltaic systems which convert solar energy to electrical energy. Sun is the first uses as a direct source of heat energy and is very common used for supplying hot water to houses and swimming pools. In photovoltaic process the solar electricity seeks to convert light from the sun directly into electricity. Photovoltaic system may be categorized as stand-alone photovoltaic system for solar vehicles applications, grid-connection photovoltaic system and building systems.

The stand-alone solar systems are not connected to a grid. Stand-alone solar power systems have been used for a long time in areas where no public grid is available. It may vary widely in size and application ranging from wrist watches or calculator to remote building or spacecraft. Billinton and Karki presenteda simulation method and its objective provides to help system planner decide on appropriate installation sites, selection of PV arrays or diesel units in capacity extension and optimal PV penetration levels when utilizing PV energy in small isolated system[17]. Koutroulis E et al. have developed a methodology for the optimal sizing of hybrid, stand-alone PV/WG system. In this the selection standards for commercially available system device we discussed, the optimal number and type of PV modules, WGs and PV battery chargers, the PV module's tilt angle and the normal capacity[18]. Friling et alpresented the Performance Enhancement of the heat transfer of building integrated photovoltaic modules[19]. Fanni L *et al.* presented comprehensive analysis of gains and losses of fully-integrated flat roof amorphous silicon photovoltaic plants[20].

Photovoltaic power generation widely used in remote application with small power requirements where the distribution running cost was not feasible. As on reasonable price of PV power, the use of photovoltaic for grid-connected application is increasing. However, the high cost of PV modules and large area they require continue to be difficulties t using PV power to supplement existing electrical utilities. Both of these problems the approach is the integration of photovoltaic into building materials[14].

3. Photovoltaic system for Power generation

A photovoltaic power generation system contains of multiple components like cells mechanical and electrical assembly and mountings and means of adaptable and/or modifying the electrical output. These systems are valued in peak kilowatts (kWp) which is an amount of electrical power that a system is predictable to deliver when the sun is directly overhead on a clear day. A grid connected system is linked to a huge independent grid which in most cases is the public electricity grid and feeds power into the grid. They vary in Size from few kWp for residential purpose to solar power station up to tens of GWp. This is a form of dispersed electricity generation. Poponi evaluated the prospects for diffusion of photovoltaic (PV) technology for electricity generation in grid-connected systems by the methodology of experience bends that is used to expect the different levels of increasing world PV shipments required to reach the calculated break-even prices of PV systems, supposing different trends in the relationship between prices and the rise in cumulative shipments[21]. Al-Hasan et al. discussed optimization of the electrical load pattern in Kuwait using grid connected PV systems as the electric load demand can be fulfilled from both the photovoltaic array and the utility and found during the performance evaluation that the peak load matches the maximum incident solar radiation in Kuwait, which would highlight the role of using the PV station to minimize the electrical load demand and a significant decrease in peak load can be achieved with grid connected PV systems[22]. Rehman *et al.* utilized monthly average daily solar radiation and sunshine duration data to study the delivery of radiation and sunshine duration over Saudi Arabia and also examined the renewable energy production and economical assessment of a 5 MW installed capacity photovoltaic based grid connected power plant for electricity generation[23].

Ito *et al*. studied a 100 MW very large-scale photovoltaic power generation (VLS-PV) system which is to be installed in the Gobi and assessed its potential from economic and environmental viewpoints inferred from energy payback time (EPT), life cycle CO_2 emission rate and generation cost of the system[24]. Zhou *et al*. performed the economic analysis of power generation from moving solar chimney power plant (FSCPP) by evaluating cash flows during the whole service period of a 100 MW plant[25]. Muneer *et al*. discovered the long term predictions of large scale PV generation in arid/ semi-arid locations, around the globe and its transmission using hydrogen as the energy vector[26]. Cunow et al. described the megawatts plant at the new Munich Fir Centre that represents a significant advance in large PV plant technology and the components employed, operational control and costs[27].

Bhuiyan *et al*. studied the economics of stand-alone photovoltaic power system to exam its feasibility in remote and rural areas of Bangladesh and related renewable generation with non-renewable generators by determining their life cycle cost by the method of net present value study showed that life cycle cost of PV energy is lower than the cost of energy from diesel or petrol generation in Bangladesh and thus is economically feasible in remote and rural areas of Bangladesh[28].

4. Hybrid solar power generation system

Hybrid power generation system combines a renewable energy source with other forms of generation; usually a conventional generator powered by diesel is even another renewable form of energy like wind. Such hybrid system serves to reduce the consumption of non-renewable fuel.

Barton *et al.* presented a novel method of modeling an energy store used to match the power output from a wind turbine and a solar PV array to varying electrical load and validated the method against time stepping methods showing god agreement over a wide range of store power grades, store productivities, wind turbine capacities and solar PV capacities[29]. Katti and khedkarapplication of wind-alone, solar-alone, and combined wind PV generation for utilization as stand-a-lone generation system, to be used as the remote areas which were based on the site matching and an energy flow strategy that satisfies the need with optimum unit sizing by[30]. Deshmukh *et al*. presented methodology to model hybrid renewable energy system (HRES) components, HRES design and their evaluation showing that the hybrid PV/wind energy systems are becoming gradually popular and highlighted, the matters related to penetration of this systems in the present distribution network as it provides prospects of incorporating in power generation capacity to recover power quality, due to the isolated generation[31]. El-Shatter *et al.* designed a hybrid photovoltaic (PV)-fuel cell generation system using an electrolyze for hydrogen generation and applied a fuzzy progression model (FRM) for maximum power point tracking to extract maximum available solar power from PV arrays under variable insolation condition[32]. Maclay *et al*. developed a model of a solar-hydrogen powered residence, in both stand-a-lone and grid parallel configuration using Matlab/ Simulink that assesses the feasibility of employing a recreating fuel cell (RFC) as an energy storage devices to be used with photovoltaic (PV) electrical generation and investigated the design requirement of RFC sizing, battery sizing, charge/discharge rates, and state of charge limitations[33]. Zervas *et al*. studied of hybrid power generation system comprising of the following main modules: Photovoltaic Array (PV), Electrolyze, Metal Hybrids Tanks, and Proton Exchange Membrane Fuel Cells (PEMFC), its can efficient to store solar energy by transforming it to hydrogen, which is the fuel supplied to the fuel cell al[34].

Helal *et al*. conducted a techno economic study to analyze the economic feasibility of three alternative design and the design option include a diesel- assisted PV-RO plant, a fully diesel option include a diesel driven RO plant and a fully solar-driven PV-RO plant and performed detailed cost calculation for each one of the suggested configuration to assess their feasibility and cost effectiveness[35]. Schmid and Hoffmann presented simulation showing that PV systems with energy storage connected to prevailing diesel generators that can be turned off during the day deliver the lowest energy costs[36].

5. Light absorbing material

All solar cells require a light absorbing material which is present-day within the cell structure to absorb photons and generate free electrons via the photovoltaic effect. The photovoltaic (PV) effect is the basic of the transfer of light to electricity in photovoltaic, or solar cells. Sunlight, which is pure energy, on striking PV cell, imparts sufficient energy to some electrons (negatively charged atomic particles) to increase their energy level and thus free them. A build-in-potential barrier in the cell acts on these electrons to produce a voltage, which in turn is used to drive a current through a circuit.

5.1 *Silicon*

Bruton asserted that silicon technology has been the leading one for the source of power modules into photovoltaic applications and the likely changes are a growing proportion of multi-crystalline silicon and monocrystalline silicon existence used for high-efficiency solar cells while thinner wafers and ribbon silicon technology continue to grow[37]. Braga *et al*. reviewed the current advances in chemical and metallurgical ways for photovoltaic (PV) silicon production and found that production of (solar-grade silicon) SoGSi (expand the acronym) can be five times extra energy efficient than the conventional Siemens process that uses more than 200 kWh/kg[38]. Goetzberger *et al*. briefed the history of photovoltaic material and tried to look at possible future scenarios with silicon as min concern[39]. Vander Zwaan and Rabble presented current PV production cost ranges, both in terms of capacity installation and electricity generation, of single crystalline silicon and other thin film technology assessing possible cost reductions expected according to the learning-curve methodology[40]. Aouida *et al*. investigated the structural and optic stability of porous silicon layers (PSLs) planned to be used in silicon solar cells technology with UV irradiation applied to PS-treated solar cells improving their PV characteristic[41]. Keogh et al. suggested that testing of silicon solar cells under natural sunlight is simpler, cheaper, and more accurate than all but the most careful simulator measurements[42]. Hanoka discussed a silicon ribbon development method, String Ribbon comparing it with the two other vertical ribbon technologies discussing the characterization of this ribbon, particularly dislocated distribution and detailed the growth progress of 100 μm ribbon[43]. Schlemm et al. presented a magnetic field enhanced linear microwave plasma source and its application for removal of silicon nitride anti-reflective and passivation layers on photovoltaic cells[44]. McCann et al. showed that excellent bulk lifetimes and surface passivation can be preserved with a low pressure chemical vapour deposition (LPCVD) silicon nitride layer put on a silicon wafer, even following high-temperature treatment provided a thin layer of silicon oxide is present under the nitride[45]. Adamian *et al*. investigated the possibility of using porous silicon layers as antireflection coating instead of anti-reflection coatings in common silicon solar cells (ZnS) and complete comparison of the photovoltaic and optical characteristic of investigated samples of solar cells with ZnS antireflection coating and with porous silicon antireflection coating[46]. Balenzategui *et al.* focused on the measurement of the angular response of solar cells based on different silicon technologies and analyzed the sources of aberration from the theoretical response, especially those due to the surface reflectance[47].

5.1.1 *Amorphous Silicon*

Amorphous silicon (a-Si) is the non- crystalline form silicon. It is the well-developed of the thin film technology having been on the market for more than 15 years. It is widely used in pocket calculation, but it also powers some private homes, building and remote facilities. It its simplest form, the cell structure has a single sequence of p-i-n layers. However, single layer cell suffer from significant degradation in their output (in the range 15-35%) when exposed to the

Sun. the mechanism of degradation is called Staebler-Wronski Effect, after its discoverers.UnitedSolar Syatems Crop. (UniSolar) pioneered amorphous-silicon solar cells and remains a major maker today, as does Sharp and Sanyo.

Yang *et al*. discussed the advances made in amorphous-Si PV technology that directed to the achievement of an AM 1.5, 13% stable cell efficiency and set the foundation for the spectrum splitting triple-junction structure being manufactured by the roll-to-roll continuous deposition process[48]. Lund *et al*. reported on the laboratory and field studies being undertaken on the nature of the Staebler-Wronski effect in amorphous silicon cells and how the stability of these cells is affected by different operation conditions and proposed a number of possible way to reduce the Staebler-Wronski effect in a Si:H solar cells[49].

5.1.2 *Crystalline Silicon*

Crystalline silicon photovoltaic is the most widely used photovoltaic, crystalline silicon photovoltaic are modules built using crystalline silicon solar cells (c-Si), developed from the microelectronic technology industry. Crystalline silicon solar cells have high efficiency, making crystalline silicon photovoltaic an interesting technology where space is at a premium. Crystalline silicon proposals to improve the efficiency when compared to amorphous silicon while still using only a small amount of material. The commercially available multi-crystalline silicon cells have efficiency around 14-19%.

Green *et al*. Developed crystalline silicon glass (CSG) solar cell technology, the advantages of standard silicon wafer-based technology with that of thin-films, with the deepest likely manufacturing cost of these contenders and confirmed efficiency for small pilot line modules already I the 8-9% energy conversion efficiency range, on the path to 12-13%[50]. Shah *et al*. proposed that intrinsic microcrystalline silicon deposited at temperature as low as 200-250 °C by the WHF-GD (very high frequency-glow discharge) method has been used successfully as photovolataically active material within p-i-n and n-i-p type solar cells[51]. Lipinski *et al*. investigated double porous silicon (d-PS) layers formed by acid chemical engraving on a top surface of n+/p multi-crystalline silicon solar cells with the aim to improve the act of standard screen-printed silicon solar cells, the PS layers helping as an antireflection coating with the efficiency of the solar cells with this structure is about 12%[52]. Franklin et al. described the novel sliver cells made of single crystal silicon solar cells that proposal the potential for a 10-20 times lessening in silicon consumption for the same sized solar module, though additional benefit, in an industrial production environment, of requiring 20-40 times rarer wafer starts per MW than for conventional wafer-based technologies[53].

The manufacture of crystalline silicon PV module is divided into several steps, starting with wafer cutting, cell fabrication and module assembly. In wafer stage, solar-grade multicrystalline or single crystal silicon ingots are sliced into wafer 0.2 mm thick. During the cell stage, a p-n junction is formed by dopant diffusion, and electric contacts are created by applying and sintering metallization pastes. In the module stage, the cells are connected physically and electronically and are then encapsulated by glass and plastics (ethylene-vinyl acetate [EVA], Tedlar, *etc.*).

5.2 *Organic and polymer cells*

Jorgensen *et al.* presented a thoughtful of stability/degradation in organic and polymer solar cell devices and discussed the method for studying and clarifying degradation and enhancing through the stability for better active material, encapsulation, application of getter materials and UV filters[54]. Bernede *et al*. studied different cell configurations: two-layer D/A organic solar cells deposited by vacuum evaporation and bulk D/A hetero junction material based on a discontinuous D/A network thin film obtained by spin coating[55]. Wei *et al*. demonstrated efficiency white organic light-emitting device based on excelled with higher luminance and luminous efficiency and this bi-functional device with electroluminescence (EL) and PV performance is promising to be used as white displays or backlight source in the upcoming as it can be charged by solar energy through additional apparatus free of work and can also be used as an optional sensor to UV light[56].

5.3 *Hybrid photovoltaic cells*

A hybrid solar cell contains of a combination of both organic and inorganic semiconducting materials.

The unique properties of inorganic semiconductors with the film-forming properties of the conjugated polymers[57]. Organic materials usually are inexpensive, easily process able, and their functionality can be tailored by molecular design and chemical synthesis. Further the inorganic semiconductors can also be manufactured as process able Nano particulate colloids. By varying the size of the nanoparticles, their band gap can be tuned and their absorption/emission spectra can be tailored[58].

An effective strategy for hybrid solar cell fabrication is to use blends of Nano crystals with semi conductive polymers as bulk hetero junction[57-62]. Exactions formed upon photo excitation are separated freely charged carriers very efficiently at interfaces between organic semiconductors and inorganic semiconductor nanoparticles in a hybrid compound thin film. The n-type and p-type solubility components in the same solvent are in important problem. Commonly the organic semiconductors are dissolved in organic solvents, while the inorganic semiconducting nanoparticles are also easily dissolved in aqueous solvents. Using ligand exchange, the nanoparticles can be made soluble in common organic solvents. Hybrid solar cells have been demonstrated in conjugated polymer blends containing CdSe, CuInS2, CdS, or PbS Nano crystals.

High surface tension of very small inorganic Nano crystals makes them unbalanced, and thus they have a tendency to produce by a process called "Ostwald ripening". Therefore, nanoparticles are synthesized commonly shielded by an organic ligand. These ligands prevent the combination and oxidation of the nanoparticles and can alter the dispersion characteristics of the particles into the polymer matrices[57, 60]. This organic ligand, further it is a barrier for transport of charges from nanoparticle to nanoparticle. So the hybrid solar cells, such ligands have to be removed to ensure intimate electrical contact between the nanoparticles.

5.4 *Thin film technology*

As the name implies, thin-film technology are made of layers of semiconductors typically a few microns thick (approximately 100 times thinner than those used in conventional single and multi-crystalline silicon technologies). The property is enabling by the absorption coefficient of these semiconductors being higher than that of crystalline silicon, resulting in lower material use and thus cheaper technologies. A thin- film solar cell is a second generation solar cell that is complete by depositing one or more thin layers, or the photovoltaic material of thin-film (TF) on a substrate, such as glass, plastic or metal. Thin-film solar cells are commercially used in many technologies, including cadmium telluride (CdTe), copper indium gallium dieseline (CIGS), and amorphous thin-film silicon (a-Si, TF-Si).

Barnett *et al*. investigated that solar cells utilizing thin-film polycrystalline silicon can be achieve photovoltaic power conversion efficiencies greater than 195 as a result of light trapping and back surface passivation with optimum silicon thickness[63]. Aberle reviewed the most promising thin-film c-Si PV technologies that have arisen during the last 10 years and found that three different types of thin-film c-Si PV technologies (SILVER, hybrid, CSG) can be transferred to industrial production[64]. Ito et al. present techniques to TiO_2 film fabrication for dye-sensitized solar cells that consists of pre-treatment of the working photo electrode by $TiCL_4$, variation in layers thickness of the transparent nanocrystalline-TiO_2 and claim of a topcoat light-scattering layer as well as the adhesion of an anti-reflecting film to the electrode's surface resulting in a conversion efficiency of global air mass 1.5 (AM 1.5, 1000W/m^2) solar light to electric power over 10%[65]. Sathyamoorthy *et al.* discussed the electrical transport properties of flash evaporated Zinc Phthalocyanine thin films and studied the DC conduction mechanism in these films (Al-ZnPc-Al structure) at altered temperatures along with the field dependence behavior on activation energy and possible conduction mechanism in the ZnPc films under DC field[66].

The manufacturing stage for thin-film PV technologies is relatively simple compared with crystalline silicon (resulting in an additional cost advantage). Thin-film PV manufacturing typically relies on a series of semiconductor-layer depositions on a glass or stainless steel substrate followed by module fabrication steps (*e.g.*, encapsulation) similar to those used for crystalline silicon technologies. Other flexible substrates can sometimes be used to produce building integrated PV products.

6. Performance and reliability

Researchers and scientists had proposed many methods for evaluation of performance of a photovoltaic system. A brief review of some methods is present here.

Li *et al*. investigated the operational performance and effectiveness characteristic of a small PV system installed at the City University of Hong Kong and the amount of solar irradiance data filling on the PV panel was determine using the luminous efficacy approach[67]. Yu *et al*. developed a novel two-mode maximum power point tracking (MPPT) control algorithm the modified constant voltage control and incremental conductance method (IncCond) method to improve the efficiency of the 3 kWPV power generation system at different insolation condition that provides excellent performance at less than 30% insolation, covering the whole insolation area without additional hardware circuitry[68]. Jaber *et al*. developed a computer-simulation model of the behavior of a photovoltaic (PV) gas-turbine hybrid system, with a compressed-air store, to assess its performance as well as to predict the total energy-conversion efficiency and found that hybrid plant produces approximately 140% more power per unit of fuel expended compared with corresponding conventional gas turbine plants and lower rates of pollutant emission to the atmosphere per kWh of electricity generated[69]. Keogh *et al*. existing a new tester (commonly used for measuring solar cells and modules) design that is simple, low cost, and reduces transient errors by use of a constant voltage cell-bias circuit and it excerpts a family of I-V curves over a decade range of light intensity, which provides comprehensive information on cell performance[70]. So *et al*. analyzed evaluated the performance of a large scale grid-connected PV system and observing system that are installed at SSDP in Daegu City in order to observe the overall effect of meteorological condition on their operation characteristic for monitoring period[71].

7. Conclusion

Reducing the dependence on fossil fuel and addressing the priority issues of environment, the solar energy will play an increasing important role in a future. Photovoltaic efficiency and manufacturing costs not much not the point that photovoltaic power generation can replace conventional coal-gas, nuclear-powered generating facilities.PV/T is a technology combining PVs and solar thermal components of solo module to enhance the solar conversion efficiency of the system and make economic use of the space. Photovoltaic power generation is quiet more costly than conventional system in general. On the other hand, huge variations in cost of conventional electrical power, and other influences, such as cost of supply, create situation in which the use of PV power is economically sound. The some application of photovoltaic power generation used in remote area such as communications, villages and homes in developing countries, water pumping, camping, and boating. Also the application of grid-connection such s electric utility generation facilities and residential rooftop installations mark up a slighter but more rapidly rising segment of PV use.Manufacturing and the efficiency costs not reached at that point where the photovoltaic power generation can replace conventional coal-, gas-, and nuclear-powered generating facilities. PV cost is much more than conventional power. Moreover, as technological developments narrow the cost gap, as more applications are becoming economically feasible at an accelerating rate. Many difficulties, related like development of reasonable, clean and unlimited solar energy technologies for long time period and the huge benefits, desirable to policies to unlock the extensive potential of solar energy for appropriate system planning and power operation system to supply excellent and dependable power electric source.

References

[1] Solar Cells - Chemistry Encyclopedia - structure, metal, equation, Thepn Junction. Chemistryexplained.com. Retrieved on 2015-11-10.

[2] **Jump up^ Pearce, Joshua**. "Photovoltaics - A Path to Sustainable Futures". Futures, **34**(7) (2002), 663. doi:10.1016/S0016-3287(02)00008-3.

[3] **Jump up to: a b c d M. Bazilian, I. Onyeji, M. Liebreich, I. MacGill, J. Chase, J. Shah, D. Gielen, D. Arent, D. Landfear** and **S. Zhengrong**. "Re-considering the economics of

photovoltaic power" (PDF). Renewable Energy. **53**, (2013), 329. doi:10.1016/j.renene.2012.11.029.

[4] **Jump up^ Palz, Wolfgang**. Solar Power for the World: What You Wanted to Know about Photovoltaics. CRC Press. (2013), 131-. ISBN 978-981-4411-87-5.

[5] **Bushong Steven**. Advantages and disadvantages of a solar tracker systemhttp://www.solarpowerworldonline.com/2016/05/advantages-disadvantages-solar-tracker-system/. (2016). Missing or empty |title= (help).

[6] Jump up^ "Grid connect solar power FAQ - Energy Matters".

[7] Jump up^ http://scool.larc.nasa.gov/lesson_plans/CloudCoverSolarRadiation.pdf

[8] **P.E. Tomaszewski**. Jan Czochralski-father of the Czochralski method. *J. Cryst Growth*, **236**(1-3) (2002), 1.

[9] Energy conversion: development of solar cells. Britannica.online, http://www.eb.com:180-cgi-bin/g? DocF¼macro/5002/13/245.html; (1998).

[10] The history of PV. http://www.pvpower.com/pvhistory.html; (1998).

[11] **Zweibel Kenneth** and **Herch Paul**. Basic photovoltaic principles and methods. New York: Van Nosstrand Reinhold Company, Inc.; (1984).

[12] **M. Hammonds**. Getting power from the sun: solar power. *Chemistry and Industry,* **6** (1998), 219e28.

[13] **D. Coiante** and **Barra**. Can photovoltaics become an effective energy option. *Solar Energy Materials and Solar Cells,* **27** (1992), 79e89.

[14] **Singh** and **Girish Kumar**. "Solar power generation by PV (photovoltaic) technology: a review." *Energy,* **53** (2013), 1.

[15] **G. Kumaresan, R. Sridhar** and **R. Velraj**. Performance studies of a solar parabolic trough collector with a thermal energy storage system. *Energy*, **47** (2012), 395e402.

[16] **G.D. Rai**. Non-conventional energy sources. 4th ed. New Delhi, India: *Khanna Publisher*, (2006).

[17] **R. Billinton** and **R. Karki**. Reliability/cost implications of utilizing photovoltaics in small isolated power systems. *Reliability Engineering and System Safety,* **79** (2003), 11e6.

[18] **E. Koutroulis, D. Kolokotsa, A. Potirakis** and **K. Kalaitzakis**. Methodology for optimal sizing of stand-alone photovoltaic/wind-generator systems using genetic algorithms. *Solar Energy,* **80** (2006), 1072e88.

[19] **N. Friling, M.J. Jimenez, H. Bloem** and **H. Madsen**. Modeling of heat dynamics of building integrated and ventilated photovoltaic modules. *Energy and Buildings,* **41** (2009), 1051e7.

[20] **L. Fanni, A. Virtuani** and **D. Chianese**. A detailed analysis of gains and losses of afully integrated flat roof amorphous silicon photovoltaic plant. *Solar Energy*, **85** (2011), 2360e73.

[21] **R. Alazraki** and **J. Haselip**. Assessing the uptake of small-scale photovoltaic electricity production in Argentina: the PERMER project. *Journal of Cleaner Production*, **15** (2007), 131.

[22] **A.Y. Al-Hasan, A.A. Ghoneim** and **A.H. Abdullah**. Optimizing electrical load pattern in Kuwait using grid connected photovoltaic systems. *Energy Conversion and Management*, **45** (2004), 483.

[23] **S. Rehman, A. Bader Maher** and **A. Al-Moallem Said**. Cost of solar energy generated using PV panels. *Renewable and Sustainable Energy Reviews*, **11** (2007), 1843.

[24] **T. Muneer, M. Asif** and **J. Kubie**. Generation and transmission prospects for solar electricity: UK and global markets. *Energy Conversion and Management,* **44** (2003), 35-52.

[25] **E. Cunow** and **B. Giesler**. The megawatt solar roof at the new Munich Trade Fair Centre-an advanced and successful new concept for PV plants in the megawatt range. *Solar Energy Materials & Solar Cells,* **67** (2001), 459.

[26] **MMH Bhuiyan, M. Ali Asgar, R.K. Mazumder** and **M. Hussain**. Economic evaluation of a stand-alone residential photovoltaic power system in Bangladesh. *Renewable Energy,* **21** (2000), 403.

[27] E. Cunow and B. Giesler. The megawatt solar roof at the new Munich Trade Fair Centre-an advanced and successful new concept for PV plants in the megawatt range. *Solar Energy Materials & Solar Cells,* **67** (2001), 459.

[28] **MMH Bhuiyan, M. Ali Asgar, R.K. Mazumder** and **M. Hussain**. Economic evaluation of a stand-alone residential photovoltaic power system in Bangladesh. *Renewable Energy,* **21** (2000), 403.

[29] **P.B. John** and **G.I. David**. A probabilistic method for calculating the usefulness of a store with finite energy capacity for smoothing electricity generation from wind and solar power. *Journal of Power Sources,* **162** (2006), 943.

[30] **P.K. Katti** and **M.K. Khedkar**. Alternative energy facilities based on site matching and generation unit sizing for remote area power supply. *Renewable Energy,* **32** (2007), 1346.

[31] **M.K. Deshmukh** and **S.S. Deshmukh**. Modeling of hybrid renewable energy systems. *Renewable and Sustainable Energy Reviews,* **12** (2008), 235.

[32] ThF El-Shatter, M.N. Eskandar and M.T. El-Hagry. Hybrid PV/fuel cell system design and simulation. *Renewable Energy,* **27** (2002), 479.

[33] **J.D. Maclay, J. Brouwer** and **G. Scott Samuelsen**. Dynamic analyses of regenerative fuel cell power for potential use in renewable residential applications. *International Journal of Hydrogen Energy,* **31** (2006), 994.

[34] **P.L. Zervas, H. Sarimveis, J.A. Palyvos** and **N.C.G. Markatos**. Model-based optimal control of a hybrid power generation system consisting of photovoltaic arrays and fuel cells. *Journal of Power Sources,* **181** (2008), 327.

[35] **A.M. Helal, S.A. Al-Malek** and **E.S. Al-Katheeri**. Economic feasibility of alternative designs of a PV-RO desalination unit for remote areas in the United Arab Emirates. *Desalination,* **221** (2008), 1-16.

[36] **L.A. Schmid** and **C.A.A. Hoffmann**. Replacing diesel by solar in the Amazon: short-term economic feasibility of PV-diesel hybrid systems. *Energy Policy,* **32** (2004), 881-98.

[37] **T.M. Bruton**. General trends about photovoltaics based on crystalline silicon. *Solar Energy Materials & Solar Cells,* **72** (2002), 3.

[38] **A.F.B. Braga, S.P. Moreira, P.R. Zampieri, J.M.G. Bacchin** and **P.R. Mei**. New processes for the production of solar-grade poly crystalline silicon: A review. *Solar Energy Materials & Solar Cells,* **92** (2008), 418.

[39] **A. Goetzberger** and **C. Hebling**. Photovoltaic materials, past, present, future. *Solar Energy Materials & Solar Cells,* **62** (2000), 1.

[40] **B. van der Zwaan** and **A. Rabl**. Prospects for PV: a learning curve analysis. *Solar Energy,* **74** (2003), 19.

[41] **S. Aouida, M. Saadoun, M.F. Boujmil, M. Ben Rabha** and **B. Bessais**. Effect of UV irradiations on the structural and optical features of porous silicon: application in silicon solar cells. *Applied Surface Science,* **238** (2004), 193-8.

[42] **W.M. Keogh** and **A.W. Blakers**. Accurate measurement using natural sunlight, of silicon solar cells. *Progress in Photovoltaics: Research and Applications,* **12** (2004), 1.

[43] **J.I. Hanoka**. An overview of silicon ribbon growth technology. *Solar Energy Materials & Solar Cells,* **65** (2001), 231.

[44] **H. Schlemm, A. Mai, S. Roth, D. Roth, K.M. Baumgartner** and **H. Mueggeb**. Industrial large scale silicon nitride deposition on photovoltaic cells with linear microwave plasma sources. *Surface and Coatings Technology,* **174-175** (2003), 208.

[45] **M. McCann, K. Weber** and **A. Blakers**. Surface passivation by rehydrogenation of silicon-nitride-coated silicon wafers. *Progress in Photovoltaics: Research and Applications,* **13** (2005), 195.

[46] **Z.N. Adamian, A.P. Hakhoyan, V.M. Aroutiounian, R.S. Barseghian** and **K. Touryan**. Investigations of solar cells with porous silicon as antireflection layer. *Solar Energy Materials & Solar Cells,* **64** (2000), 347.

[47] **J.L. Balenzategui** and **F. Chenlo**. Measurement and analysis of angular response of solar cells. *Solar Energy Materials & Solar Cells,* **86** (2005), 53.

[48] **J. Yang, A. Banerjee** and **S. Guha**. Amorphous

silicon based photovoltaics-from earth to the "final frontier". *Solar Energy Materials & Solar Cells,* **78** (2003), 597.

[49] **C.P. Lund, K. Luczak, T. Pryor, J.C.L. Cornish, P.J. Jennings, P. Knipe** and **F. Ahjum**. Field and laboratory studies of the stability of amorphous silicon solar cells and modules. *Renewable Energy,* **22** (2001), 287.

[50] **M.A. Green, P.A. Basore, N. Chang, D. Clugston, R. Egan, R. Evans, D. Hogg, S. Jarnason, M. Keevers, P. Lasswell, J.O. Sullivan, U. Schubert, A. Turner, S.R. Wenham** and **T. Young**. Crystalline silicon on glass (CSG) thin-film solar cell modules. *Solar Energy*, **77** (2004), 857.

[51] **A. Shah, E. Vallat-Sauvain, P. Torres, J. Meier, U. Kroll, C. Hof, C. Droz, M. Goerlitzer, N. Wyrsch** and **M. Vanecek**. Intrinsic microcrystalline silicon (mc-Si:H) deposited by VHF-GD (very high frequency-glow discharge): a new material for photovoltaics and optoelectronics. *Materials Science and Engineering B*, **69-70** (2000), 219.

[52] **M. Lipinski, P. Panek, Z. Swiatek, E. Beltowska** and **R. Ciach**. Double porous silicon layer on multi-crystalline Si for photovoltaic application. *Solar Energy Materials & Solar Cells*, **72** (2002), 271.

[53] **E. Franklin, V. Everett, A. Blakers** and **K. Weber**. Sliver solar cells: high-efficiency low-cost PV technology. *Advances in Opto Electronics,* (2007).

[54] **M. Jorgensen, K. Norrman** and **F.C. Krebs**. Stability/degradation of polymer solar cells. *Solar Energy Materials & Solar Cells*, **92** (2008), 686.

[55] **J.C. Bernede, H. Derouiche** and **V. Djara**. Organic photovoltaic devices: influence of the cell configuration on its performances. *Solar Energy Materials & Solar Cells,* **87** (2005), 261.

[56] **H. Wei, W. Li, M. Li, W. Su, Q. Xin, J. Niu, Z. Zhang** and **Z. Hu**. White organic electro-luminescent device with photovoltaic performances. *Applied Surface Science,* **252** (2006), 2204-8.

[57] **E. Arici, N.S. Sariciftci** and **D. Meissner**. *AdV. Funct. Mater*, **2** (2003), 13.

[58] **H. Weller**. Angew. Chem., *Int. Ed. Engl.* **32** (1993), 41.

[59] **W. Hunyh, J. Dittmer** and **A.P. Alivisatos**. *Science,* **295** (2002), 2425.

[60] **E. Arici, D. Meissner, F. Scha¨ffler** and **N.S. Sariciftci**. *Int. J. Photoenergy*, **5** (2003), 199.

[61] **N.C. Greenham, X. Peng** and **A.P. Alivisatos**. *Phys. ReV. B,* **54** (1996), 17628.

[62] **W. Huynh, X. Peng** and **A.P. Alivisatos**. AdV. Mater. 1999, 11, 11

[63] **A.M. Barnett, J.A. Rand, R.B. Hall, J.C. Bisaillon, E.J. DelleDonne, B.W. Feyock, D.H. Ford, A.E. Ingram, M.G. Mauk, J.P. Yasko** and **P.E. Sims**. High current, thin silicon-on-ceramic solar cell. *Solar Energy Materials & Solar Cells,* **66** (2001), 45.

[64] **G. Aberle Armin**. Fabrication and characterisation of crystalline silicon thin film materials for solar cells. *Thin Solid Films*, **511-512** (2006), 26-34.

[65] **S. Ito, T.N. Murakami, P. Comte, P. Liska, C. Gratzel, M.K. Nazeeruddin** and **M. Gratzel**. Fabrication of thin film dye sensitized solar cells with solar to electric power conversion efficiency over 10%. *Thin Solid Films,* **516** (2008), 4613.

[66] **R. Sathyamoorthy, S. Senthilarasua, S. Lalithaa, A. Subbarayana, K. Natarajana** and **Xavier Mathew**. Electrical conduction properties of flash evaporated Zinc Phthalocyanine (ZnPc) thin films. *Solar Energy Materials & Solar Cells*, **82** (2004), 169.

[67] **DHW Li, GHW Cheung** and **CL Joseph**. Analysis of the operational performance and efficiency characteristic for photovoltaic system in Hong Kong. *Energy Conversion and Management*, **46** (2005), 1107.

[68] **G.J. Yu, Y.S. Jung, J.Y. Choi** and **G.S. Kim**. A novel two-mode MPPT control algorithm based on comparative study of existing algorithms. *Solar Energy*, **76** (2004), 455.

[69] **J.O. Jaber, S.D. Odeh** and **S.D. Probert**. Integrated PV and gas-turbine system for satisfying peak-demands. *Applied Energy*, **76** (2003), 305.

[70] **W.M. Keogh, A.W. Blakers** and **A. Cuevas**.

Constant voltage I-V curve flash tester for solar cells. *Solar Energy Materials & Solar Cells*, **81** (2004), 183.

[71] **J.H. So, Y.S. Jung, B.G. Yu, H.M. Hwang** and **G.J. Yu**. Performance results and analysis of large scale PV system. *In: IEEE 4th World Conference on Photovoltaic energy conversion*, **2** (2006).

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Conventional and renewable energy scenario of India: present and future

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Abstract

This paper presents a review about conventional and renewable energy scenario of India.Energy is one of the major parameters for establishing growth and progress of the country, rather the standard of living depends directly upon the per capita energy consumption.In India most of the power generation is carried out by conventional energy sources, coal and mineral oil-based power plants which are depleted day by day as population increase and contribute heavily to greenhouse gases emission. Due to this world are moving for renewable energy source such as solar energy, wind energy, tidal energy, geothermal energy and ocean energy. Last 30 years has been a period of exuberant hunt of activities related to research, development, production and demonstration at India. India has obtained application of a variety of renewable energy technologies for use in different sectors too. This paper presents current status, major achievements and future aspects of renewable energy in India. In this paper evaluationof current energy policies for conquering the obstructions and implementing renewables for the future is also been presented.

Key words : Conventional Energy, Renewable energy, Solar Energy.

1. Introduction

Renewable energy (RE) has become an important agenda of India's energy planning process especially since climate change has taken centre stage in the domestic and international policy arena. With high economic growth rates and over 17.32 percent of the world's population, India is a significant consumer of energy resources. India, at 1.27 billion people, is the second most populated country in the World. Despite the global financial crisis, India's energy demand continues to rise. India consumes its maximum energy in Residential, commercial and agricultural purposes in comparison to China, Japan, Russia, EU-27 and US[1].

To demonstrate its commitment to renewable energy, the government has set aggressive targets for renewables and several incentives and policy initiatives at the Central and State levels have been put in place both for grid connected and off-grid renewable energy.

1.1 *Why are Renewable Sources better than Oil Resources?*

A broad comparison between renewable sources of energy and oil resources based on some factors is given below, see Table 1. It indicates that renewable resources are the future for the country in the energy sector and there is a Need to completely unleash the potential of these resources.

2. Renewable Energy Scenario in India

Solar Energy : Radiant light and heat from the sun, has been harnessed by humans since ancient times using a range of ever-evolving technologies. Solar radiation, along with secondary solar-powered resources such as wind and wave power, hydroelectricity and biomass, account for most of the available renewable energy on earth. Only a minuscule fraction of the available solar energy is used. India is both densely populated and has high solar insolation, providing an ideal combination for solar power in India. The solar energy received on

Table 1. Difference between renewable energy and oil resources

S.N	Kind	Renewable sources of energy	Oil Reserves
1	Availability	They are abundant in nature	Oil reserves are limited in nature
2	Regeneration	Can be Regenerated; Inexhaustible resource	Ore is drained, can't be regenerated
3	Emission	Zero emission Releases	Greenhouse gases
4	Environmental	effect of use There is no adverse effect on Environment. The whole system is pollution free and environment Friendly.	Harmful to the environment
5	Transportation	Used where it is available or transported where needed	Has to be transported from its source site for further processing, exposing the environment to pollution from accidents
6	Distribution	Evenly distributed in World.	Uneven distribution which leads to flow gap and price fluctuations
7	Development	Leads to more Sustainable development i.e. more jobs Opportunities	Lesser sustainable Development
8	Storage	Need storage between Production and consumption.	Portable form of energy. Easy to store
9	Climate Change	Depends on altercation of climate	Do not depend on weather modifications
10	Area	Large amount of land is Required	Not large geographical area is required
11	Geopolitical implications	Reduces our reliance on oil, Safe guarding national security. Allows for self-sufficiency [3]	Over-reliance on oil as a resource can undermine a country's energy Security. [3]
12	Cost	High Capital and Maintenance cost.[4]	Cost of producing is low since they are Naturally available. Furthermore they are cheap to transform from one form of energy to Another. [4]
13	Energy Supply	Once generated, they produce high amount of Energy.	Limited supply only

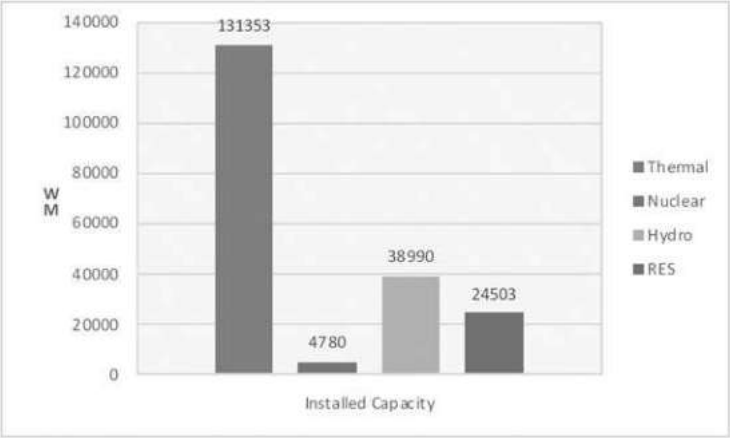
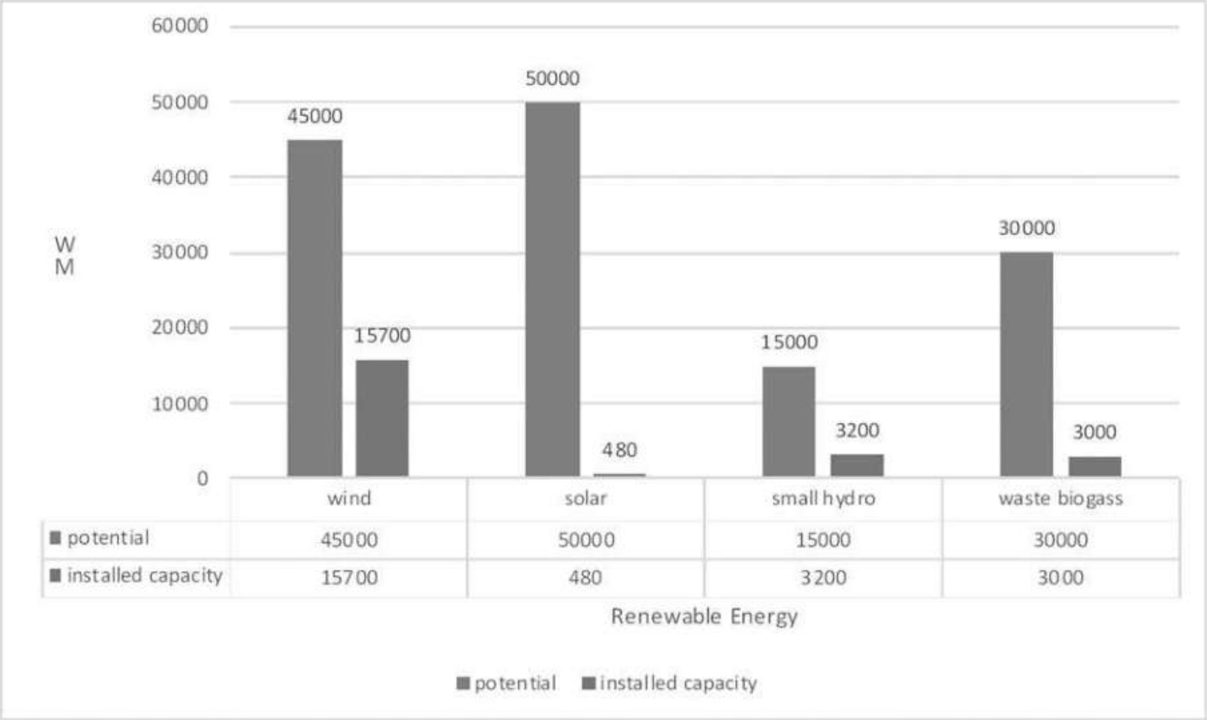


Table 2. State policy for Solar Energy

State	Month of release	Target addition
Andhra Pradesh	September 2012	Has not set a target
Chhattisgarh	October 2012	500-1,000 MW by 2017
Gujarat	October 2009	500 MW
Karnataka	September 2011	350 MW
Kerala	November 2013	500 MW by 2017 and 2,500 MW by 2030
Madhya Pradesh	January 2012	
Punjab	December 2012	1,000 MW by 2022
Rajasthan	2011	12,000 MW by 2022
Tamil Nadu	October 2012	3,000 MW by 2015
Uttarakhand	September 2013	500 MW by 2017
Uttar Pradesh	1st Quarter of 2013	500 MW by 2017

the earth are 20000 times of global requirements. In solar energy sector, some large projects have been proposed, and a 35,000 km² area of the Thar Desert has been set aside for solar power projects, sufficient to generate 700 to 2,100 gigawatts. India is endowed with rich solar energy resource. The average intensity of solar radiation received on India is 200 MW/km square (megawatt per kilometre square). With a geographical area of 3.287 million km square, this amounts to 657.4 million MW. However, 87.5% of the land is used for agriculture, forests and fallow lands 6.7% for housing, industry, *etc.*, and 5.8% is either barren, snow bound, or generally inhabitable. Thus, only 12.5% of the land area amounting to 0.413 million km square can, in theory, be used for solar energy installations. Total energy consumption % in India is, by type combustible.renewable and waste 27.2 Hydro 1.8 Oil 23.7 Nuclear 0.8 Coal/Peat 40.8 Natural



	wind	solar	small hydro	waste biogass
■ potential	45000	50000	15000	30000
■ installed capacity	15700	480	3200	3000

Table 3. Overview of solar policy

	Tamil Nadu	Andhra Pradesh	Karnataka	Punjab	Madhya Pradesh	Uttar Pradesh	Rajasthan	Total/average
Allocation date	June 2013	June 2013	Apr 2012	July 2013	May 2012	July 2013	Mar 2013	Most of the allocations happened in the first half of 2013
PPAs signed as on September 2013 (MW)	0	60	60	0	225	0	75	420
Tariff (INR/kWh)	6.48 (with an escalation of 5% p.a. for the first 10 years)	6.49	7.94-8.5 (60 MW) 5.51-8.05 (130 MW)	7.2-8.63	7.9-8.05	8.01-9.27	6.45	7.59
New PPAs expected to be signed by the year end (MW)	500	80	100	230	0	120	0	1330
Further allocations (MW)	None	500	None	None	None	None	RfS for 1 MW x 50 announced	550
Delayed projects (MW)	NA	NA	50	NA	120	NA	NA	170
Expected commissioning date of projects under deployment	Dec 2014	Mar 2014 (50 MW) Dec 2014 (110 MW)	Dec 2014	Dec 2014	Mar 2014	Dec 2014	Mar 2014	250 MW by March 2014; 1,240 MW by Dec 2014
Expected period of procurement	Jan 14 - Mar 14	Jan 14 - Mar 14	Ongoing	Jan 2014 - Mar 2014	Ongoing	Jan 2014 - Mar 2014	Ongoing	Most of the procurements will take place between Jan-Mar 2014

Table 4. Total energy consumption in India

S.N	Equipment	Units
1	Number of solar street lighting systems	55,795
2	Number of home lighting systems	342,607
3	Solar lanterns	560,295
4	Solar photovoltaic power plants	1566 kW
5	Solar water heating systems	140 km^2 of collect or area
6	Box-type solar cookers	575,000
7	Solar photovoltaic pumps	6,818

Table 5. Renewable Energy Capacity in MW

Source	Installed capacity by end of 11th Plan (March 2012)	Current installed Capacity (March 2015)	Target as per 12th Plan (March 2017)	Revised Targets till 2022
Solar Energy	941	3383	10941	100000
Wind Energy	17352	22645	32352	60000
Biomass Power	3325	4183	6125	10000
Small Hydro	3395	4025	5495	5000
Total	24914	34351	54914	175000

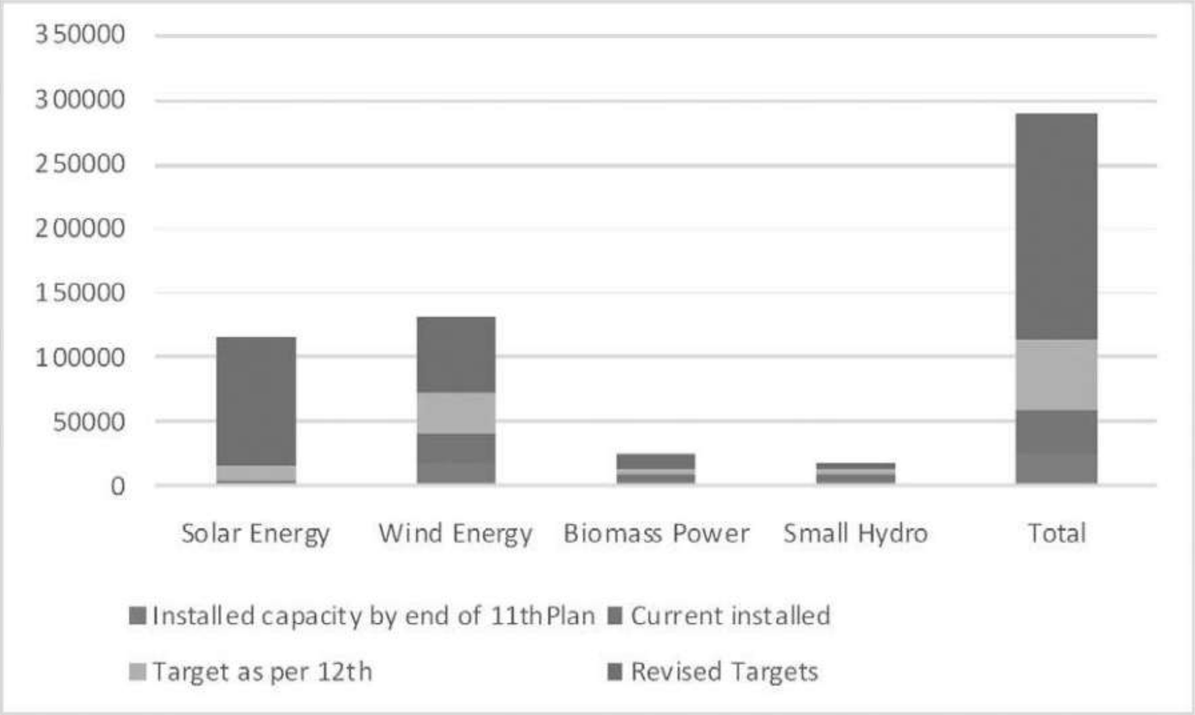


Fig. Chart for Renewable energy in India gas 5.6 other renewables 0.2 Even if 10% of this area can be used, the available solar energy would be 8 million MW, which is equivalent to 5,909 mtoe (million tons of oil equivalents) per year (Leone, 2011). In July 2009, India unveiled a $19 billion plan, to produce 20 GW of solar power by 2020.Under the plan, solar-powered equipment and applications would be mandatory in all government buildings including hospitals and hotels. On November 18, 2009, it was reported that India was ready to launch its National Solar Mission under the National Action Plan on climate change, with plans to generate 1,000 MWof power by 2013[6]. India has a vast potential for renewable energy sources, especially in areas such as solar power, biomass and wind power. The current installed capacity of renewable energy is around 92204 MW, constituting about 7.3 percent of India's total installed generation capacity. Technological breakthroughs for cost effective photovoltaic technology could generate a quantum leap in the renewable energy sector since India is well endowed with solar insolation (average of 6 kWh/sq.mt./day). India plans to announce increased subsidies for solar-power generation, as the country looks to scale up production of renewable energy and show it is committed to mitigating climate change. India just had 2.12 megawatts of grid-connected solar generation capacity. As part of the National Solar Mission, the ministry aims to bolster the annual photovoltaic production to at least 1,000 megawatts a year by 2017. With an installed capacity of 123 GW, the country currently faces energy shortage of 8 percent and a peak demand shortage of 11.6 percent. In order to sustain a growth rate of 8 percent, it is estimated that the power generation capacity in India would have to increase to 306 GW in the next ten years which is 2.5 times current levels. However, as of October 2009[7], India is currently ranked number one along with the United States in terms of installed Solar Power generation capacity.

3. Conclusion

There is an urgent need for transition from petroleum-based energy systems to one based on renewable resources to decrease reliance on depleting reserves of fossil fuels and to mitigate climate change. In addition, renewable energy has the potential to create many employment opportunities at all levels, especially in rural areas. So Isolated systems, whose cost depends on load factor are needed to be linked with rural industry. Innovative financing is also a requirement. Mainstreaming of renewables is very essential. Energy security, economic growth and environment protection are the national energy policy drivers of any country of the world. The need to boost the efforts for further development and promotion of renewable energy sources has been felt world over in light ofhigh prices of crude oil. A disparaging part of the solution lies in promoting renewable energy technologies as a way to addressconcerns about energy security, economic growth in the face of rising energy prices, competitiveness, health costs and environmental degradation. The cost-effectiveness of Wind and Small Hydro power energy should also be taken into account. An emphasis should be given on presenting the real picture of massive renewable energy potential; it would be possible to attract foreign investments to herald a Green Energy Revolution in India.

References

[1] **D.S. Arora, S. Busche, S. Cowlin, T. Engelmeier, H. Jaritz, A. Milbrandt** and **S. Wang**, "Indian renewable energy status report" NREL, (2010).

[2] **Rijul Dhingra, Abhinav Jain, Abhishek Pandey** and **Srishti Mahajan**. Assessment of Renewable Energy in India. *International Journal of Environmental Science and Development*, **5**(5), (2014).

[3] **V. Verneker**, "Distributed Renewable Energy Generation in India, "M.Sc. thesis, *Dept. of Sustainable Energy & Environment,* Cardiff University, Cardiff, United Kingdom, (2008).

[4] **S. Guru**, "Renewable energy sources in India, is it viable?" Working Papers Series, *Julian Simon Centre for Policy Research*, (2002).

[5] India Ministry of Non-Conventional Energy Sources (MNES)http://mnes.nic.in/

[6] Details of Solar power in India available at: http://en.wikipedia.org/wiki/Solar_power_in_India

[7] Future Perspectives for Renewable Energy in India available at: http://www.alternative-energy-news.info/future-renewable-energy-india/

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Study of activation energy and thermodynamic parameters of bismuth sulfide by thermogravimetric analysis

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Abstract

Bismuth sulfide chalcogenide was successfully synthesized inside the ampoule by conventional high temperature solid state solvothermal reaction of bismuth and sulfur. It was prepared by adjusting stoichiometric amount of the bismuth and sulfur heated in evacuated sealed quartz ampoule at 850 °C for 12h, which is easy to be maintained and controlled. The key step was only adjusting the sulfur content. Synthesized powder was characterized by Energy dispersive Analysis by Energy Dispersive X-ray Spectroscopy (EDXS) and Thermo Gravimetric Analysis (TGA) in an air atmosphere. TGA curves were used to study the decomposition step of the isolated compounds. Activation energy (E_α) for decomposition has been calculated using Broido method. The thermodynamic parameters such as change in enthalpy (ΔH), change in entropy (S) and Gibb's free energy (ΔG) are estimated. TGA analysis shows a remarkable thermal stability with addition of sulfur content.

Key words : Bismuth sulfide, Solid State Solvothermal Route, EDXS, TGA, Activation energy by Broido method, Thermodynamic parameters.

1. Introduction

The chalcogenides are recently attracting of all the concern because of their practical applications in various fields such as thermoelectric devices and optoelectronics. Bismuth sulfide occurs in nature as the mineral bismuthinite. It has a trigonal prismatic crystal structure. In the past few year, main group metal chalcogenides, AV_2BVI_3 (where, A=As, Sb, Bi and B= S, Se, Te)[1] have received ever increasing attention as a valuable semiconductor. Bismuth sulfide has a direct band gap between 1.2 - 1.7 eV.[2] Also, due to its high figure of merit (ZT) value, it is widely used as a thermoelectric-cooling material based on the Peltier effect[3].

Various types of Bi_2S_3 nanomaterials including nanobeads,[2] nanowires,[4,5] nanotubes,[6] nanoribbons[7] and nanorods,[1,8] *etc.* have been synthesized using different types of techniques. This method is a well established approach for fabricating inorganic materials with desired micro/nano structures and controlled crystalline orientation. The advantage of this approach is it allows materials to be prepared at temperature substantially below those required by traditional solid state reaction route.[9] In this paper we have synthesized Bi_2S_3 with excess sulfur content in ampoule by conventional high temperature solid state solvothermal route. It may be predicted that up scaling of this method will lead to large quantities of bismuth sulfide with high purity and novel morphologies.

Thermal behavior of the chalcogenides is very important for the researcher in various branches. It is widely used in chemicals, Textiles, Aerospace, Metals, Auto, Government, Academic, Petrochem, Polymers, *etc.* Over a dozen thermal methods can be recognized, which differ in the properties measured and the temperature programs. These are used for quality control and research applications on industrial products, such as polymers, pharmaceuticals, clays and minerals, metals and alloys.[16,23,24] The well-established thermogravimetric analysis (TG) has been reliably and widely used over many decades in studying thermal behavior and properties of various types of material and evaluating the thermal parameters for their degradation processes[17,18].

The aim of this research is to study the degradation and evaluation of the kinetic and thermodynamic parameters by Broido method to obtain degradation kinetics data. In presence study the thermal behavior (TGA) of the bismuth sulfide was studied and kinetic parameters were determined by Broido method[19]. The present author evaluates some of the parameters, such as activation energy, changes in enthalpy, changes in entropy and Gibb's free energy using Broido method.

Thermogravimetric analysis (TGA) provides a rapid method for determining the Temperature-Decomposition (TD) profile of a compound material and the kinetics of its thermal decomposition. Only knowledge of the reaction process mechanism enables a proper approach to intrinsic kinetic[22]. A group of techniques in which a physical property of substances and/or its reaction products is measured as a function of a temperature whilst the substance is subjected to a controlled temperature program[25].

2. Experimental Details

The starting materials were analytical grade, which were purchased from Loba Chemie Pvt. Ltd. And used as received without further purification.

In this process, Bi_2S_3 was synthesized from its constituent elements, Bi and S, weighed in atomic stoichiometric proportion (2:3) and sealed in a quartz ampoule, in which pressure of 10^{-2} mbar was achieved. Samples have been prepared with 5%, 10% and 15% excess sulfur content, respectively, in the raw mixture in evacuated ampoules. The melting of elements mixed in ampoules was then carried out in an indigenous electric furnace. The temperature of the furnace was raised from room temperature to 1150 K at the rate of 3K/min. The ampoule was kept at 1150 K for 12 h to ensure homogenous crystallization. It was cooled down up to room temperature inside the furnace at a cooling rate of 4K/min. The solid ingot was taken as powdered to a mean particle size of ~100 μm using the process of grinding and then sieving.

3. Results and Discussion

In order to investigate the compositional analysis of the synthesized Bi2S3 compounds EDXS analysis were carried out with an accelerating voltage of 30 kV.

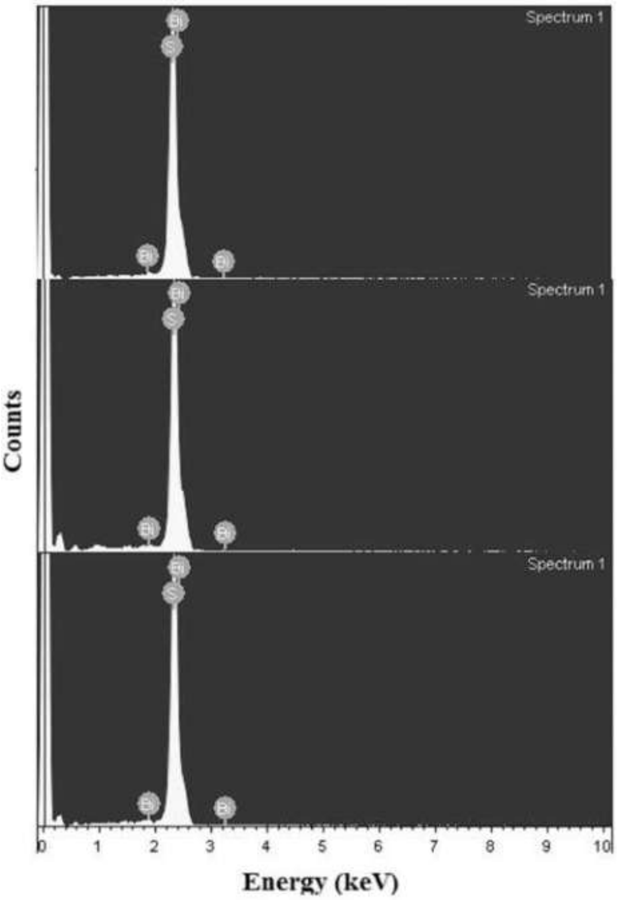

Fig. 1. Plot of EDXS images of Bi_2S_3 compound prepared with 5%, 10% and 15% excess sulfur in raw mixture

Fig. 1, shows the results of EDXS measurements. The EDXS results confirmed the presence of Bi & S elements with the expected Bi:S ratio ~ 2:3. The EDXS reveals that the required phase has present. Moreover, the S-content in sample Bi_2S_3 + 5% is very low, as expected, because of the low melting point and highly volatile nature of the sulfur. Excess sulfur has taken in the raw mixture in order to improve the sulfur incorporation in the compound. The good stoichiometry occurs for the sample Bi_2S_3 + 10% and Bi_2S_3 + 15%. This is due to the presence of excess sulfur vapour in the sealed ampoule, which allows the formation of Bi_2S_3 phase under the sulfur environment during the growth process.

Thermogravimetric analysis (TGA) experiments were undertaken to understand synergism between bismuth and sulfur. Samples were prepared with sulfur-to-bismuth ratio designed to give the correct stoichiometry for Bi_2S_3. Changes in the mass of a sample are studied while the sample is subjected to controlled temperature program. The temperature program is most often a linear increase in temperature, but, isothermal studies can also be carried out, when the changes in sample mass with are followed. TGA is inherently quantitative, and therefore an external powerful thermal technique, but gives no direct chemical information. The ability to analyze the volatile products during a weight loss is of great value. Sample were prepared with bismuth to sulfur ratio designed to give the correct stoichiometry for Bi_2S_3 compound prepared with 5%, 10% and 15% excess sulfur in raw mixture. TGA data were collected on TGA/851 (METTLER TOLEDO). An experiment runs to ambient temperature up to 700°C in an air atmosphere. The balance sensitivity is usually around one microgram, with a total capacity of a few hundred milligrams. A typical operating range for the furnace is ambient to 1500°C, with heating rates up to 10°C/min. Thermocouple as a temperature sensor is placed close to the sample. Heating is automatically resumed, at a constant rate, until the next significant weight loss event. By this process, we are able to nicely resolve closely occurring decomposition events and provide better quantitative analysis of a sample. The samples were 1-4 mg and contained in platinum pan. Thermogram is graph of mass versus temperature. Sometimes given as "%" of original mass. Temperature - mass points were collected every 1 sec. Mass (mg) vs. Temperature curve has been shown in Fig. 2 showed clearly a stage of decomposition. TGA curve did not show an appreciable mass loss in the temperature range 273-393 K, 273-423 K and 273-443 K, respectively and stability is increased with sulfur content and weight loss decreases with it.

For the compounds, Bi_2S_3 + 10%, there is one major loss of weight between the stage of degradation began at 402 K and terminated in 534 K, Bi_2S_3 + 10% the stage of degradation began at 413 K and terminated in 543 K, Bi_2S_3 + 15% the stage of degradation began at 433 K and terminated in 553 K, and observed mass loss was 42%, 53% and 50%, indicating the highest weight loss occur with 10% excess sulfur.

It can be seen that the mass losses obtained from the TG curves that calculated for the decomposition product (*i.e.* final reside) are good agreement for the

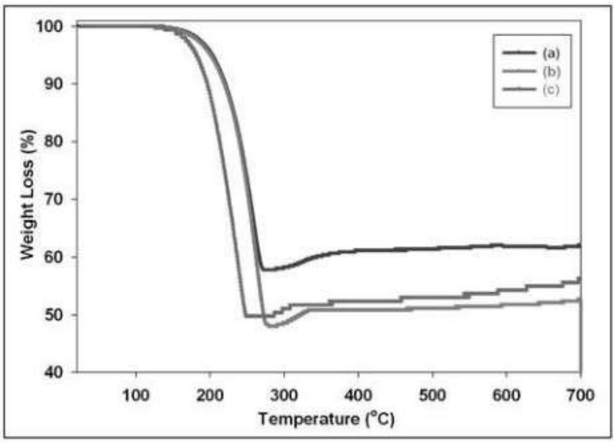

Fig. 2. Plot of TGA curve of Bi_2S_3 compound prepared with (a) 5%, (b) 10% and (c) 15% excess sulfur in raw mixture (Model: Perkin Elmer, Pyris-6 TGA, COE, Vapi)

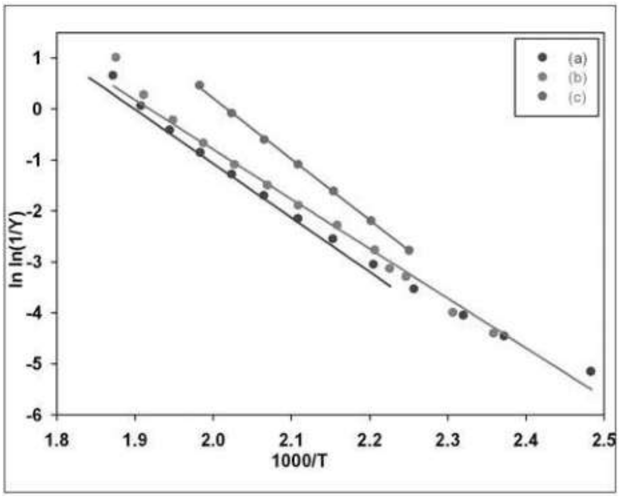

Fig. 3. Plot of ln (ln 1/y) vs. 1000/T for Bi_2S_3 compound prepared with (a) 5%, (b) 10% and (c) 15% excess sulfur in raw mixture

entire decomposition step. Thermal degradation studies of the Bi_2S_3 compound prepared with 5%, 10% and 15% excess sulfur in raw mixture indicated that these compounds were thermally stable up to 393 K, 402 K and 423 K respectively. Degradation of these compounds occurs in single stage and harmony with the literature[17].

As shown in Fig. 3, ln (ln 1/y) vs. 1000/T gives an excellent approximation to a straight line indicating a very smooth thermal degradation. The activation energy E and frequency factor A can be calculated from the slope and intercept, respectively.

Kinetic Studies : A variety of methods exist for analyzing the kinetic features of all types of weight loss or gain, either with a view to predictive or to understand the controlling chemistry. In order to determine kinetic parameters in a solid-state degradation reaction, usually several equations[11,19] have been proposed as means of analyzing a TG curve. In the kinetic studies of the thermal system, the mass temperature relation, which can determine the behavior of the degradation reactions, can be examined. In the present study, four equations such as FC (Freeman-Carroll), HM (Horowitz-Metzger), CR (Coats-Redfern), and B (Broido) were used for calculating the activation energy (E), exponential factor (A) and thermodynamic parameters (G, H and S). The kinetics was studied for the stage of degradation of the complex[19].

Broido[11, 19] has developed a model and put forward the following equation for calculations of kinetic parameters from the TGA curve.

$$In\left[In\frac{1}{y}\right] = \left(\frac{-E_\alpha}{R}\right)\frac{1}{T} + \left[\frac{RZ}{eA\Phi}\bullet T^2\right] \qquad (1)$$

Here, $Y = \frac{W_t - W_\alpha}{W_0 - W_\alpha}$, R is a gas constant and Z can be deduced from the relation:

$$Z = \frac{E_\alpha \Phi}{RT^2 m} \exp\left(\frac{E_\alpha}{RT}\right) \qquad (2)$$

Here, W_t, W_0 & W_α are weight of active material at absolute Temperature T, weight of the material taken initially and weight of the material at the end of the reaction respectively. Y is the fraction of the number of initial molecules not yet decomposed.

The plot of ln (ln 1/y) vs. 1000/T gives an excellent approximation to a straight line indicating a very smooth thermal degradation of the bismuth sulfide is as shown in Fig. 3. The slope is related to energy of activation as,

$$E_\alpha = -2.303 \times R \times \text{slope} \qquad (3)$$

The activation energies (E_α) for the processes corresponding to the major steps in various TGA curves were estimated by fitting the degree of disassociation (α) over the respective temperature ranges to equations by Broido relation. The changes

Table 1. Calculated values of weight loss and frequency factor.

Sr. No.	Bi_2S_3	Stage	Stability Temperature T (°K)	Weight Loss T (°K)	Weight Loss (%)	Frequency Factor (A)
1.	$Bi_2S_{3+5\%}$	1st	393	402-534	42	18.67
2.	$Bi_2S_{3+10\%}$	1st	402	433-543	53	20.15
3.	$Bi_2S_{3+15\%}$	1st	423	433-553	50	24.10

Table 2. Activation energy and thermodynamic parameters from Broido relation.

Sr. No.	Bi_2S_3	E_α (eV)	ΔS (eV/°K)	ΔH (eV/mole)	ΔG (eV)
1.	$Bi_2S_{3+5\%}$	-5.724×10^{20}	-1.395×10^{21}	-4.853×10^{22}	61.13×10^{22}
2.	$Bi_2S_{3+10\%}$	-6.493×10^{20}	-1.389×10^{21}	-5.00×10^{22}	62.80×10^{22}
3.	$Bi_2S_{3+15\%}$	-7.4109×10^{20}	-1.489×10^{21}	-5.191×10^{22}	68.26×10^{22}

in enthalpy (ΔH) were estimated by employing the relations,

$$\Delta H = E_\alpha - 2\,RT \tag{4}$$

Here, *A, h, k, T* are Frequency factor, Planck's constant, Boltzmann's constant, average temperature respectively and the Gibb's free energy,

$$\Delta G = \Delta H - T\,\Delta S \tag{5}$$

The changes in entropy (ΔS) was derived from the relation,

$$\Delta S = 2.303\ R \log\left(\frac{Ah}{kT}\right) \tag{6}$$

A TGA measurement is the residual mass of the sample at a given temperature, usually given as a percentage of the original sample mass:

$$M_{res}(\%) = \frac{M_{r.T}}{M_S}\ 100\% \tag{7}$$

Where, M_{res} (%) is the residual mass expressed as a percentage, ($M_{r.\ T}$) is the mass remaining at as specific temperature (T) in grams, M_s is the initial mass of the sample in grams.

According to this method, the plot of ln ln (1/Y) versus 1/T gives straight lines as shown in Fig. 3, and activation energy E and frequency factor A can be calculated from the slope and intercept, respectively.

A negative value of activation energy (E_α) shows the rate of reaction decreases with increase in temperature. For an exothermic reaction *ΔH* is taken to be negative associated with heat releasing reactions. The entropy can be interpreted as a measure of disorder indicates that the less disorder of the system because the number of particles decreases. The negative values of entropy indicate that reaction were slower than normal and account for the non-spontaneous nature of degradation reactions of the compounds were supported by positive value of *ΔG* shows endergonic reaction in all the cases. In general, it can be concluded that it is possible to obtain Bismuth sulfide with in thermal stability and more applicable from the economic view point. Calculations of the Gibb's free energy of activation illustrate that bismuth sulfide is thermodynamically more stable with addition of sulfur content.

4. Conclusions

Bi_2S_3 compound prepared with 5%, 10% and 15% excess sulfur in raw mixture was synthesized from its constituent elements via facile, conventional and low cost strategy by conventional high temperature solid state solvothermal route in the evacuated quartz ampoules. The EDXS results confirmed the presence of Bi & S elements with the expected Bi:S ratio ~ 2:3. The EDXS reveals that the required phase has present. The present work is the first ever report including the reaction mechanism of thermal decomposition and application of the theory namely Broido method for the stage of decomposition of the material. Thermal analysis reveals that compounds of bismuth sulfide are structurally stable in the temperature range ca. 393 - 423 K and stability is increased with addition of sulfur content and weight loss decreases with it. After this temperature range compounds become thermally decomposes with the evaluation of oxygen and sulfur. It is a convenient and efficient for producing pure metal sulfides. It can also be extended to the 423 K and stability is increased with addition of sulfur content and weight loss decreases with it. After this temperature range compounds become thermally decomposes with the evaluation of oxygen and sulfur. It is a convenient and efficient for producing pure metal sulfides. It can also be extended to the preparation of some other types of novel structures and morphologies of bismuth sulfide by different techniques with unique properties.

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References

[1] **Y. Wang, J. Chen, P. Wang, L. Chen, Y.B. Chen** and **Wu L-M**, *J. of Phy. Chem.*, **113C** (2009) 16009.

[2] **Z. Xingfu, Z. Xin** and **Danyu Zhan** *et.al.*, *Nanotechnology*, **17** (2006), 3806.

[3] **L. Wenjing, M. Chen, X. Wang** and **L. Weimin**, *Chem. Mate.*, **19** (2007), 872.

[4] **M. Shao, W. Zhang, Z. Wu** and **N. Youbao**, *J. of Crystal Growth*, **265** (2004), 318.

[5] **X. Chen, X. Wang, A. Chnghua** and **J. Liu** *et al.*, *J. of Crystal Growth*, **256** (2006), 368.

[6] **L.D. Zhao, Zhang B-P, Liu W-S, Zhang H-L** and **Li J-F**, *J. of Solid State Chemistry*, **181** (2008), 3278.

[7] **J. Tianhao, L. Guanrao, Q. Xingyi, Y. Qinglin, D. Yuan** and **G. Lin**, *Chinese Science Bulletin*, **51** (2006), 655.

[8] **J. Fang** and **F. Chen** *et. al.*, *Mat. Rec. Soc. Symp. Proc,* (2002) 730.

[9] **Y. Yu, C.H. Jin, R.H. Wang, Q. Chen** and **Peng L-M**, *J. Phy. Chem. B*, **109** (2005), 18772.

[10] **Broido**, *J. Poly. Sci.,* **7A**(2), 1761.

[11] **T.K. Patil**, *J. of Advanced in Applied Science Research,* **4** (2013), 115.

[12] **C. Duval**, *Inorganic Thermogravimetric Analysis*, 2nd Edn. (Elsevier, London) (1963), 264.

[13] **S. Gupta** and **M.N. Ansari**, *Indian J. of Chemistry,* **44A** (2005), 1608.

[14] A Dictionary of Physics, 5th Edn (OXFORD University Press, London), (2006).

[15] **A. Jana, C. Bhattacharya** and **J. Datta**, *Electronics Acta*, **55** (2010), 6553.

[16] **E. Karapinar, I. Gubbuk** and **B. Taner** *et. al.*, *Journal of Chemistry,* (2013), 7.

[17] **T. Chang, K. Wu** and **C. Liao** *et. al.*, *Polymer degradation and stability*, **62**(2) (1998), 299.

[18] **S. Arora, V. Patel** and **A. Kothari**, *Material Chemistry and Physics;* **84**(2-3) (2004), 323. **T. Chang, K. Wu** and **C. Liao** *et. al.*, *Polymer degradation and stability,* **62**(2) (1998), 299.

[19] **K.K. Shrivastava, S. Srivastava** and **M.T. Alam**, *Int. J. Pharmaceutical Biological and Chemical Science*, **2** (2013), 26.

[20] **T. Robert**, A. Kerr *et. al.*, *Tribology Transactions,* **53** (2010), 22.

[21] **S. Solanki, I. Patel** and **N. Shah**, 58th DAE-Solid State Physics Symposium, *AIP Conf. Proc.,* **1591** (2014), 1473.

[22] **Bojan Jankovic**, Cellulose; © Springer Science+Business Media Dordrecht (2014).

[23] **D. Skoog** *et. al.*, Principles of instrumental analysis, 5th edition, Harcourt Publishers, (2001).

[24] **S. Anandham**, *Thermal Analysis.*

[25] **R. Mackenzie**, *Thermochim. Acta*, **28**(1) (1979).

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Renewable energy options in Uttarakhand state of India

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Abstract

Present investigation is aimed on the study of renewable energy options in Himalayan state Uttarakhand. This paper deals with present status of Uttarakhand in production of renewable energy and potential for increasing production and adoption of more renewable energy options. Methodology of the present investigation includes data collection through study of Government publications of national and international level on energy statistics and survey of Himalayan ecology. At present Uttarakhand have 1.86 GW power production capacities, which is 0.76% of total power capacity (245 GW) of India. Similarly Uttarakhand shares 0.21 GW renewable energy power capacities, which is 0.66% of total renewable energy capacity of India. Presently most of the renewable energy in Uttarakhand comes from Small Hydro Projects (SHP) that amounts to 0.175 GW. Thus major part (83%) of renewable energy in Himalayan state Uttarakhand comes from SHP and only small fraction from other renewable energy resources. The part of solar energy production is 0.005 GW. At present there is no wind energy plant in Uttarakhand, but state has potential of 0.534 GW. Beside solar and wind energy, there are hot water springs available in Uttarakhand, which can serve directly thermal energy or may produce electricity. Large amount of available biomass is one more option of renewable energy.

Key words : Uttarakhand, renewable energy, wind energy, geothermal energy, biomass energy.

1. Introduction

Energy consumption by any society is indicator of the development of that society. In the fast pace of growth, energy demand is increasing year by year. Conventional source of energy like, fossil fuel cannot meet the requirements of ever growing demand. More and more energy is required for present generation and it must be made available for future generation also. In this energy scenario, search for other energy options are inevitable. For sustainable growth of mankind, renewable energy resources must be harnessed with full potential. Solar energy, wind energy, tidal wave energy, ocean energy, geothermal energy and biomass energy are options of renewable energy sources. At present India consumes 6% of total world energy, whereas population of India is 18% of the total world population[1]. Share of renewable energy power capacity in India is 13.1% of total power capacity in the country, which is 5% of total world renewable energy power capacity[2]. At present Uttarakhand have 1.86 GW power production capacities, which is 0.76% of total power capacity (245 GW) of India. Similarly Uttarakhand shares 0.21 GW renewable energy power capacities, which is 0.66% of total renewable energy capacity of India. Most of the renewable energy in Uttarakhand comes from Small Hydro Projects (SHP) that amounts to 0.175 GW. Thus major part (83%) of renewable energy in Himalayan state Uttarakhand is derived from SHP and only small fraction from other renewable energy resources. Present value for solar energy production is 0.005 GW. There is no wind energy plant in Uttarakhand at present, but state has potential of 0.534 GW[3]. The present paper is aimed to study other renewable energy options in Uttarakhand beside solar energy.

The status and the potential of those renewable energy sources which are compatible with Himalayan ecology will be discussed in the following.

2. Methodology

Methodology of the present investigation includes study of data published by Government authorities of national and international level on energy statistics. The potential of new sources of renewable energy in Uttarakhand has been looked for through studies of specific topology and ecology of Uttarakhand.

3. Results and Discussions

Recently, on May 10, 2016, EY (Ernst & Global Limited, UK) has announced that India ranks third in Renewable Energy Country Attractiveness Index (RECAI), based on investment and deployment in the area of renewable energy. In India current installed capacity of renewable power is 34.5 GW, which has to be increased as 175 GW till 2022[2]. Presently electricity production in Uttarakhand is 1.86 GW, in which 1.65 comes from hydroelectricity and 0.21 from renewable energy. Table 1 shows the status of Uttarakhand in India in electricity production. Among various options of renewable energy most of the energy (0.175 GW) is meet by Small hydro projects (SHP) in Uttarakhand. A comparison of grid interactive renewable energy of Uttarakhand and whole country has been presented in Table 2. This table shows that presently no wind energy is produced in Uttarakhand. However, according to Ministry of New and Renewable Energy (MNRE), estimated potential of wind energy in Uttarakhand is 2.271 GW. The estimated potential of renewable energy in Uttarakhand is given in Table 3. This table includes data on energy produced through wind, SHP, biomass, co-gen bagasse and waste. In light of Himalayan topology and ecology some of the renewable energy sources are discussed here in context to Uttarakhand in the following.

3.1 *Wind Energy*

The occurrence of wind with suitable speed and aerodynamic condition are vital factors for harnessing wind energy. On the basis of topology, open seas, coastal areas, hills, valley, terrace and saddle are good sites of wind energy harvesting. Low depression saddles with water divides or river valleys have good potentials for wind energy. They have suitable aerodynamic conditions and are commonly found in rural Garhwal Himalayas. In local dialect these are

Table 1. Status of Uttarakhand in India in electricity production during 2013-2014 (GW) [3].

S.N.	Particular	India	Uttarakhand	% of Uttarakhand in India
1	Hydro	39.49	1.65	4.2
2	Thermal	168.25	0	0
3	Nuclear	4.78	0	0
4	Renewable Energy	31.69	0.21	0.7
5	Total	245.25	1.86	0.8

Table 2. Grid interactive renewable energy (GW) during 2013-2014 [3].

S.N.	Particular	India	Uttarakhand	% of Uttarakhand in India
1	Biomass	4.013	0.030	0.75
2	Waste	0.106	0	0
3	Wind	21.136	0	0
4	Small hydro project	3.803	0.175	4.6
5	Solar	2.6	0.005	0.19
6	Total	31.7	0.209	0.66

Table 3. Potential of Renewable Energy (GW) in Uttarakhand estimated during 2013-2014 [3].

S.N.	Particular	India	Uttarakhand	% of Uttarakhand in India
1	Wind Energy	102.772	0.534	0.52
2	SHP	19.749	1.708	8.65
3	Biomass	17.538	0.024	0.137
4	Co-Gen Bagasse	5	0	0
5	Waste	2.556	0.005	0.2
6	Estimated Potential	147.615	2.271	1.54

known as Khals. In these regions, there is change in altitude and change in air pressure. During the day time, the air in the valleys is heated, consequently pressure decreases. After sunset the temperature decreases, thus an increase in pressure is observed at the top of mountains (mountain summits). As a result, the cool air drains from summits to valleys during night. After sunrise the surface air of the valley again warms up. Typically, a temperature difference of 0.5°C produces winds of 5m/s at 10m above ground which is good wind energy potential. Survey records indicate that about 135 Khals have been formed in between the Alaknanda catchment in the north and the Ramganga catchment in the south[4]. The potential of wind energy in Uttarakhand has been estimated as 0.534 GW (Table 3).

Till now only one wind farm has been proposed in Uttarakhand on a hill top, in Bachhelikhal in Tehri district. Three wind turbines will be set up with a capacity of 800 kW each at Bachhelikhal to produce 2.4 MW of wind energy. The estimated cost is Rs 12.5 crore[5].

3.2 *Geothermal Energy*

Inside the earth crust, lots of molten rocks, metals and minerals are present. As one go towards the centre of earth the temperature increases continuously. There exists a temperature gradient of about 30°C/km towards the depth from earth crust. The high temperature is due to radioactive radiations emitted inside the earth crust. Hence a large amount of energy exists inside earth in form of heat known as geothermal energy. Geothermal resources are available in the following form :

i. Hydrothermal or hydro-geothermal energy (heat absorbed in ground water)
  - Dry steam
  - Wet steam
  - Hot water

ii. Geo-pressured resources

iii. Hot dry rocks

iv. Magma

Geothermal sites are available mainly at the boundaries of tectonic plates. These are also the regions of earthquakes and volcanoes. This energy can be used directly for heating purpose in domestic and industrial sector or can be converted into electricity. In India, Geological Survey of India has identified about 340 geothermal hot springs in the country[6]. There are about 50 hot springs in Uttarakhand. The surface temperature of water of hot springs of Uttarakhand varies from 25°C-90°C[7]. In the Uttarakhand region, more than 50 individual occurrences of moderate to high temperature springs have been reported along the banks of the major rivers - Tons, Yamuna, Bhagirathi, Mandakini, Alaknanda, Dhauli Ganga, and Kali. Some of the wellknown hot springs are located in Tapoban, Suryakund (Yamnotri), Gagnani, Badrinath, Garam Pani near Nainital, and Gaurikund (near Sonprayag). Several hot springs occur between Pala and Gangnani, north of Uttarkashi. Presently they are used only for holy dip and bathing purpose. However they are the potential resource for producing electricity and for direct use as thermal energy to heat the space.

3.3 *Biomass Energy*

Biomass energy may be tapped as Co-generation with waste of sugar, paper, fertilizer, chemical, textile and other industries, using biomass/agro residue and waste and urban, municipal and industrial liquid/ solid Waste. Uttarakhand has an estimated potential of about 220 MW for cogeneration. It is estimated that about 20 million Metric Tons of agro residues and agro industrial/ processing waste is produced annually in Uttarakhand. It holds promising potential for generating decentralized power of about 300 MW. At present about 1000 Metric Tons of Municipal, Urban and Industrial solid/liquid waste is being produced every day in the State[8]. Introducing scientific processing and treatment of this waste would lead to power generation along with abatement of environmental pollution.

In this context electricity generation through Pine needles is a new approach. According to the Uttarakhand Renewable Energy Development Agency (UREDA), the total area of Pine forest in the state is about 3.43 lakh hectare. These pine forests produce about 20.58 lakhs tonnes of dry biomass every year in the state. Avani Bio Energy, an NGO based out of Uttarakhand has set up a plant to produce 9 kW capacities in Pittorgarh in 2009. In 2014, the same company has set up another plant of 120 kW at Chachreda village in Pithoragarh to sell it to state grid[9].

4. Conclusion

From above discussion it can be concluded that beside solar energy, other renewable energy options are also available in Uttarakhand in form of wind, geothermal and biomass energy. Government and private companies may take initiatives to harness this energy to utilize the full potential of Uttarakhand Renewable energy sources.

5. Acknowledgements

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References

[1] India Energy Outlook, World Energy Outlook Special Report 2015.

[2] Renewable Energy in India: Growth and Targets, Ministry of New and Renewable Energy (MNRE) 13 May 2015.

[3] Energy Statistics 2015, Central Statistics Office, Ministry of Statistics And Programme Implementation, Government of India, New Delhi.

[4] **D.P. Kothari, K.C.singal** and **R.Ranjan**, Renewable Energy Sources and Emerging Technologies Second Edition, *PHI Learning Pvt. Ltd. New Delhi*, (2016), 171.

[5] Business Standard, New Delhi/Dehra Dun (2011).

[6] **Oum Prakash Sharma** and **Poonam Trikha**, Geothermal Energy and Its Potential in India, Renewable Energy Akshay Urja, **7**(1), 2013.

[7] **Vijay P. Dimri**, Geothermal Energy Resources in Uttarakhand, India, *J. Ind. Geophys. Union* **17**(4), (2013) 403-408.

[8] Uttarakhand state govt. Policy for harnessing Renewable energy sources, Annexure of G.O.No.263 /I (2) / 2008 -04 (8)-96/2001, dated 20-1-2008.

[9] Electricity generation using pine needles in uttarakhand, Avani Bio Energy, (NGO), Pithoragarh.

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Study of controlled atmosphere cold storage

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Abstract

Major cold storages existing in India are all having 50 years old technology. These are basically refrigeration units with no or minimum control on hhumidity, let aside aatmosphere ccontrol ssystems. As a result the aapples stored in it gets non-crispy and freshness is gone, India is a ssecond llargest pproducer of ffruits & vvegetables in the world but there is great loss by spoiling them worth Rs 40000 crores every year. Invest in apples is not like in gold but put up in a controlled atmosphere cold storage (CACS) and it will earn gold, this only way to keep fruit and vegetable as farm fresh. Have you ever wondered how the apples & other fruits from Australia & China come to Indian market and still fresh and crispy? And we define the non-crispy (Bhus-Bhus) apples a "Cold Storage Apple".

Key words : Humidity, Atmosphere, Domestic Products, Economy, Surging.

1. Introduction

Over the years India has achieved a significant position as one of the fastest growing economy in the world. In a robust demonstration of its nascent strength India has emerged as one of the stars of global economics in recent years, growing at 5.1 per cent in 2012 and 6.9 per cent in 2013, emerging as the second fastest growing economy in the world, thus breaking all previous barriers and surging ahead in the new millennium. However, agriculture growth rate has not been significant, but it remains an important contribution factor in India Gross Domestic Product (GDP). This is due to the fact that the country in mainly based on the agriculture sector and employs around 65% of the total population in India. The

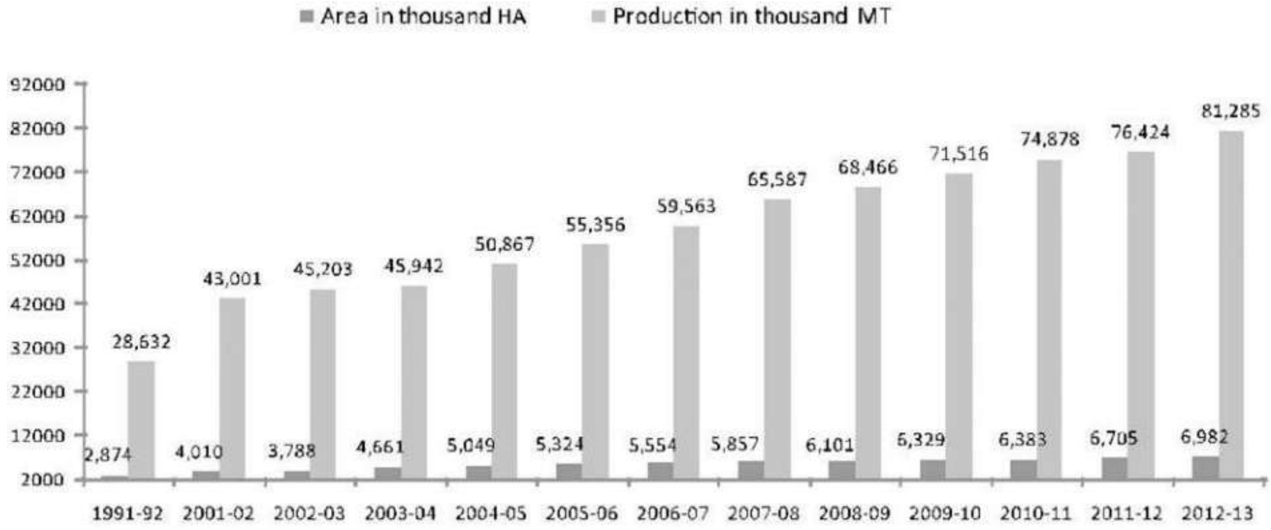


Fig. 1. Rankin cycle TS Diagram for subcritical and ultra supercritical

agriculture sector contributed around 18% to India GDP in 2007. Within the agriculture sector horticulture plays a very important role. Bestowed with varied agro-climatic conditions, India is favourable for growing a large number of horticultural crops such as fruits, vegetables, root tuber, aromatic and medicinal plants and spices and plantation crops like coconut, areca nut, cashew and cocoa. Presently, Fruit crops occupy around 30 per cent of India's gross cropped area, producing 268,842 metric tonnes during 2012-13.

2. Current status of post harvest technology in India

- India is the largest producer of milk and the second largest producer of fruits, vegetables.
- Fruit production in India has recorded a growth rate of 3.9% on an annual basis
- Total food grain production now stands at about 255 Million Metric tons whereas horticultural output is more than about 268 Million Metric tons.
- The value of losses of crops and livestock produce at national level was estimated by CIPHAT Ludhiana as Rs. 44143 crores at 2009 wholesale prices.
- It is estimated that 7% of the grain rots in fields and open godowns.
- Annual wastage of fruits and vegetables is estimated to range from 20% to 30% having value of Rs. 8000 crores annually.
- Against the total production of more than 500 MMT of horticultural & non- horticultural produces, the total cold storage capacity is estimated approximately 31 MMT, which is not even 10% of the total production.
- A study conducted by the National Spot Exchange Ltd. (NSEL) in December, 2010. estimated a cold storage requirements of 61.13 million tons in the country
- Most of the cold storage are stand alone normal cold storage. Capacity of the state of the art Controlled Atmosphere Cold Storage chambers is very small.

3. Govt. Initiatives to Develop the Controlled Atmosphere Cold Storages

NHB (National Horticulture Board) & NHM National Horticulture Mission provides capital investment subsidy for construction/expansion/ modernization of cold storages: Back-ended subsidy @35% in developed areas and @50% in growing areas of the project cost @ Rs 10,000/- per MT for normal cold storages, @ Rs 20,000 per MT for Controlled Atmosphere Cold Storages.

4. Use of Controlled Atmosphere (CA) storage

Controlled Atmosphere (CA) storage is used to extend the storage life of seasonal perishable produce when refrigeration alone is not sufficient. This technique can be used for many fruits and vegetables and, historically has been the principle storage method for the world's apple crop.

CA storage is a completely natural process that changes the ratio of the constituent gases in the normal atmosphere so that the respiration activity of the produce being stored is reduced to a minimum. Apples are the pre-eminent product stored under CA conditions but it is also an important storage technique for many other commodities. The list of products that can have some benefit from CA storage is very long. The following lists are not exhaustive but are products that are frequently stored on a commercial basis in controlled atmospheres. It is important to realize that local varieties, Climatic and growing conditions can have significant effects on the success of CA storage. Before committing to large scale storage of any product few of them are as follows, local testing should be done to establish the benefits and optimum CA conditions for that crop.

- Apple
- Plum
- White Cabbage
- Pear
- Cherry
- Lemon, *etc.*

5. Requirement of Controlled Atmosphere Cold Storage (CA)

Cold storage in general is the gentlest method of preserving the fruits and vegetables. It has relatively few adverse effects on the taste, texture, nutritive value, and other attributes of foods, provided simple rules are followed and storage periods are not excessive. In a controlled atmosphere (CA), oxygen is decreased and carbon dioxide increased to prolong the storage life of fruit. Generally, in typical CA storage, oxygen is decreased from the normal 21% in air to 1 - 3% and carbon dioxide is increased from 0.04% to 1.5%, depending on the commodity Temperature of the chamber maintained between 0°C to 1°C with the help of Refrigeration Machineries. Ethylene, a gas produced naturally by many commodities, can also be controlled. In CA storage we try to extend the time that produce quality is maintained, by slowing respiration and delaying ethylene production. For many fruit, both respiration and ethylene production increase after harvest, hastening the ripening and senescence processes, thereby accelerating the deterioration of the fruit.

6. Controlled Atmosphere Storage (CA) For APPLES

Eating crisp, juicy apples year-round is possible due to controlled atmosphere storage. Known simply as "CA" in the industry, controlled atmosphere storage involves careful control of temperature, oxygen, carbon dioxide and humidity. CA storage got its start in England before World War II when farmers discovered their produce kept longer if stored in an airtight room. It was up to scientists to unravel the reasons for longer storage. Apples take in oxygen and give off carbon dioxide as starches in the flesh change to sugar. In the sealed rooms, this respiratory process reduced the oxygen, thus slowing the ripening process. CA storage has come a long way since then, and researchers in Washington State have been among the leaders in this technology. CA was first used in the United States in the 1960s and Washington now has the largest capacity of CA storage of any growing region in the world.

7. Methodology

1.7.1 *Controlled Atmosphere Cold Storage Layout*

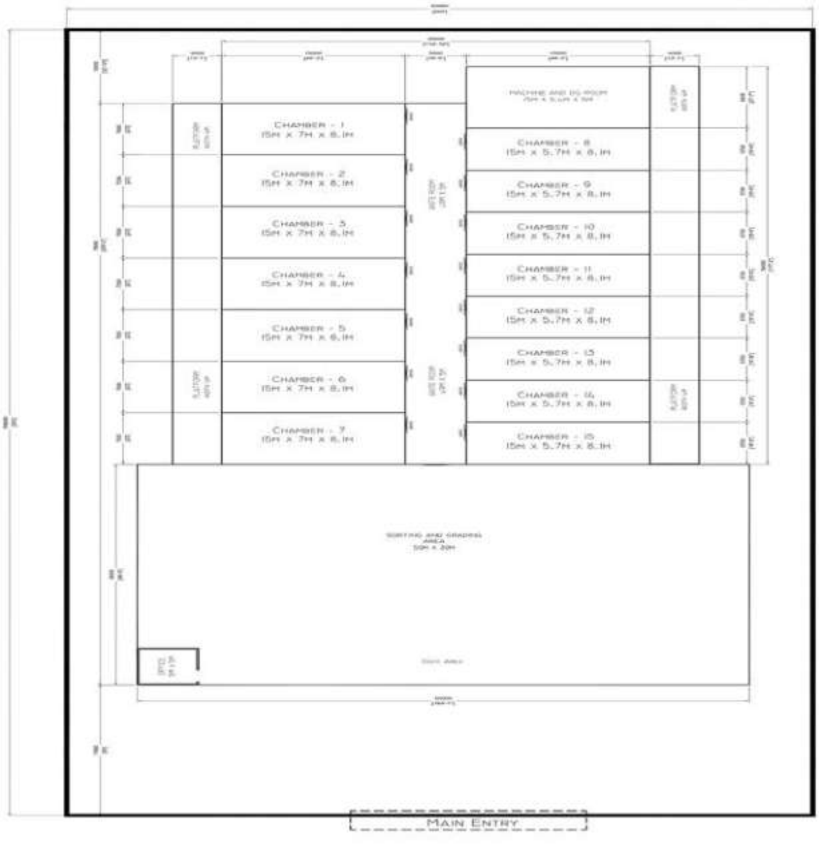


Fig. 2. CA Cold Storage Layout

CA Chamber's 1 to 7 Sizes - 15.0 Mtr × 7.0 Mtr × 8.1 Mtr - 250 MT × 7 Nos - 1750 MT
CA Chamber's 8 to 15 Sizes - 15.0 Mtr × 5.7 Mtr × 8.1 Mtr - 205 MT × 8 Nos - 1640 MT
Total Capacity - 3390 Metric Tons

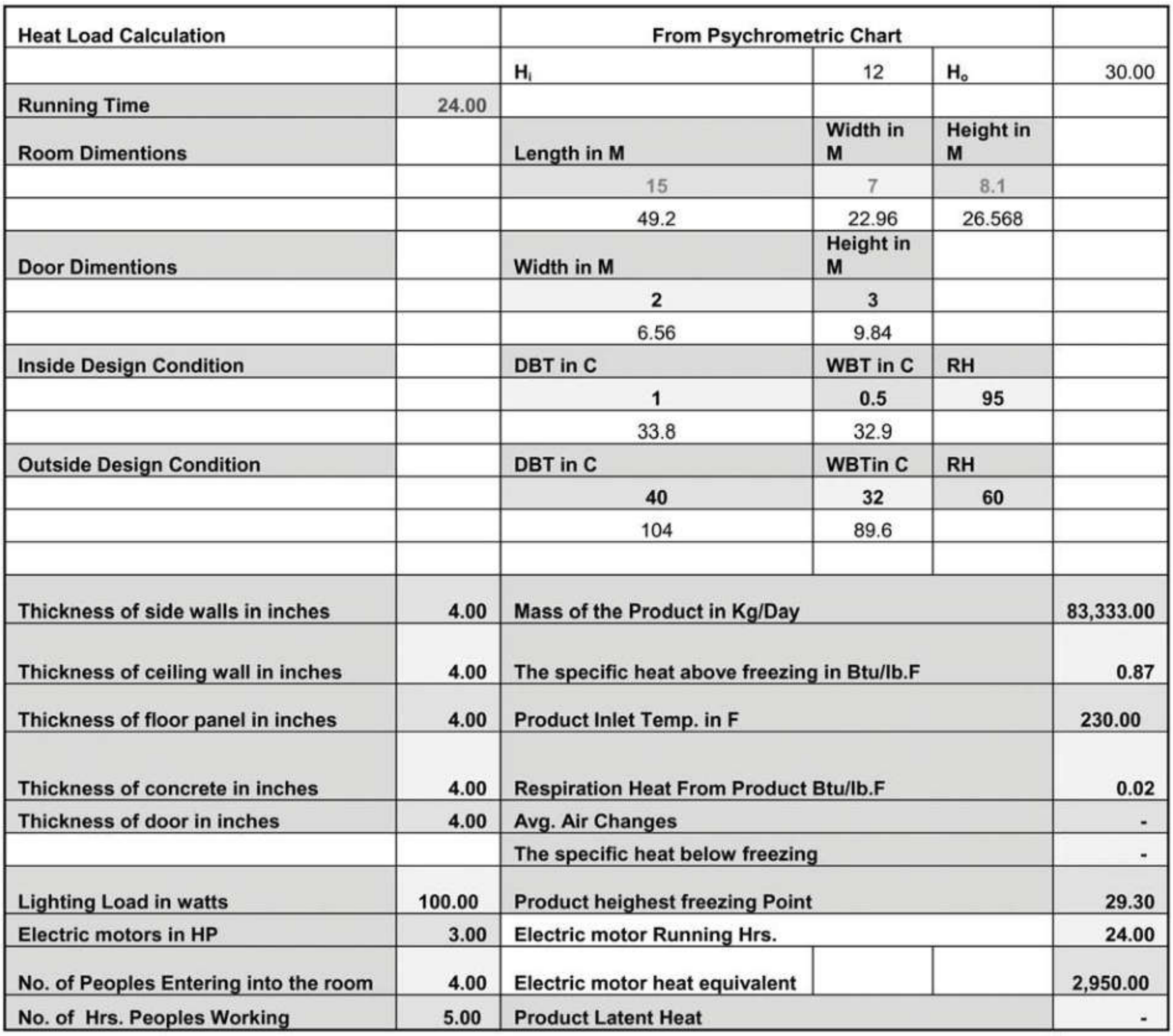
1.7.2 *Design Consideration & Hear Load Calculation*

Cold Store Design Consideration & Commodity Storage Requirements.

Type of Commodities/Produce	Apple
Ideal/Recommended Storage Conditions	
Temperature (DB in °C)	+0 to 1°C
Humidity RH (%) Range	90 to 95%
CO_2 Percentage	1 to 5%
O_2 Percentage	1 to 3%
O_2 Pull Down Duration (hrs)	48 hrs
Cooling Rate (product Temp Pull Down Duration in hrs)	7/8 cooling
Air Circulation (CMH/MT of Produce)	165 cmh/MT of produce
Produce Freezing Point °C	-1.4°C to -2.3°C
CA Chamber Dry bulb (DB in °C)	0°C to 1°C
CA Chamber RH (%)	90 to 95%
Max Storage Period (month)	10 months
Max product Temp (°C) - at the time of loading	15-20 °C
Daily Loading Rate(MT/day) in each cold chamber	82.5 (33%)
Loading Period (month)	September-October
Temperature Pull Down Rate (°C / Day)	As per 7/8 cooling
Unloading Period (months)	Jan to July
Daily Unloading Rate (MT/day) - From each cold chamber	Variable (30 MT/day)
Ante Room Conditions (T °C & RH%)	15-20 °C & 65-70%
Sorting & Grading Area (T °C & RH%)	18-22 °C & 65-70%
Special Provisions - Ethylene Control - Air Purification - Sanitation	Ethylene & the Air Purification are achieved by scrubbing the Air through Dioxide Scrubber.

Heat Gain Load on Back Side Wall

Q	= (A)(U)(TD)	3,548.94
A	- area of side wall in sq.ft	1,307.15
TD	- The temperature difference across the wall in F = = $T_{outside} - T_{inside}$	70.20
U	- The overall coefficient of heat transmission in BTU/sq.ft/F = 1/R	0.04
H_i	- Convection Coefficient of inside wall	1.65
H_o	- Convection Coefficient of outside wall	4.00
X	- Thickness of Wall in inches	4.00
K	- Thermal Conductivity	0.16
R	- Overall Thermall Resistance = $1/H_i + x/k + 1/H_o$	25.86



Heat Load Calculation		**From Psychrometric Chart**			
		H_i	12	H_o	30.00
Running Time	24.00				
Room Dimentions		**Length in M**	**Width in M**	**Height in M**	
		15	7	8.1	
		49.2	22.96	26.568	
Door Dimentions		**Width in M**	**Height in M**		
		2	**3**		
		6.56	9.84		
Inside Design Condition		**DBT in C**	**WBT in C**	**RH**	
		1	**0.5**	**95**	
		33.8	32.9		
Outside Design Condition		**DBT in C**	**WBTin C**	**RH**	
		40	**32**	**60**	
		104	89.6		
Thickness of side walls in inches	**4.00**	**Mass of the Product in Kg/Day**			**83,333.00**
Thickness of ceiling wall in inches	**4.00**	**The specific heat above freezing in Btu/lb.F**			**0.87**
Thickness of floor panel in inches	**4.00**	**Product Inlet Temp. in F**			**230.00**
Thickness of concrete in inches	**4.00**	**Respiration Heat From Product Btu/lb.F**			**0.02**
Thickness of door in inches	**4.00**	**Avg. Air Changes**			**-**
		The specific heat below freezing			**-**
Lighting Load in watts	**100.00**	**Product heighest freezing Point**			**29.30**
Electric motors in HP	**3.00**	**Electric motor Running Hrs.**			**24.00**
No. of Peoples Entering into the room	**4.00**	**Electric motor heat equivalent**			**2,950.00**
No. of Hrs. Peoples Working	**5.00**	**Product Latent Heat**			**-**

Heat Gain Load on Door Side Wall

Q = $Q_{Wall} + Q_{Door}$	3,548.94
Q of Wall	3,373.68
A - area of side wall in sq.ft	1,242.60
TD - The temperature difference across the wall in F = = $T_{outside} - T_{inside}$	70.20
U - The overall coefficient of heat transmission in BTU/sq.ft/F = 1/R	0.04
H_i - Convection Coefficient of inside wall	1.65
H_o - Convection Coefficient of outside wall	4.00
X - Thickness of Wall	4.00
K - Thermal Conductivity	0.16
R - Overall Thermall Resistance = $1/H_i + x/k + 1/H_o$	25.86

Heat Gain Load on L & R Side Walls

Q	= (A)(U)(TD) in BTU/Hr	1,656.17
A	- area of side wall in sq.ft	610.00
Q of Door		175.26
A	- area of side wall in sq. ft	64.55
TD	- The temperature difference across the wall in F = = $T_{outside}$ - T_{inside}	70.20
U	- The overall coefficient of heat transmission in BTU/sq.ft/F = 1/R	0.04
H_i	- Convection Coefficient of inside wall	1.65
H_o	- Convection Coefficient of outside wall	4.00
X	- Thickness of Door	4.00
K	- Thermal Conductivity	0.16
R	- Overall Thermall Resistance = 1/ H_i + x/k + 1/ H_o	25.86
TD	- The temperature difference across the wall in F = = $T_{outside}$ - T_{inside}	70.20
U	- The overall coefficient of heat transmission in BTU/sq.ft/F = 1/R	0.04
H_i	- Convection Coefficient of inside wall	1.65
H_o	- Convection Coefficient of outside wall	4.00
X	- Thickness of Wall in inches	4.00
K	- Thermal Conductivity	0.16
R	- Overall Thermall Resistance = 1/H_i + x/k + 1/ H_o	25.86

Heat Gain Load on Ceiling Wall

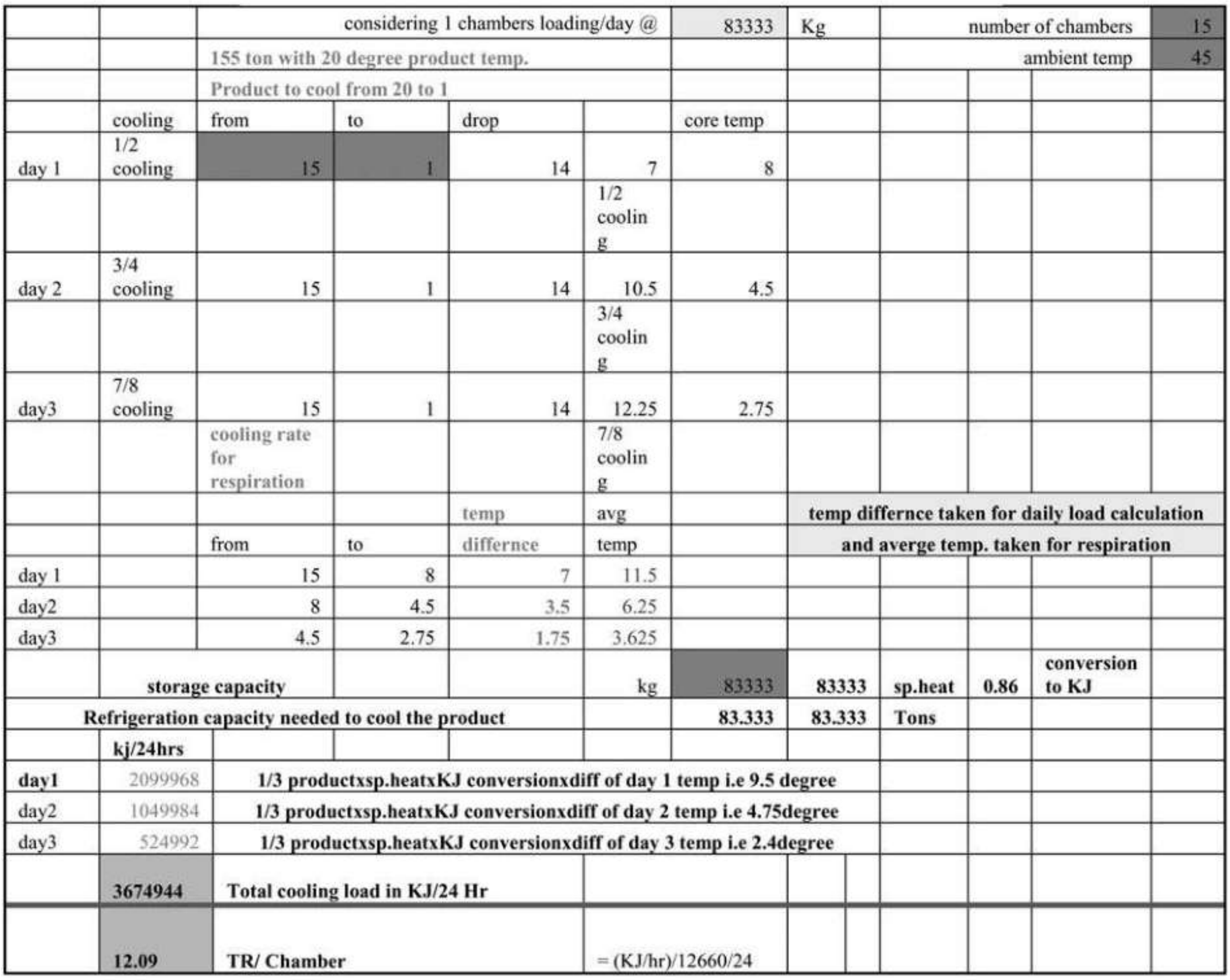
Q	= (A)(U)(TD)	3,066.99
A	- area of side wall in sq.ft	1,129.63
TD	- The temperature difference across the wall in F = = $T_{outside}$ - T_{inside}	70.20
U	- The overall coefficient of heat transmission in BTU/sq.ft/F = 1/R	0.04
H_i	- Convection Coefficient of inside wall	1.65
H_o	- Convection Coefficient of outside wall	4.00
X	- Thickness of Wall in inches	4.00
K	- Thermal Conductivity	0.16
R	- Overall Thermall Resistance = 1/ H_i + x/k + 1/ H_o	25.86

Heat Gain Load on Floor

Q	= (A)(U)(TD)	1,561.42
A	- area of side wall in sq.ft	1,129.63
TD	- The temperature difference across the wall in F = = $T_{outside}$ - T_{inside}	36.20
U	- The overall coefficient of heat transmission in BTU/sq.ft/F = 1/R	0.04
H_i	- Convection Coefficient of inside wall	1.65
H_o	- Convection Coefficient of outside wall	4.00
X	- Thickness of Wall in inches	4.00
K	- Thermal Conductivity	0.16
R	- Overall Thermall Resistance = 1/H_i + x/k + 1/H_o	26.19
X	- Thickness of concrete in inches	4.00
K	- Thermal Conductivity	12.00

Heat Gain Load on L & R Side Walls	1,656.17
Heat Gain Load on Back Side Wall	3,548.94
Heat Gain Load on Door Side Wall $Q = Q_{Wall} + Q_{Door}$	3,548.94
Heat Gain Load on Ceiling Wall	3,066.99
Heat Gain Load on Floor	1,561.42
Total Transmission Load Btu/Hr	**13,382.46**
Total Equipment Load in TR	**1.12**

Equipment Load	
Lighting load = Load × 3.42 × No. of Hrs. in BTU/hr	1,710.00
Electric Motors = Load of Motor × Heat Eqult. × No. of Hrs.	8,850.00
Peoples = No. of People × No. of Hrs. × Heat Eqult.	19,000.00
Total Equipment Load in BTU/hr	**29,560.00**
Total Equipment Load in TR	2.46.00



		considering 1 chambers loading/day @				83333	Kg	number of chambers			15
		155 ton with 20 degree product temp.						ambient temp			45
		Product to cool from 20 to 1									
	cooling	from	to	drop		core temp					
day 1	1/2 cooling	15	1	14	7	8					
					1/2 cooling						
day 2	3/4 cooling	15	1	14	10.5	4.5					
					3/4 cooling						
day3	7/8 cooling	15	1	14	12.25	2.75					
		cooling rate for respiration			7/8 cooling						
				temp	avg		**temp differnce taken for daily load calculation**				
		from	to	differnce	temp		**and averge temp. taken for respiration**				
day 1		15	8	7	11.5						
day2		8	4.5	3.5	6.25						
day3		4.5	2.75	1.75	3.625						
	storage capacity				kg	83333	**83333**	**sp.heat**	**0.86**	**conversion to KJ**	
Refrigeration capacity needed to cool the product						**83.333**	**83.333**	**Tons**			
	kj/24hrs										
day1	2099968	**1/3 productxsp.heatxKJ conversionxdiff of day 1 temp i.e 9.5 degree**									
day2	1049984	**1/3 productxsp.heatxKJ conversionxdiff of day 2 temp i.e 4.75degree**									
day3	524992	**1/3 productxsp.heatxKJ conversionxdiff of day 3 temp i.e 2.4degree**									
	3674944	**Total cooling load in KJ/24 Hr**									
	12.09	**TR/ Chamber**			= (KJ/hr)/12660/24						

Product Load

Sr. No	Description	Load Detail in TR
1.	Transmission Load	1.12
2.	Equipment Load	2.46
3.	Product Load	12.09
4.	Total Heat Load/Chamber	15.67
5.	Safety Factor - 10%	1.57
6.	Total Heat Load	17.24

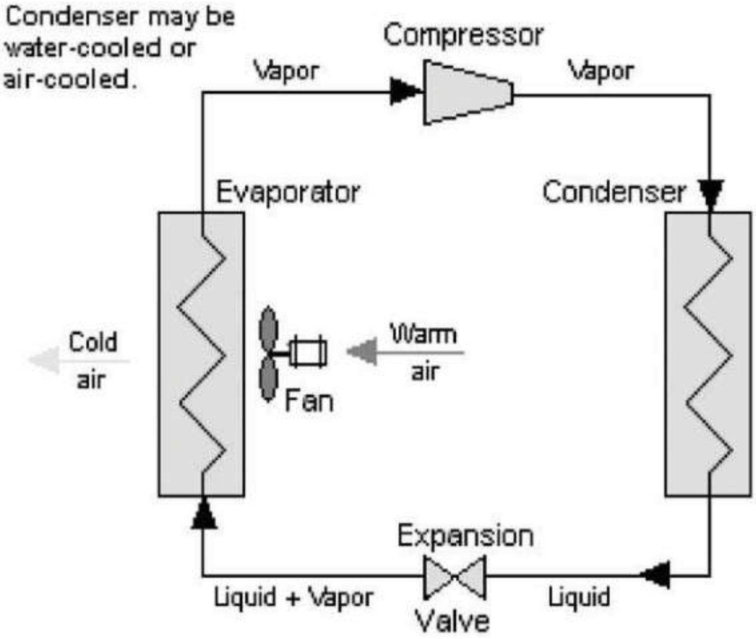
Total Heat Load for 15 Chambers

Note : Holding Load/Chamber in Kw - (Product Load × (Respiration rate/ton))/12660/24/0.284

During Holding we can save energy by using the Variable Frequency Drives @ 34% only.

1.7.3 *Refrigeration Equipments*

Major Components/Working Principle :



Typical single stage vapor compression refrigeration

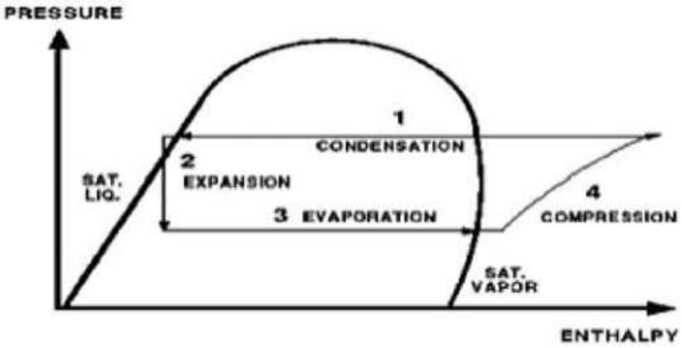


Fig. 3. Working Principle

1.8. Benefits of ammonia & glycol refrigeration system

- Ammonia free cooling system.
- Using glycol achieving the humidity faster.
- No weight loss in the product.
- Plc based temperature and humidity monitoring, results no shrinkage in apples.
- Ammonia charging is very less just about 400 kg

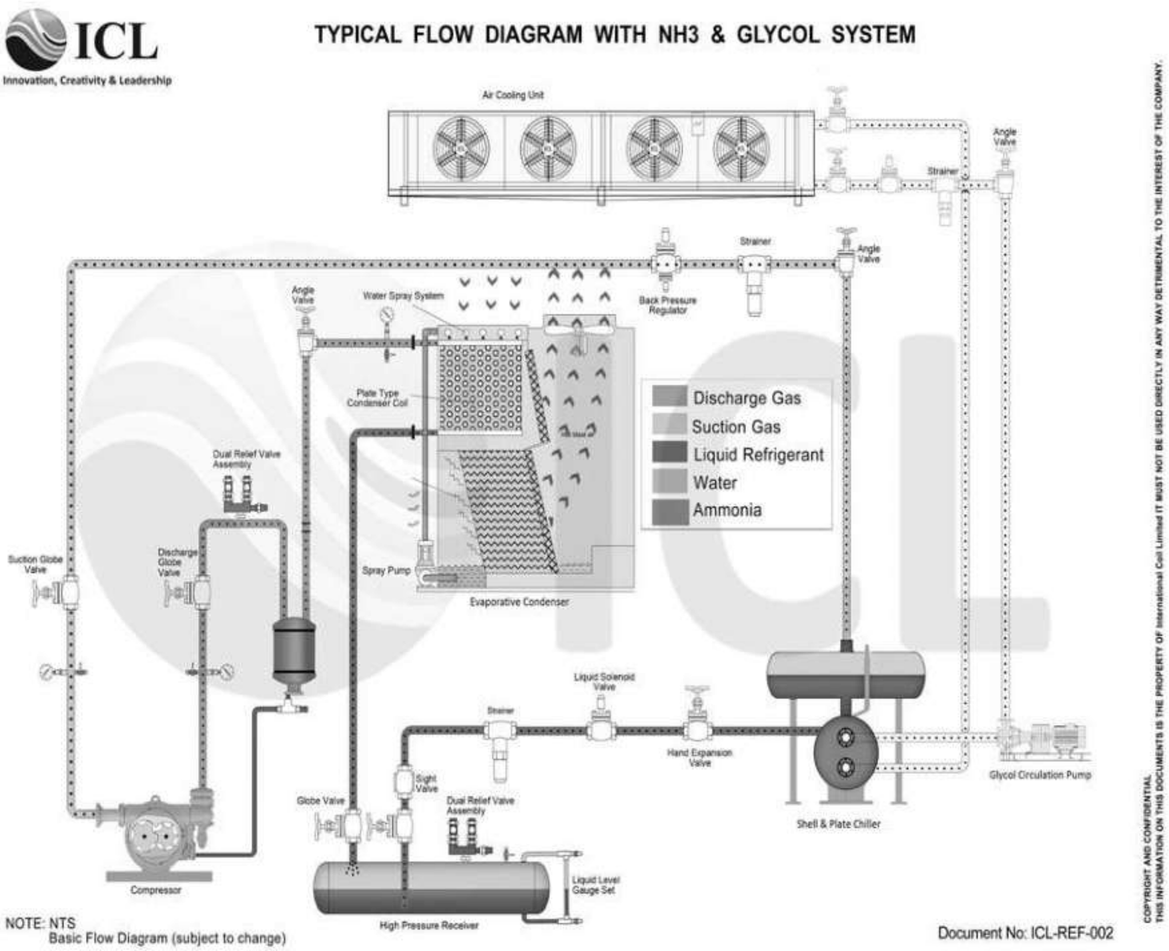


Fig. 4. Refrigeration Flow Diagram

1.8.1 *Controlled Atmosphere Equipments*

Fig. 5. Nitrogen Generator

Fig. 6. CO_2 Scrubber

Fig. 7. Valve Station

Fig. 8. GAS Analyzer

Nitrogen Generators : Nitrogen Generator is being used to reduce the % of Oxygen Value inside the chamber by increasing the % of Nitrogen inside the chamber.

1.8.1.1 *CO_2 Scrubber*

CO_2 Scrubber is being used to maintain the desired % of CO_2 Value inside the chamber.

Valve Station : These are all pneumatic operated valves being used for aspiration and delivery purpose of N_2/CO_2 gases.

1.8.1.2 *Gas Analyzer/Controller*

These regulates and monitoring the level of O_2/CO_2.

9. Conclusion

To safe guard the interest of the Farmers, Controlled Atmosphere System was developed in India especially for Apples, in earlier days the farmer had no facility to store their product after harvesting, which was forcing them to sell their product immediately after the harvesting at a cheaper price due to arrival of bulk quantity in market. With the controlled atmospheric technology the farmer can store their product for 6-8 months so that they can sell their product as per the requirement of the market, which can fetch them better price instead of getting low price when the product is in Bulk.

India has a good resource base, adequate research and development infrastructure and excellence in several areas of horticultural interest. Production and postharvest processing activities within the country have, therefore, been changing at a rapid rate. The demand for horticultural produce in India is on the rise, owing to increasing populations, changing food habits, the nutritional value of horticultural crops and a greater emphasis on postharvest management, processing and value addition. Advantages of growth can be harnessed with well planned strategies, so as to ensure a positive future outlook.

Food safety is of growing importance in food production, processing and marketing. Investment in food safety, while assuring risk-free ventures related to horticulture, will increase the cost of fresh produce and the processing of fruits and vegetables. Efforts geared toward improving production technologies for fruits and vegetables will become meaningful only if the effective postharvest technology is developed and wastage is reduced. Thus, proper growth of postharvest technology of fruits and vegetables is vital for development of India's economy.

References

[1] Postharvest Management of Fruit and Vegetables in the Asia-Pacific Region,

[2] Published By Asian Productivity Organization and Food and Agriculture Organization of the United Nations

[3] Ministry of Food Processing Industry - www.mofpi.nic.in

[4] International Coil Ltd - www.icl-tech.com.

[5] Principle of Refrigeration by Roy Dossat.

[6] National Horticulture Board - www.nhb.org.in

[7] Ashrae Hand Book of Refrigerant

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1. W.F Bruce and L.F Fieser, *J. Am. Chem. Soc.,* **60** (1938) 1017.
2. J.B. Birks, Photophysics of Aromatic Molecules, Wiley Interscience, New York (1970) 225.
3. C.R. Tilford, New Developments in Barometric Range Pressure Standards, Proceedings of NCSL Symp., Washington D C, (1988) 35.1-35.15.
4. G. Klingenberg and H. Bauer, Final Report-CCM.V-K1 *Metrologia,* **41** (Techn. Suppl) 2004.

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WHO took up the malaria in Global Technical Strategy 2016 - 2030 in May 2015 as a part of Sustainable Development Goals 2030 which aims to reduce malaria deaths and the disease at least 90 % and eliminate malaria in at least 35 countries by 2030. This goal of WHO can only be achieved by the high will power of the entire world for the humanitarian.

REFERANCE :

- Bhargava Y. S. (1982): Malaria – A guide to health workers, Aravali Publication, Rajasthan
- Bedi Yashpal (1988) : Social and preventive medicine, Rawat Publication, Jaipur
- Department of Planning and Statistics, (2012 - 13): Socio - Economic Development of DNH since it liberation, Administration of DNH, Silvassa
- Govt. of India (1995): Operational Manual for Malaria Action Programme, Ministry of Health and Family Walfare, Shamnath Marg, Delhi
- Hussain Reshma, Karniq Yashwant (1986) Dadra and Nagar Haveli, Achchooti Aur Akeli, Indian red cross society, Dadra & Nagar Haveli
- Lele, P. S. (1987) Dadra and Nagar Haveli: past and present, published by S. P. Lele, Dadra and Nagar Haveli, Silvassa
- Mishra, R. P. (1970): Medical Geography of India, National Book Trust, New Delhi.
- Malaria Institute of India, Delhi (1958), Manual of Malaria Eradication Operation, Delhi
- Shelar S. K. (2006): A Geographical Study of Resurgence of Malaria in Nashik Division, Maharashtra: A study in Medical Geography, Unpublished Ph. D. Thesis submitted to Dr. H. S. Gaur Central University, Sagar (M. P.)

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08

Study Of NLO Properties Of Grown Copper Tartrate Crystals By Single Diffusion Gel Method

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Abstract-

Copper tartrate crystals were grown successfully by a simple gel technique using single diffusion method. The optimum growth conditions were established by varying different parameters such as pH of gel solution, gel concentration. gel setting time, concentration of reactants etc, Copper tartrate crystals were obtained blushes & opaque The maximum size of the grown crystals was observed about 6 x 5 x3mm^3. These grown crystals were characterized by, XRD,FT-IR, UV & SEM.

Keywords- Silica gel, grown Copper tartrate crystals, XRD,FT-IR, UV & SEM.

INTRODUCTION

Systematic study of the growth and properties of crystals is covered under the subject of crystal growth. It is a subject of multidisciplinary nature. The growth of crystals occurs either in nature or artificially in laboratory.

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The Mother Nature grows a variety of crystals in the crust of Earth, which are the natural mineral crystals and often considered as precious stones. However, the demand of the modern day science and technology has tempted scientists to synthesize and grow several new varieties of crystals. This has brought the field of Crystal Growth into the limelight. As a result the congeries of crystals is ever expanding day by day. The growth of crystal occurs not only in the crust of earth or in laboratory but also in a living body. Many crystals, particularly, bio-materials and proteins, cause various ailments and health related problems. The urinary stones are usually composed of either pure or mixed crystals of calcium oxalate, i.e., bone and joint diseases, are caused by crystals such as calcium pyrophosphate and monosodium tartrate monohydrate. There are other crystals which play important role in various ailments, for this bio-crystallization occurring in human body causes suffering and it is not desirable to occur.

The advancement of science and technology in the recent years. Has replaced the traditional & laboratories experimental technique of analysis by sophisticated. Instrumental technique of analysis. Which gives more accurate results, for characterize of grown crystal a large number of technique are available. The subject of crystal growth was treated as a part of crystallography and never had an independent identity until the last century. It is important to note that both structural crystallography and the science of crystal growth emerged from curiosity about the large variety in crystal forms existing in nature.(1-4)The growth of single crystals of various substances has gained considerable attention of several investigators. Sophisticated and strenuous equipments have been developed and employed for growing a wide variety of crystals; either may be due to lack of natural crystals or their non availability in the required purified form. The growing methods are to be selected, depending on the nature of crystals for which it has to be used for specific purpose. A variety of crystal required for the purpose of research & applications can be grown in silica gel. The gel medium being chemically inert, good single crystals are essential for the variety of scientific & commercial purposes.

MATERIALS AND METHODS

Copper tartrate shows poor solubility in water hence it was thought worthwhile to grow such a kind of material by chemical reaction at controlled rate using gel method. Gel was prepared by using tartaric acid & sodium. The chemicals use for the growth of copper tartrate crystals; all chemicals were of AR grade. Take 7ml of tartaric acid (1M) in a small beaker. To tartaric acid add sodium metasilicate solution. (1M) drop by drop with constant stirring. Then the pH of solution maintains to 4 to 4.5, then pH is measured with digital pH meter.

Transfer the mixture in the borosilicate glass test tube in diameter is 2.5 cm & in length is 25 cm. Then cover its mouth with cotton plug .Its is transparent initially, after 2/3 days, it turns onto milky & gel converted into semisolid with little amount of water on the top of the surface which is called water of syneresis. Such gel can not be used for reaction as it has not set. It vibrates with the small mechanical jerks allows the water of syneresis to evaporate completely. It may take one week & it does not vibrate with the small mechanical jerks i.e. called "Setting of gel".

After setting of gel, allow the aging of the gel. Aging makes gel the harder and reduces the diameter of the capillaries present in the gel. Take the copper chloride ($Cucl_2$) required concentration was then poured slowly along the sides of the test tube to avoid breaking of the gel. Copper chloride solution acted as upper reactants ions through the narrow pores of the silica gel leads to reaction between these ions and the ions present in the gel as lower reactant.(5-8).

The following reaction was expected inside the gel.

$CuCl_2 + C_4H_6O_6 \rightarrow C_4H_4O_6Cu + 2HCl$

Copper Chloride + Tartaric acid→Copper tartrate

Crystals of copper tartrate are bluish opaque, diamond shaped. Maximum sizes of the grown crystals are 3mm x 4mm and thicknesses about 2 to 3mm are obtained.

Different parameters such as concentration of reactants, pH of gel, impurities in the solvent, gel setting time, gel aging time, etc. have considerable effect on growth rate. Near gel interface dendrites growth is observed due to fast growth rate. However as the reactants percolates through the gel, the controlled reaction occurs below interface the depth of 3 to 4 cm. Hence good quality, bluish opaque crystals having well developed faces are observed. Optical micrograph of the grown crystal it shown fig. it shows bluish colored & opaque crystal of copper tartrate Table 1 gives the various conditions for copper tartrate crystals grown in silica gel.Optimum condition of copper tartrate crystal.

Table 1 Various optimum conditions for growing crystals were found

Various process parameter	Optimum conditions
Density of sodium meta silicate solution	1.05 g/cm^3
Concentration of tartaric acid	1 M
Volume of Tartaric acid	7 ml
Concentration Copper chloride	1 M
Volume of sodium meta silicate solution	19 ml
pH of the mixture	4 to 4.5
Room Temperature	30^0c
Gel setting time	96 Hours

In present work Figure 1 illustrates different morphologies of pure copper tartrate crystals grown under different conditions of growth. Some bluish opaque crystals were observed. Figure 2 shows single bluish opaque crystal.

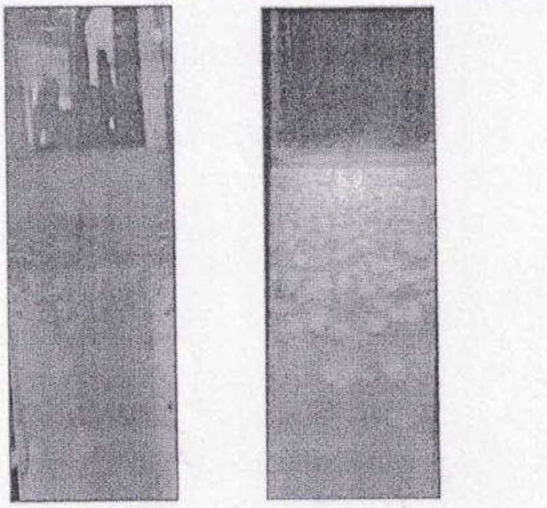


Fig. 1 shows inside test tube copper crystal

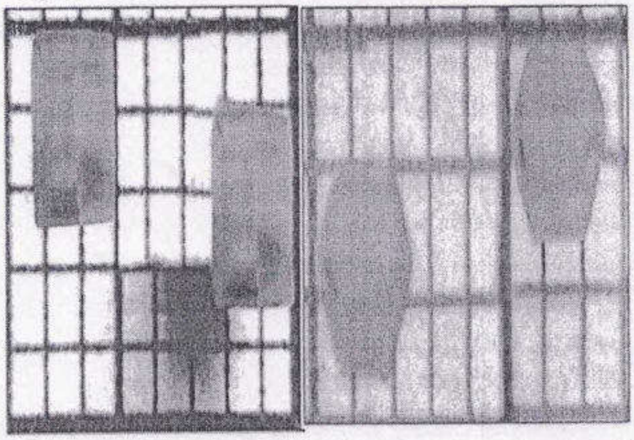


Figure 2 shows the Blushes & opaque crystal

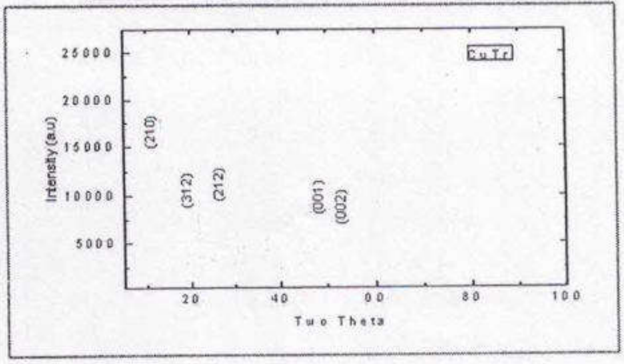
RESULTS AND DISCUSSION

XRD of Copper tartrate Crystal

X-ray diffractogram is useful in the analysis of crystal structure. Cell parameters, 'd' values, unit cell volume and lattice system etc, can be evaluated using X-ray diffractogram. X-ray diffractogram of gel grown copper tartrate was recorded using powder rotation photograph method on 'Minislex Regaku' X-ray diffractometer at department of Physics, Savitribai Phule University, Pune. CuKá-radiation (wavelength ë=1.54051 A^0) was used. The sample was rotated in the range (2è), 20^0-80^0. The scanning speed was kept 10^0/min .The recorded x-ray diffractogram is shown in graph 1. XRD pattern in graph 1 shows very sharp peaks having high intensity which leads to extremely good crystalline perfection of the copper tartrate crystals. The powder diffraction data of copper tartrate is as shown in the table 2 from this powder diffraction data, observed'd' values and (hkl) were computed. The computer program, POWD (Integrative powder diffraction and indexing program version 2.2) was used to calculated'd' values and (hkl).

Table 2 Unit cell parameter

System	Orthorhombic
a	8.3650?
b	12.845?
c	8.768?



Graph 1 XRD of Copper tartrate crystal

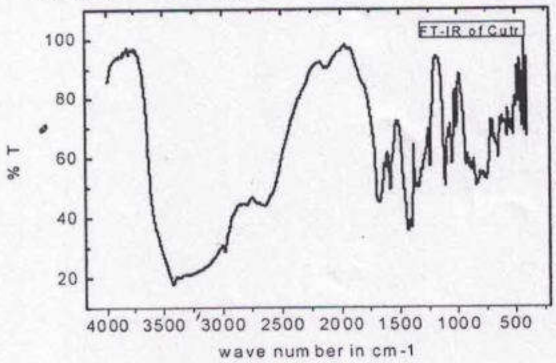
FT-IR of Copper tartrate crystal

Fourier transforms infrared spectroscopy (**FTIR**) is a technique which is used to obtain an infrared spectrum of absorption photoconductivity or Raman scattering of a solid, liquid or gas. An FTIR spectrometer simultaneously collects high spectral resolution data over a wide spectral range. This confers a significant advantage over a dispersive spectrometer which measures intensity over a narrow range of wavelengths at a time.The term Fourier transform infrared spectroscopy originates from the fact that a fourier transform (a mathematical process) is required to convert the raw data into the actual spectrum. Fourier transform spectroscopy is a less intuitive way to obtain the same information. Rather than shining a monochromatic beam of light at the sample, this technique shines a beam containing many frequencies of light at once, and measures how much of that beam is absorbed by the sample. Next, the beam is modified to contain a different combination of frequencies, giving a second data point. This process is repeated many times. Afterwards, a computer takes all these data and works backwards to infer what the absorption is at each wavelength. The FT-IR spectrum of the copper tartrate was recorded in the KBr phase in frequency range 400-4000cm^{-1}, using SHIMADZU spectrometer at Department of chemistry, North Maharashtra University Jalgaon. Graph 2 shows FT-IR spectrum of copper tartrate crystals. The recorded IR spectrum was compared with the standard spectra of functional groups. A broad band due to stretching vibrations of hydroxyl, water and C- H groups. Table 3 shows FT-IR spectral and vibrational assignments of copper tartrate.(9-10).

Table 3 shows FT- IR spectral and vibrational assignments of copper tartrate

Wave number cm^{-1}	Intensity	Assignments
3640-3610	s, sh	O-H stretch
3500-3200	S,b	O-H stretch
3300-2500	m	O-H stretch
2260-2100	w	-C= C- stretch
1760-1665	s	C=O stretch
1470-1450	m	C-H bend
1320-1000	s	C-O stretch
850-550	m	C-Cl

Where m = medium,w = weak,
sh = sharp,s = strong



Graph-2

Shows IR spectrum of copper tartrate crystals

UV OF COPPER TARTRATE

UV-VIS Spectrophotometry is used to determine the absorption or transmission of UV/ VIS light (100to1100nm) by a sample. It can also used to measure concentrations of absorbing materials based on developed calibration curves of the material. A spectrophotometer is employed to measure the amount of light that a sample absorbs. The instrument operates by passing a beam of light through a sample and measuring the intensity of light reaching a detector. The beam of light consists of a stream of photons. When a photon encounters an analytic molecule (the analytic is the molecule being studied), there is a chance the analytic will absorb the photon. This absorption reduces the number of photons in the beam of light, thereby reducing the intensity of the light beam. The absorption spectra of the given sample are recorded by UV-2450 spectrophotometer .A sample is placed in the UV/VIS beam and a figure of the absorbance versus the wavelength is obtained. The energy band gap is determined using this spectrum with the help of relation

Band gap energy (eV) =
1240/wavelength (nm).

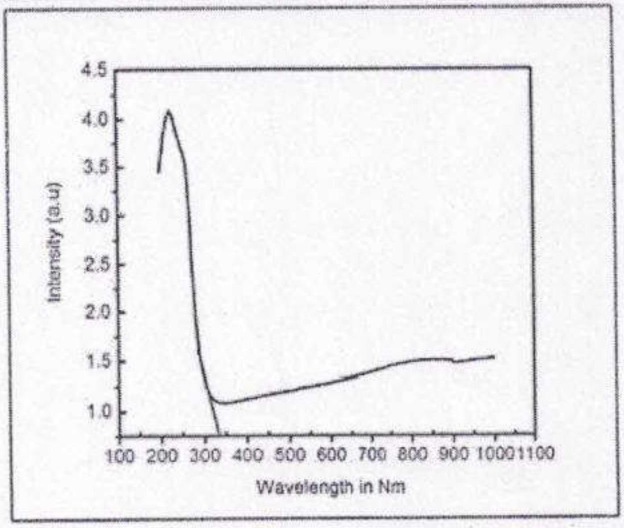
Graph 3 shows UV absorption spectra of copper tartrate crystals. From the spectrum, it has been inferred that copper tartrate crystals have sufficient transmission in the entire visible and IR region. The absorption coefficient is high at lower wavelength and the wide transparency from 340 nm suggesting their suitability for second and third harmonic generations of the 1064 nm radiation.(11-12). The band gap energy of the copper tartrate crystals with the obtained wavelength are calculated using the following simple conversion equation;

Band gap energy (eV) = 1240/ wavelength (nm).Band gap energy is presented in the table 3.

Table 3

Value of band gap energy for copper tartrate grown crystals:

Crystals	Band gap energy (eV)
Copper tartrate	3. 64

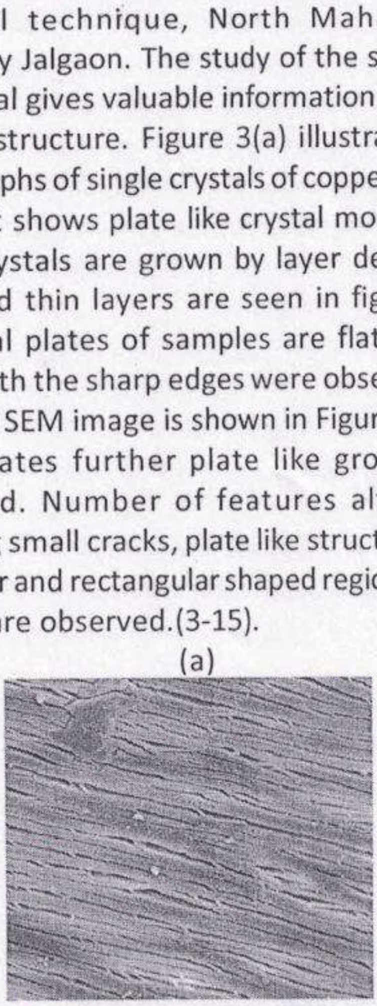


Graph 3 shows UV absorption spectra of copper tartrate crystals

SEM OF COPPER TARTRATE

In the present work powdered sample of copper tartrate crystals was examined by using SEM technique at the University Department of chemical technique, North Maharashtra University Jalgaon. The study of the surface of the crystal gives valuable information about its internal structure. Figure 3(a) illustrates SEM photographs of single crystals of copper tartrate crystal. It shows plate like crystal morphology. These crystals are grown by layer deposition. Thick and thin layers are seen in figure. The individual plates of samples are flat and the plates with the sharp edges were observed. An enlarged SEM image is shown in Figure 3(b).On some plates further plate like growth was observed. Number of features altogether including small cracks, plate like structures, and triangular and rectangular shaped regions on the surface are observed.(3-15).

(a)



(b)

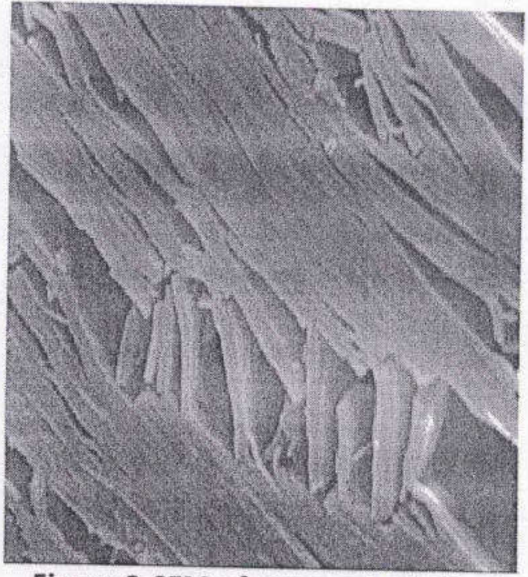


Figure 3 SEM of Copper tartrate

4 CONCLUSIONS

From the above studies we observed that. Gel growth method is suitable for growing crystals of copper tartrate. Different habits of copper tartrate crystals can be obtained by changing parameters like gel density, value of pH, concentration of supernatant etc.it is investigated that copper tartrate crystals have NLO properties.

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REFERENCES

1. H.K. Henisch., "Crystal Growth in Gels", Dover Publication inc p – **17**,1996.
2. N. Srinivasan & S. Natarajan., "Indian J. Phys" **70** A563, 1996.
3. A. Elizabeth, C.Joseph. and M.A. Ittyachan., "Bull. Material Sci." **24**, 4,431. 2001
4. K.C. Joseph and M.J. Joshi., "Indian J.Phys" **76**A 159, 2002
5. S.J. Shitole and K.B. Saraf., "Bull. Mater.Sci.";**24**(5) ;461 – 8., 2001
6. S.J.Shitole and K.B. Saraf, "Crystal .Res. Technology";**37**(5);440 – 5. 2002
7. D.S. Bhavasar, K.B. "Crystal Res. Technology";**37** (1); 51 – 5. 2002
8. S.J.Nandre,S.J.Shitole and R.R.Ahire., "Advances in applied science research", **2**(2): 134-139. 2011,
9. K.Nakamoto "Infrared Spectra of inorganic and co-ordination Compounds" (New York;Johm wiley and sons Inc) 2nd edn. 1970.
10. N.S.Patil,,P.A.Savale.,S.K.Bachhav and S.T.Pawar.,"Archives of physics Research", **2**(1) : 39-47. 2011
11. D.K.Sawant., H.M.Patil and D.S.Bhavasar., "Pelagia research library, DCS", **2** (3), 63, 2011.
12. D.K.Sawant., H.M.Patil and D.S.Bhavasar., "Scholars Research Library Archives of Physics research" **2** (2), 67, 2011.
13. S.J.Nandre,S.J.Shitole and R.R.Ahire., "Scholar research Library Archives of Physics Research",**3**(1), 70,2012,
14. S.J.Nandre,S.J.Shitole.,S.S.Sonawane and R.R.Ahire.,"International Journal of Basic and Applied Research".**1**, 125, 2012.
15. S.J.Nandre,S.J.Shitole and R.R.Ahire., "Journal of Scientific Review". **4**(1), 203, 2012

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A Scientific Approach towards Social Media

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Abstract

Social Media is the produce of science and technology. It encompasses most of the fields via Educational, social, industrial, economical, political and cultural aspects. It has become a part of everyone's life. Even children from KG have at least a little knowledge about how to handle smart phone a digital device. Social media is defined as a relationship that exists between network and people. A very common and widely used example of social media would be internet, whatsapp, and blog writing. It is a means of exchanging ideas, feelings, personal information, pictures and videos. It can be used for educational purposes with scientific approach.

Introduction and Discussion

Here we are discussing on scientific approach towards social media. When a number of computers and terminal equipment are to be connected together to form an integrated system, a well understood standard method of communication and physical interconnection should be established. Let we define it as the use of software technology to ease human life. It is a network used with a scientific device either as a smart phone, Lap Top, Tab or a Personal Computer. For instance Whatsapp, Twitter, E Mail and communication on Internet. Since school education, it is heard that science is the boon or curse for human beings. However, without scientific approach no nation can be attained progress, health, peace and prosperity. After computer revolution, the speed of the development increases. while speaking in relation to India , the country achieve tremendous development in different fields ranging from agriculture, space, hygiene, medicine, trade and commerce, tourism, transportation, infrastructure and communication. The development in these fields builds the nation and nation's economy. In order to achieve perfection we must require a scientific and logical approach towards every task.

As far as we are concerning to teaching profession. We are very close to the changes whatever happened in the society. Since we are being in contact with the teenagers and youth, we know their talent and feelings. The aims and aspirations of the youth very high and they are very sensitive to adapt every change. It is said that Technology is a vital part of success equation. Therefore, it is our duty to provide them the right choice. However, an adaptive method to criticize everything is technical and scientific. The social workers blames on the technology that technology destroys the social and cultural patterns. The focus is on social media. They thought that social media has negative impact on society and youth. Using social media is nothing but simply a waste of time. The educationist and parents are worrying about the exposure of social media ruins the life of teenagers, school going children and college students. Nevertheless, our experiences told different stories. We have been teaching Physics to the college students. When we discussed the topics such as Mechanics, Nuclear Physics, Semiconductors, Photoelectric effect and Quantum Mechanics student found it difficult to understand. However, when we allowed students to use

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internet and social media to solve the difficult problems in the physics the number of correct replies are increased. The learners obtain respond immediately from Internet and social media from the other corners of the world. A number of talented students and researchers have been discovered through social networking sites. . Many students especially utilize social media on daily basis. It is a powerful medium in the hands of the students for group discussion and sharing their views on difficult topics. They enquire about Why? How? and What? The matter relates.Defines the questions and achieves framework. So our opinion is that social media is useful medium for the learners in every field.

Social Media and Employability

The vast majority of the students are passing out as a graduate from the universities without knowing the skills of life. They have no idea where to go now after passing graduate examinations. The poor ones are aimless and jobless. Their job is only wandering here and there in the beaten paths made by the society.

The policy makers, the political leaders, economist and social reformers are constantly talking over the problem of unemployment in the country. It is a debatable topic for group discussion on many channels and stage. Nobody has a specific idea to solve this problem. Nevertheless, science and technology come to our help to ease the problems. Students have easy, free access to resources online to help them to learn something additional qualification. The provision should be made for the undergraduate students that while they are studying their graduate courses at the same time parallel skill based on line certificate courses should be completed. It would be beneficial for them to acquire job after completing degree. The various courses such as digital marketing, digital management, business management, computing, IT, software application development, programming languages, event management and planning are available online for everyone.

Social Media is a boon for the society that provides an educational platform for vast majority of the learners at a time. It provides a network of knowledge and skills. The courses provided on network are highly skillful and beneficial. These courses are recognized by the mostly renowned universities all over the world. Therefore, it is advisable to take positive meaning of social media and make difference in the personality of the students. Make them skilful while achieving degree courses. The students should discover their hidden potential and critical thinking. The employers have choice to choose the right man for the right job. The jobless candidates have opportunity to get job through social media communication. In other words, social media itself creates lot of job avenues to youngsters. It is a source of motivational and inspirational force for the jobless member of the society. It will provide them social equity, dignity and reduction of poverty.

Conclusion:

The above discussion makes us to conclude that if we have a scientific approach towards social media then it is useful and beneficial for the cause of welfare of society. It helps to develop the career, personality, and way of living, way of thinking and the way of behaviour of the users especially the youngsters of the society. Only we have to develop scientific approach.

Reference

1. Beiser, Arthur. Concepts of Modern Physics: McGraw-Hill International Book Company. Singapore. 1984. Print.
2. Castells, M 2009, *Communication Power*, Oxford University Press, Oxford.
3. Dahlgren, P 2009, *Media and political engagement: citizens, communication, and democracy,* Cambridge University Press, New York.
4. Laud, B.B. Electromagnetics: Wiley Eastern Limited. New Delhi. IInd edit. 1992. Print.
5. Rajaraman, V. Fundamentals of Computers. Prentice Hall of India, New Delhi. 2011 print.

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NANOTECHNOLOGY APPLICATIONS: Current and future Nanotechnology applications Nanomaterials, Nano-electronic Nano-medecine and bio nanotechnology applications

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Abstract

Currently, nanotechnology is described as revolutionary discipline in terms of its possible impact on industrial applications. Nanotechnology offers potential solutions to many problems using emerging nanotechniques. Depending on the strong interdisciplinary character of nanotechnology there are many research fields and several potential applications that involve nanotechnology. In this section we provide a brief overview about some nanotechnology and nanoscience current developments. Obviously it can't provide an exhaustive report of the developments in nanoscience and nanotechnologies in all scientific and engineering fields. We are going to consider three main categories (broad nanotechnology categories).

Key words –nano-wire, carbon tubes nano-powder

Introduction

- Nanomaterials;
- Nano-electronic (information and communication technology);
- Nano-medecine and bio nanotechnology.

We can define nanomaterials as those which have nanostructure components with at (less than 100nm). Materials with one dimension in the nanoscale are layers, such as a thin films or surface coatings. Materials that are nanoscale in two dimensions are nanowires and nanotubes. Materials that are nanoscale in three dimensions are particles quantum dots (tiny particles of semiconductor materials). Nanocrystalline materials, made up of nanometer-sized grains, also fall into this category. Two principal factors cause the properties of nanomaterials to differ significantly from other materials: increased relative surface area, and quantum effects. These factors can change or enhance properties such as reactivity, strength and electrical properties, optical characteristics. Nanomaterials and Nanotechnology applications

Nanomaterials in one dimension –

In this category belong nanomaterials such as thin films and engineered surfaces. This type of nanomaterials can't be really considered as a new material considering that have been developed and used for decades in fields such as electronic device manufacture, chemistry and engineering.

Nanomaterials in two dimensions-

Two dimensional nanomaterials such as tubes and wires. Inorganic nanotubes see nano-natural a typical example of inorganic nanotubes example. Halloysite nanotubes are hollow tubes with high aspect ratios that are tens to hundreds of nanometers (billionths of a meter) in diameter, with lengths typically ranging from about 500 nanometers to over 1.2 microns (millionths of a meter).

Carbon nanotubes see carbon nanotubes section of nanocompositech.com

Nanowires

Nanowires are ultrafine wires or linear arrays of dots, formed by self-assembly. They can be made from a wide range of materials. Semiconductor nanowires made of silicon, gallium nitride and indium phosphate have demonstrated remarkable optical, electronic and magnetic characteristics.

Nano scale in three dimensions –

Nanoparticles are often defined as particles of less than 100nm in diameter. Fullerenes (carbon 60): Spherical molecule formed of hexagonal carbon structure recently discovered1986.

Dendrimers- are spherical polymeric molecules, formed through a nanoscale hierarchical self-assembly process.(trivial definition: 3d polymer),Quantum dots: for an exhaustive treatment of a subject see quantum dots companies with more white papers about quantum dots and their applications.

We shortly list a number of applications considering current and future application of nanomaterials previous scheduled.

Cosmetics applications of nanoparticles- (e.g sunscreen lotions: ray absorbs properties)

Nanocomposites materials- nanoparticles silicate nanolayer (clay nanocomposites) and nanotubes can be used as reinforced filler not only to increase mechanical properties of nanocomposites but also to impart new properties (optical, electronic etc.).

Nanocoatings-surface coating with nanometer thickness of nanomaterials can be used to improve properties like wear and scratch-resistant, optoelectronics, hydrophobic properties.

Hard cutting tools-current cutting tools (e.g mill machine tools) are made using a sort of metal nanocomposites such as tungsten carbide, tantalum carbide and titanium carbide that have more wear and erosion-resistant, and last longer than their conventional (large-grained) materials.

More performed paint using nanoparticles to improve paint properties.

Fuel cells-could use nano-engineered membranes to catalytic processes for improve efficiency of small-scale fuel cells.

Displays- new class of display using carbon nanotubes as emission device for the next generation of monitor and television (FED field-emission displays).

Using nanotechnology based knowledge may be producing more efficient, lightweight, high-energy density batteries.

Nanoparticles can be used as fuel additivities and catalytic more efficient materials.

Other feasible nanotechnology applications

Nanospheres in lubrificants technology like a sort of nano balls bearing Nanoscale magnetic materials in data storage device. Nanostructure membranes for water purification.Nanoelectronic (information and communication technology).In some sense, electronic miniaturization has been the true driving force for nanotechnology research and applications. The main aim in this area is understand nanoscale rules and mechanism in order to implement new ICT systems more economic, little and reliable. It's a sure thing that silicon era is on the way up. Only nanotechnology can radically change ICT systems in order to continue to follow Moore's law. Nanotechnologies are therefore expected to enable the production of smaller, cheaper devices with increasing efficiency.

Nanotechnology applications in nanoelectronic area

The Current nanotechnology applications concern

- **Computer chips;**
- **Information storage;**
- **Sensors;**

Bio-nanotechnology and Nano-medecine

Bio-nanotechnology is concerned with biological nanostructures and is a strong interdisciplinary matter (chemical, biological and the physical sciences.) Biological systems are the most perfect nanosystems one can image. Bimolecular structures possess highly specific morphology and functions and somehow nanotechnologist must study there in depth in order to understand general nanotechnology aspects.

Nanotechnology applications in bio-nanotechnology and Nano-medecine

Bio nanotechnology is a new research that may product great break through in applications in the field of medicine such as disease diagnosis, drug delivery and molecular imaging that has been already intensively researched.

Current and particularly future applications regard

Electronics information and communication technology

In this area, "smart" molecules may be integrated into devices for specific ICT applications, in order to obtain a protein based transistor. For this and other type of nanotech application will be important understand the fundamental electronic properties of bio molecules in particular the mechanisms by which electronic charge is transferred between them and metals semiconductors and novel nanoelectronic properties of Carbon Nato Tubes.

Drug delivery systems

One of the most potential applications of nanotechnology might be related to gene and drug delivery system on order to improve therapy efficacy. The challenge is devise nanoparticles capable of targeting specific diseased cells, which contains both therapeutic agents that are released into the cell and an on-board sensor that regulates the release. As related approach already in use is that of polymer based drug delivery systems but the functionalities previous outlined are obviously more powerful.

Medical Imaging for diagnosis

Nanotechnologies already use quantum dots or synthetic chromospheres to selected molecules (e.g proteins) for intracellular imaging. Also incorporation of naturally fluorescent proteins has been experimented which, with optical techniques allow intracellular biochemical processes to be investigated directly.

Reference

1) Ehud Gazit, Plenty of room for biology at the bottom: An introduction to bionanotechnology. Imperial College Press, 2007, ISBN 978-1-86094-677-6

2) *"Nanobiology"*. Swiss Nanoscience Institute.

2) Ng, CK; Sivakumar K; Liu X; Madhaiyan M; Ji L; Yang L; Tang C; Song H; Kjelleberg S; Cao B. (4 Feb 2013). "Influence of outer membrane c-type cytochromes on particle size and activity of extracellular nanoparticles produced by Shewanella oneidensis". Biotechnology and Bioengineering. **110** (7): 1831–7. doi:10.1002/bit.24856. PMID 23381725.

3) Nolting B, "Biophysical Nanotechnology". In: "Methods in Modern Biophysics", Springer, 2005, ISBN 3-540-27703-X

4) Venkatesan M, Jolad B, editors. Emerging Trends in Robotics and Communication Technologies (INTERACT). 2010 International Conference on . Nanorobots in cancer treatment; 12/3-5; Chennai: IEEE; 2010. doi:10.1109/INTERACT.2010.5706154

5) "Nanobiology: from physics and engineering to biology". IOP Science.

6) "The Nanobiology Imperative". Historianofthe Future.com.

7) Zadegan, Reza M.; Norton, Michael L. (June 2012). "Structural DNA Nanotechnology: From Design to Applications". Int. J. Mol. Sci. **13** (6): 7149–7162. doi:10.3390/ijms13067149. PMC 3397516. PMID 22837684.

18. Growth of Mixed Copper-Lithium Tartrate Crystals by Single Diffusion Gel Method

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Abstract

Single crystals of Mixed Copper-Lithium tartrate have been grown using single diffusion silica gel method. Effect of various parameters such as gel pH, gel aging, gel density and concentration of reactants on the growth of these crystals have been studied. Crystals having different morphologies and habits were obtained. The pH of the gel (4.2) concentration of upper reactant (0.5 M) Conc of lower reactant (0.5M) at room temp 30°c are found to be critical. In the present work few dendrite, semitransparent faint bluish crystals of mixed copper lithium tartrate were obtained Maximum size of grown crystal was 1mm x 1mm x 2mm

Keywords: Gel technique, Mixed crystals of Copper-lithium tartrate.

Introduction

The advancement in the science of the solid state and material science depend upon the availability of good quality single crystals. Consequently, tremendous amount of efforts has been made on the development of crystal growth techniques, each having its own importance and potentiality with certain limitation. The new rapidly developing branches of science and technology, such as quantum electronics, quantum and non linear optics, semiconductor instrumentation, Laser and masers etc. all involves the use of single crystals and their singular properties. So several techniques have been developed and are still being to be developed in rapid succession to synthesize better and better quality of crystals, which are rare in nature, or not yet grown in laboratory.[1-4]

Experimental Procedures

Good crystals of mixed Lithium -Copper tartrate can be grown in gels in different way. The single diffusion method was employed in the present work for the growth of Lithium - Copper tartrate crystals. The crystallization apparatus used essentially consists of simple glass tubes of length 25cm and diameter 2.5 cm .Double distilled water was used for the dilution throughout the study. Tartaric acid, Sodium Meta silicate, Lithium chloride, and cuprous chloride solutions were prepared by dissolving these compound in an appropriate amount of distilled Alcohol (Methanol and Ethanol) to give the required molarities. Gel of required specific gravity were prepared by adding tartaric acid to the solution of sodium Meta silicate. Calculated amount of redistilled water and a stock solution was kept ready for doing further experiments. Care has been taken to avoid excessive local ion concentration which may otherwise cause premature local gelling and make the final medium inhomogeneous and turbid. The Tartaric acid solution of particular strength was taken in a 100ml beaker and sodium meta silicate solution of a suitable specific gravity was added drop wise using a tephlon cock burette,with constantly Stirring the solution in the beaker by magnetic stirrer, stirring is done to avoid the pH variation in with time value This solution was gently poured in to the test tube without giving chances for the formation of the bubbles. Then test tubes were closed with rubber corks or cotton to prevent evaporation and contamination of the exposed surface. by dust particles of atmosphere.

The gels in the range 4 to 4.2 was usually found to set in 4 to 8 days depending on the environmental temperature After ensuring firm gel setting, the saturated solution of mixture of LiCl and CuCl (supernatant) of particular strength was poured over the set gel with the help of pipette The solution being allowed to fall along the wall of the test tube to prevent the gel surface from cracking. The supernatant solution slowly diffused in to the gel medium where it react with inner reactant giving rise to slow precipitation of the reactants.

The Following reaction is expected to take place, inside the gel.

$LiCl + CuCl + C_6H_6O_6 \quad CuLiC_4H_4O_6 + 2HCl$

The table 1 given the optimum conditions for growing crystals.

Table 1 The Optimum conditions for growth of Mixture Copper- Lithium tartrate Crystals.

Optimum conditions	**Copper tartrate**
Density of sodium meta silicate solution	1.04 gm/cm3
Concentration of tartaric acid	1 M
Volume of Tartaric acid	7 ml
Concentration Cuprous chloride + Lithium chloride Mixture	0.8 M

Volume of sodium meta silicate solution	18ml
pH of the mixture	4.2
Room Temperature	30^0C
Concentration of Lithium Chloride	1 M

Effect of Various Parameters on Crystal growth

Various concentrations were tried of tartaric acid & those of sodium metasilicate solutions. Were tried at different p^H values and the effect of various parameters was studied.

i) Effect of gel density

Gels of various densities were made by mixing sodium metasilicate of specific density from 1.038 to 1.04 gm/cm^3 with one mole tartaric acid at pH 4.2 constant. It was observed that the transparency of the gel decreases as the gel densities increases .Gels with higher densities set more rapidly than the gels with lower densities. It may be noted that rhombic shaped bluish crystals of mixed copper - lithium tartrate were obtained with sodium meta silicate of density 1.04 gm/cm3. It was found that increase of gel density decreases the nucleation density. This is because denser gel results in smaller pore size. This is in agreement with observations. Table 2 shows the effect of density on number of nuclei formed. In present work best quality, well semitransparent, various shape & size crystals were observed for density 1.040gm/cm^3.[5-10]

Table 2 Effect of gel density on Nucleation density (pH=4.2, Cuprous chloride solution CuCl & Lithium chloride LiCl = 1M & Tartaric acid =7ml)

Test tube No.	**Tartaric acid 1M(ml)**	**Density of gel (gm/cm^3)**	**Number of nuclei formed**	**Observations**
1	7	1.038	42	Nucleation process medium very small crystals.
2	7	1.040	38	Transparent, well.
3	7	1.042	30	Faint Bluish, semitransparent.
4	7	1.044	28	Bigger crystals are formed
5	7	1.046	21	Good, Some other small crystals
6	7	1.048	10	Good

ii) Effect of concentration of reactants

As the concentration of tartaric acid is increased more volume of sodium Meta silicate was required to adjust the pH value about 4.2 to 4.5. Increased in concentration of tartaric acid provides more tartrate ions to combine with copper ions. By increasing the aging time the concentration of tartaric acid is increased, and nucleation density increases, the fast growth rate at high conc. of tartaric acid resulted into dendrites growth. From Table 3& fig 1 shows the

Table 4 Effect of Concentration of Supernatant (pH=4.2, Aging period =140 hrs, Volume of sodium metasilicate (1.04 gm/cm^3) = 19 ml, Volume of 1M tartaric acid 7ml)

Test tube No.	Sodium Metasilicate (1.04 gm/cm^3)	Conc.of reactant in gel(tartaric acid 1M) ml	Conc. Of reactant above Gel (CuCl+ LiCl) (1M)	Number of Nuclei	Observations
1	17	7	0.2 (1:1)	4	Few nucleations, crystals size very small
2	17	7	0.4 (1:1)	7	Slightly crystal size increased
3	17	7	0.6 (1:1)	11	Well grown crystals of various shape & size
4	17	7	0.8 (1:1)	15	Faint, Bluish,crystals
5	17	7	1 (1:1)	20	SemiTransparent,
6	17	7	1.2 (1:1)	24	crystals are not isolated

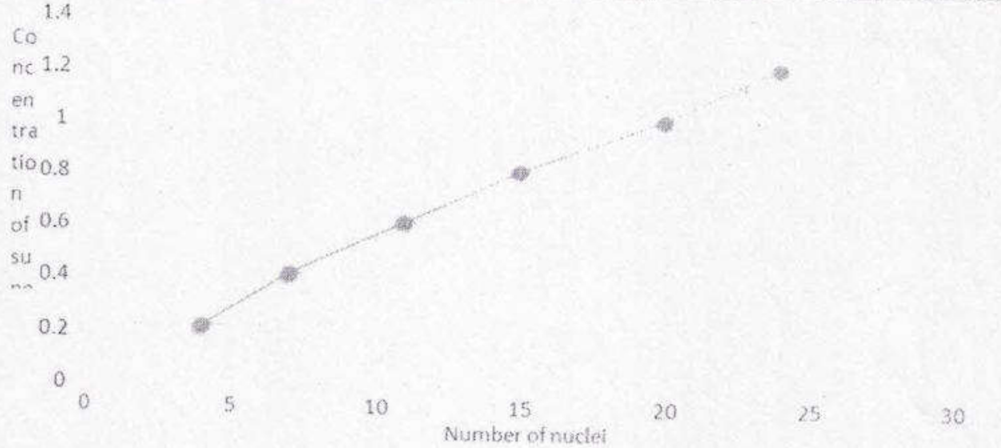

Fig. 2 Concentration of Supernatants Vs Number of Nuclei

iv) Effect of pH of gel

The pH value of gels was varied from 2 to 5 The effect of pH on growth rate was studied. It was observed that as the pH increased, the transparency of the gel decreased. In the present work good crystals of mixed cuprous/copper lithium tartrate are obtained at pH 4.2 to 4.5.The crystals growing at higher pH values were not well developed. This was due to contamination of the crystals with silica gel. It was observed that as the pH of gel increased the number of crystals decreased. Table 5 shows the effect of different pH values on the quality of crystals. Fig 3 shows the graph of gel setting time versus pH of the solution. [11-15]

Table 5 Effect of pH on gel (Aging period =120 hours, Supernant solution Cucl& LiCl=1M, Amount of 1M tartaric acid =7ml)

Test tube no.	Tartaric acid 1M (ml)	Sodium metasilicate (1.04gm/cm$^{3)}$	pH of Mixture	Gel setting time (hours)	Observations
1	7	11	3.0	-	Gel set in some days but still unstable
2	7	14	3.8	130	small crystals
3	7	16	3.9	90	Good crystals
4	7	17	4.0	80	Semi Transparent, faint bluish, opaque crystals.
5	7	19	4.1	74	Whisker growth.
6	7	21	4.2	61	Slightly increased in size
7	7	23	4.2	52	Well defined shaped

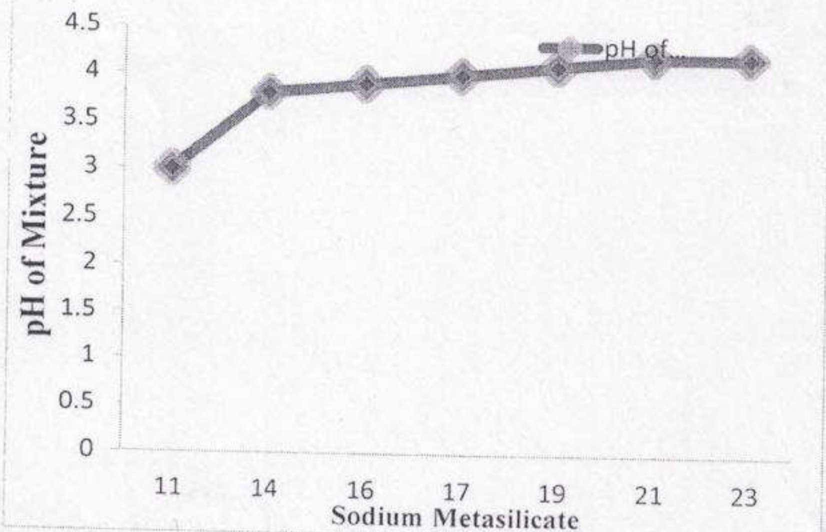

Fig. 3 pH of Mixture Vs Sodium Metasilicate

v) Morphology

Optical micrograph of the grown crystal it shown fig.4 It shows faint bluish colored & transparent crystal of copper-lithium tartrate. Varied morpholopy of grown crystals was observed under various growth conditions.

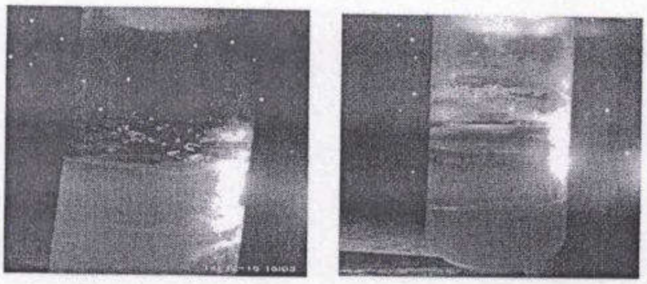

Fig. 4 Opticale photograph showing growth of Mixture copper - lithium tartrate crystals in silica gel at 0.2 to 1 M concentrations of supernatant

Conclusions

1) Gel method is found to be suitable for the growth of mixed Cu-Li tartrate crystals at room temp.2)The gel grown tartrate crystals are faint bluish color.3)The maximum size of grown crystals was found to be 2 to 4 mm.4) It was found that as pH increases, nucleation centers decreases.

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References

1. H.K. Henisch, "Crystal Growth in Gels", Dover Publication in pp – **17**,1996.
2. N. Srinivasan and s. Natarajan."Indian J. Phys" **70** A563, 1996.
3. A. Elizabeth, Joseph. and M.A. Ittyachan."Bull. Material Sci." **24**, 4,431. 2001
4. K.C. Joseph and M.J. Joshi"Indian J.Phys" **76**A 159, 2002
5. S.J. Shitole and K.B. Saraf."Bull. Mater.Sci.";**24**(5) ;461 - 8., 2001
6. S.J.Shitole and K.B. Saraf, "Crystal .Res. Technology";**37**(5);440 – 5. 2002
7. D.S. Bhavsar, K.B"Crystal Res. Technology";**37** (1); 51 – 5. 2002
8. S.J.Nandre ,S.J.Shitole and R.R.Ahire.,"Advances in applied science research", **2**(2): 134-139. 2011,
9. K.Nakamoto"Infrared Spectra of inorganic and co-ordination Compounds"
10. (New York;Johm wiley and sons Inc) 2^{nd} edn. 1970.
11. N.S.Patil,,P.A.Savale.S.K.Bachhav and S.T.Pawar"Archives of physics Research",**2**(1) : 39-47. 2011

12. D.K.Sawant., H.M.Patil and D.S.Bhavasar"Pelagia research library, DCS", **2** (3), 63, 2011.
13. D.K.Sawant. H.M.Patil and D.S.Bhavasar."Scholars Research Library Archives of Physics research" **2** (2), 67, 2011.
14. S.J.Nandre,S.J.Shitole and R.R.Ahire."Scholar research Library Archives of Physics Research",**3**(1), 70,2012.
15. S.J.Nandre,S.J.Shitole.,S.S.Sonawane and R.R.Ahire.,"International Journal of Basic and Applied Research".**1**, 125, 2012.
16. S.J.Nandre,S.J.Shitole and R.R.Ahire., "Journal of Scientific Review". **4**(1), 203, 2012.

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27. Renewable and Non-Renewable Energies for Sustainable Development

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Abstract

Various energy resources have been in use from many years ago. The problems regarding energy resources are arise due to wrong methods of their utilization. There is an urgent need for transition from petroleum based energy systems to one based on renewable energy resources to decrease dependence on depleting reserves of fossil fuels. Every human activity is related with consumption of energy. Energy is the most important factor in the development of a country. Today every country draws its energy needs from variety of sources. There are two types of energy sources: Conventional or non renewable and non conventional or renewable energy sources. A non renewable energy sources includes fossil fuels (coal, oil and gas), nuclear energy etc. Today, the world is progressing at a fast rate with the use of non renewable energy sources. Also the fossil fuel resources are fast depleting and they may come to an end within next few years. These sources have created the problem of environmental pollution. On the other hand, the renewable energy sources are available in large amount and are pollution free. So it's time to switch on to the renewable energy sources. This paper deals with some of the renewable energy and non-renewable resources, their advantages and disadvantages.

Keywords: Renewable energy sources, non renewable energy sources, solar,

Renewable and Non-Renewable Resources

They are two different kinds of sources of energy and other useful phenomena. Renewable resources are often contrasted with non-renewable resources, with people frequently debating the relative benefits of each. But what are renewable and non-renewable resources.

Renewable resources- are resources that do not run out when we use them. A good example is solar energy. When we harness the power of the sun's rays by means of solar panels affixed to our roof, we do not deplete the sun. The sun does not 'run out'; no matter how much solar energy we use. By contrast, non-renewable resources are resources that will run out as we use them. One example is oil. There is only a certain amount of oil on the planet. Oil takes millions of years to form, so, the more oil that we use; the less oil there will be left. This is one key reason why people are currently looking for renewable alternatives to non-renewable sources of energy such as oil. The practice of recycling can turn what we once thought were non-renewable resources into renewable ones. One good example here is water. It might be argued that there is only a certain amount of fresh water in the world, for example, and when we use up all of the water in a nearby reservoir or lake, and then we have no water left for our community. However, water treatment plants enable us to 'recycle' our waste water, by cleansing and sterilizing it ready for us to drink and wash in once more.

Renewable Vs. Non-Renewable Resources

There are plenty of comparisons and contrasts that can be made between renewable and non-renewable resources. Below, you will find 7 such comparisons.

1. **Types of resources-**Renewable and non-renewable resources both come from nature. However, they are both broadly different types of resources. Non-renewable resources, for example, tend to be resources that are classed as 'fossil fuels': oil, coal, natural gas and so on. Renewable resources tend to be freely available resources such as wind and solar energy.
2. **Environmental impact-**Harnessing renewable resources tends to be better for the environment. Non-renewable resources such as fossil fuels produce vast amounts of greenhouse gasses when they are burnt and this contributes to acid rain, climate change and other ecologically harmful effects. By contrast, wind and solar energy do not produce these dangerous gases.
3. **The balance between renewable and non-renewable resources-**Some renewable resources are in danger of becoming non-renewable, unless they are managed properly. One example is wood. Trees naturally grow and replenish themselves, seeding new trees every year. In theory, then, wood ought to be a renewable resource. However, if humans cut down too many trees, forests will struggle to renew themselves. This once renewable resource will become non-renewable.
4. **Convenience-**Depending on where you live, it may be more convenient to use one type of resource. For example, people who live beside windy coast lines may find that wind power is the cheapest and most convenient source of energy for them. People who live in hot countries, moreover, may find that they can generate abundant energy from solar

panels. However, people in other geographical locations may find it much cheaper and more convenient to use biomass or fossil fuels as their primary source of energy.

5. **The need for renewable resources**-By their very definition, non-renewable resources will run out one day. That means that it is essential to find a way for humanity to get all of its energy, water and other needs from renewable resources right now. It is crucial that we take measures to ensure that future generations will not end up in dire need due to our over-consumption of resources in the present.

6. **In the abstract**-Renewable and non-renewable resources can be thought of in a more abstract sense as well. For example, it might be said that ideas and creativity and renewable resources. Using our creativity and sharing our ideas does not deplete either our creativity or our stock of ideas. In fact, it often increases it! It is frequently the case that the more that we use our creativity and the more that we share our ideas, the more creativity and ideas we have to go round. Love is another example of a 'resource' that does not get depleted (and in fact can be said to increase) the more that it is used. The idea of a 'resource' does not need to be a materialistic one.

7. **Taking steps to secure renewable resources**-There are many things that we can all do right now to reduce our dependence on non-renewable resources. We can switch to solar or wind energy, or simply reduce the amount of fossil fuels that we burn by driving and flying less and using less energy around the home. Campaigning with others to ask for change at a political level is another powerful way to help to reduce humanity's need for, and use of, non-renewable resources. And, we can all start recycling, using less water and walking or cycling to work (or taking public transport) rather than driving. It is much easier to make such changes than you might think, and if big companies choose to change as well, the world will be a much cleaner, greener and sustainable living space for us all.

Advantages of Non-Conventional Sources of Energy

Cheaper and Renewable

Most of the Non-conventional Power resources are cheaper and renewable as compared to the conventional sources. Scarcity of Fossil Fuels,The overall limitation and scarcity of fossil fuels has given rise to the urgent need for exploiting alternative energy sources. Rural Energy Needs, Locally available non-conventional and renewable power resources can meet localized rural energy needs with minimum transportional cost. Inexhaustible and Environment friendly, Power from Non-conventional and Renewable is a must in order to reduce carbon dioxide (CO_2) emissions of the coal-based power plants. It is inexhaustible in nature and environment friendly.

Conclusion

This analysis of the differences between renewable and non-renewable resources has highlighted some key facts. For example, it has demonstrated that renewable resources are much more preferable to non-renewable resources, for many reasons. Renewable resources are better for the environment and better for future generations as well. These points all derive from the definition of renewable and non-renewable resources. It is precisely because renewable resources can be renewed that they are preferable to non-renewable resources. Another thing that it is important to take into account is the fact that some renewable resources are in danger of becoming non-renewable if we do not use them in a sustainable fashion. It is important for all of us to take good care of our planet – and one central way of doing so is being careful about the type and amount of resources that we use.

Renewable Energy Sources: Meaning, Advantages and Disadvantages

Meaning of renewable energy sources

Renewable energy sources are sources of energy that are not used up when they are used. So, no matter how much people use them, they will not be depleted. Renewable energy sources are automatically replenished by nature, i.e, sun's rays, water, tides, wind, air, etc. The abundant supply of renewable energy sources, contrasts with the limited supply non-renewable sources of energy, and which are used up when their energy is used. If not replenished, non-renewable sources of energy will eventually run out completely. However, there is no need to replenish renewable energy sources, and no need to worry that they will run out either. Some examples of renewable energy sources will help to illuminate things even further. Solar energy is a key example of a renewable energy resource. No matter how many solar panels we use to harness the sun's rays, we will not deplete the sun. The sun does not start to run out just because we are making use of its energy. Thus, it is a renewable energy source. Wind power is another example of a renewable energy source, for similar reasons: the act of us harnessing wind energy does not deplete the wind. But, are renewable energy sources a good thing or a bad thing? Below, you will be able to read about the main advantages and disadvantages of renewable energy.

Advantages of renewable energy sources

There are many advantages of renewable energy sources. As you will see below, many of these advantages revolve around the fact that they are an environmentally friendly option that can be used well into the future. Green energy – environment friendly-Unlike fossil fuels (which are non renewable energy sources and which release harmful substances such as CO_2 and CO when burned), renewable energy sources have a very low impact on the environment. In fact, most of them are positively environmentally friendly. Sustainable energy – limitless supply, because, crucially, they do not run out, renewable energy sources are sustainable. This makes them viable for use well into the future. Low operating cost, once they have been set up, renewable energy apparatus such as wind farms and solar panels, are very cost effective to use and operate. As such, they are nice and cheap sources of energy. Can be integrated into daily life,Renewable energy sources can be harnessed in a way that does not disrupt daily life. For example, cows can graze in the same field as wind turbines are at work, and solar panels can be placed on the roof of a family home to create a handy energy source. Able to be stored, many people do not realize this but renewable energy sources can be stored. For example, solar energy can be stored in solar panels so that it can be used even during cloudy weather or during the winter. Renewable energy sources are not as unreliable as one might think,

Disadvantages of renewable energy sources.-Unfortunately, there are also several potential disadvantages of renewable energy sources. In order to conduct a balanced evaluation of these types of energy sources, these disadvantages need to be taken into account alongside the advantages. Below, you will find a list of the key disadvantages.

1. Expensive to set up – high initial cost-Though once they are up and running they are usually very cost effective, solar panels and wind farms (as well as other renewable energy generators such as hydroelectric dams) can be costly to install. Not suitable for all climates, Solar energy generators are not suitable for very cold or dark climates, whilst wind energy generators are not suitable for parts of the world where there is not very much wind. So, not all communities throughout the world can use all type of renewable energy sources and this somewhat limits the use of this type of energy, considered on an international scale. Difficult to transport, Whilst coal or wood can simply be loaded up onto a truck and taken to wherever it needs to go, the renewable energy that is generated from (for instance) a solar panel cannot be transported so easily. This is something that may change in the future. For example, it is already possible to store the energy generated from the sun's rays in specialized cells (which may be thought of as kind of portable batteries).Not the most efficient energy sources, Fossil fuels such as coal and oil offer more energy per unit that many renewable sources of energy. This means that renewable sources of energy are not always energy efficient, and one will need to generate a lot more energy to heat a home from a renewable source compared to a non renewable source. Again, with new technologies, this may well change for the better in the future. Reliant on certain technologies, Renewable energy sources can often only be harnessed with the use of specialized technologies. For example, solar energy is captured in photovoltaic cells. At the moment, not all communities throughout the world have access to these technologies, or to the know how that enables them to be created and harnessed.

Conclusion

As non-renewable energy sources start to run out, and as the world faces the threat of substantial climate change it is imperative that we switch over to using more sustainable, greener sources of energy. Renewable energy sources such as solar energy, wind energy, wave energy and so on seem to provide a sustainable and ecologically friendly solution to our future energy needs. As can be seen from the above, there are a few disadvantages at the moment to using renewable energy resources. However, it is important to note that they are very much outweighed by the advantages of using these energy sources. In addition, with the advent of new technologies, and the development of existing ones, it is highly likely that in the future humans will be able to find simple solutions to these issues. What about you? Are there any ways in which you could switch over to using more energy from renewable sources? It may be easier than you think.

Solar Energy- Meaning, Advantages and Disadvantages

What is Solar Energy?

'Solar' just means 'from the sun'. And so, solar energy is energy that comes from the sun. Solar energy is a way of harnessing the energy in the sun's rays and using it for all sorts of things, from generating electricity in our homes to powering the pumps in a swimming pool.Solar derived energy is often also called photovoltaic energy, or 'pv' energy for short. This is because special cells or panels known as 'photovoltaic cells' are used to trap solar energy and turn it into electricity. You may know these cells by their more common name of 'solar panels'.

Advantages of Solar energy

Environmentally friendly Solar panels do not release CO_2 into the atmosphere like fossil fuels do, and they do not involve the huge risks of nuclear power. This makes them one of the most environmentally friendly energy sources around. All natural harness the power of nature, Cost effective. Once installed, solar panels cost very little to run. Compact. You can add solar panels to your roof without having to install a whole load of bulky equipment. No smells. No smoke or smells are generated from this energy source: just pure, clean energy. Storage not everyone knows this, but solar energy can be stored in the solar panels so that you can use solar energy even when it is not sunny outside, perfect for sunny climates. If you live in a country with strong sun, solar energy is perfect for you, Innovative, is part of a great technological innovation. Easy to use, once installed, it is very easy to use solar energy just turn your appliances, light switches and so on, on and off as you would do normally.

Disadvantages of Solar energy-

Not suitable for winter. On cloudy days or in the winter, you solar panels will not be able to harness so much energy. Very visible, some people feel that solar panels look unsightly on their roof. Installation costs. Some people find the costs of installing solar panels somewhat prohibitive. Maintenance. Solar panels need to be kept clean so that the sun's rays can reach them. Some people would rather not have to go to the effort of checking and cleaning the panels every couple of weeks or so. Not suitable for very heavy-duty energy. Most solar generators are perfect for homes, swimming pools and small businesses. They are not always enough to meet the energy needs of larger buildings like factories. Just a fad, some people see solar energy as just a passing fad. For this reason, they wonder whether they should buy in to this energy source as their main source of energy. Inefficient Solar panels can sometimes be quite inefficient at generating energy. Positioning Solar panels need to be positioned so that they have the best sun exposure – working out the best position for them can take some effort. Other forms of green energy are available. Hydroelectric power or biomass could be better at meeting our energy needs in an environmentally friendly way. For example, if you live on a windy coastal area hydroelectric or wind power may well be a much smart choice than solar power.

Conclusion

Solar energy is a green and surprisingly powerful source of energy that is particularly good for people and businesses that live in regions of the world with strong, regular sunshine. Fossil fuels, on the other hand, pollute our planet and they will not last forever. Thus, finding eco-friendly energy sources is imperative if we want to be able to meet our energy needs and care for our planet at the same time.

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References

1. IEA, 'World Energy Outlook', International Energy Agency, Paris, France, 2011.
2. GEA, 'Global Energy Assessment: Toward a Sustainable Future', Cambridge University Press, Cambridge, UK, 2012.

3. Prof. Dattatraya K. Chavan, Prof. L. S Utpat, Prof. Dr. G. S. Tasgaonkar, SandeepShinde, Sameer G.Patil,'Renewable Energy Sources-The Ultimate Source of Survival & Management of resources', IJCER , Vol. 2, Issue No.2,470-474, Mar-Apr 2012.
4. 'AkshayUrja', Ministry of New and Renewable Energy, Govt. of India, Volume 5, Issue1, August 2011.
5. Source: 'India Ministry of Non-Conventional Energy Sources'. Overview of Renewable Energy Potential of India, GENI, Global Energy Network Institute, pp. 17, October 2006
6. REN21, 'Renewable 2012', Global Status Report, REN21 Secretariat, Paris, France, 2012.
7. IPCC, 'Special Report on Renewable Energy Sources and Climate Change Mitigation', Cambridge University Press, Cambridge, UK, 2007.
8. 'Solar Electric generating System,' Next Era energy resources, http://www.nexteraenergyresources.com/content/where/portfolio/pdf/segs.pdf, January, 2013.
9. Debajit Patil, 'Renewable Energy in North East India; Issues and prospects', International Conference on Energy and Environmental Technologies for Sustainable Development,85- 93, Oct. 8-10, 2003.

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19. Utilization of Solar Energy from Generation to Generation - A Review

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Abstract

This review paper represents, the basic need of modern civilization is energy and its production from fossil fuels causes hazardous effect on the environment. This motivates to use the clean energy sources. Solar energy has best potential to fulfill the energy demand in future. Sunlight is not only the most plentiful energy resource on earth, but it is also one of the most versatile, abundantly available and free of cost throughout on the planet, converting readily to electricity, fuel and heat without emitting pollutant elements. The time line of solar energy research shows the development of photovoltaic technology. The way of conversion of sun energy into electrical energy divides the photovoltaic technology into different generations.This review paper also comprises peace full, traditional and scientific use of solar energy.

Keywords –Solar energy, Traditional use of solar energy, PV solar cell

Introduction

The energy plays the most crucial role in the modern human civilization. Mankind uses the fossil fuels as energy source from millions of years. Presently, most of the energy demand (upto 90%) is fulfilled from the fossil fuels in the form of coal, natural gases, petroleum product etc. The burning of theses fuels emits the gases like CO_2, CH_4, NO_x, sulphur etc. and remains their residuals in an environment. These gases are also known as greenhouse gases. The green house gases traps the infra-red radiation within the earth's atmosphere, thereby increasing the "global" atmospheric temperature (approximately 4°C of earth temperature will increase in this century) [1-3]. During the past few decades, all nations have become extremely concerned with the effect of global warming. The emission of these gases depends on the use of the fossil fuels and cut down the dependency on fossil fuels is one solution to reduce effect of global warming.

Dependency on renewable energy sources in power sector is a need of the universe, since fossil fuel resources are rapidly depleting and responsible to emission of greenhouse gases. The transformation of energy policies is not individual government effort but world-wide political issue. The several nations have been transfer their energy policies; towards utilization of clean energy sources instead of use of fossil fuels.

Clean energy sources will play vital role in the future which includes: wind, geothermal, biomass, tidal and hydroelectric etc. out of these none of the technology is scalable to fulfil future energy demands. Only solar energy is having potential to fulfil the energy demand in future. For a scale, consider; sun provides 130TW energy daily. Current global energy consumption occurs at the rate of 13.5TW, projected to rise to 40.8TW in 2050. Today, in just one hour, the sun provides enough power to supply our energy needs for an entire year which is available free of cost. In the universe and particularly country like India, an average intensity of solar received is 200 MW/km (megawatt per square kilometer) with 250-325 sunny days in year [4]. Hence, solar energy is having capacity to fulfill the energy demand of urban civilization without harming the environment.

If we can make the solar energy as targets of day-to-day consumption of energy in various forms.At least 60 per cent of our energy requirement shall come from solar energy sources. This will stop us of becoming over dependents on gulf countries for petroleum, fuel and obviously this will diminish the cost of war.

Discussion

Traditional history of solar energy

Before we thought about the scientific use of solar energy we continued to use solar energy without giving an appropriate scientific term. Depending on the language and culture we call this solar energy in different terms but certainly people around the world used solar energy even to –day with less or large quantity depending on availability of sun rays during the day time.

Before the development of leather industry and leather tanning process, people by and large used the sun rays to heat the hide to produce sun dried hide to manufacture leather goods. In the desert of Arab where water is scarce, leather bag made out of sun dried hide was the only container for carrying water from distant places. In Africa, during in their tribal rivalry, the tribes used to use shield made out of sun dried hide. Similarly, there can be several examples which can be given in respect of leather industry and such hide still being used as raw material in many of the places where technology of tanning could not reach.

In spite of development of paper technology handmade paper remained as one of the most sought after product in the market, whether it is in interior Arunachal Pradesh or in developed Bombay. The drying technology for this industry continued to be sun dried methods and this is largely believed that sun dried paper to have certain better quality perhaps due to slow process of drying or perhaps due to exposure to ultra to slow process of drying or perhaps due to exposure to ultra violet ray. In our domestic front except certain countries like U.S.A., Canada etc. where automatic driers have reached home, in all other countries we still dry our clothing under the sun. It is largely believed that keeping the cloth under the sun kills the germs since sun rays has got disincentive effects. It is also believed that pickles do not get spoil if they are kept under the sun intermittently.

Above all we got our food from plant either directly or indirectly and the nutrition that we get from our food is due to sun rays since the same is prepared by the plant with the help of sun rays only. We all know regarding the traditional use of solar energy but it has become so much part of our life that we do not bother to identify the same. If we give a little more thinking perhaps it will not difficult for us to identify such things and if we think of writing the volumes can be little. Since this book is proposed with the objective of scientific application of solar energy there is no need to write about the traditional use further, leaving the same for the thinking process for the readers to carry on the rest of the duty.

History of Photovoltaic Systems

In 1839, Edmund Becquerel a French physicist has discovered photoelectric effect. This discovery motivates to the scientist all over the world to make an efficient energy device that will convert maximum sun energy into electricity. The photovoltaic device having potential to convert sunlight into electrical potential by a sequence of events: the absorption of light, generation of charge carriers (electrons and holes) and the transport of charge carriers to electrodes.

Types of Solar Cells

The photovoltaic (PV) cells generate electric power under illumination of natural or simulated sunlight. The human being develops such devices for the generation of energy; these devices can be categories into different types on the basis of stepwise development [10].

First Generation Solar Cells

The basic building block of first generation (1G) solar cells technology is Silicon; either single crystalline Silicon (s-Si) or multi-crystalline Silicon (mc-Si). The conventional PV cell modules are built by 200-250 micron thick crystalline Silicon wafer and majority of the cost utilize to extraction crystalline Silicon from sand, then to purify and finally the doping of phosphorous and boron to make p-type and n-type Silicon. The 1G PV cells are operated on the simple p-n junction diode principle were electron-hole charge generated under illumination of a light and its separation occurs in a p-n junction: i.e. at the interface of p-type and n-type semiconductor generates a built-in potential. At the junction itself, a depletion region free of mobile carriers is formed, in which the electric field is present. The commercial production of 1G solar cell modules started since 1963 and now about 90% of global PV cells market is concerned by 1G solar cell. The efficiency of 1G ranges from 14% to 19%.

Second Generation Solar Cells

Second generation (2G) of PV cells market is based on; to remove the unnecessary material production cost to obtain pure Silicon and search alternative to crystalline Silicon. 2G PV cellsare fabricated by single junction devices; keeping in mind that to reduce the processing cost of material; while maintaining the efficiencies of 1G PV. 2G solar cells are fabricated by amorphous-Silicon (a-Si), CuInSe (CIS), CuIn(Ga)Se_2 (CIGS), CdTe/CdS and polycrystalline Silicon (p-Si) deposited on low-cost substrates such as glass, polymers and metals. 2G PV cells technologies is based on efficient light trapping properties of CdTe, CIS, CIGS and a-Si than c-Si or mc-Si, also the thickness of absorbing materials ranges in 1-10 micron, hence responsible to reduce the production cost of the PV devices. Meanwhile 2G technology has been received much attention in the last few years, due to their imperative parameters such as, it requires less semiconducting material to fabricate the PV modules, can be synthesized on flexible substrate and light weight structures. The 2G technology can be categories into three types as follows.

A) **Amorphous Silicon PV cells:** The PV cells constructed with a-Si showsefficiency range from 4% to 8%. The PV cells of a-Si are advantages because it can be deposited on comparatively low cost large area substrates or even flexible substrate, but the major drawback is reduction in power output with time.

B) **Cadmium telluride PV cells:** These types of solar cells are cheapest in thin film PV technology and having efficiency 16%. But toxicity of cadmium and availability of tellurium are the major problems with these types of solar cells; hence limits its use.

C) **CIS and CIGS PV cells :** These types of solar cells are most successful in PV industries and have been commercialized by many companies. (e.g. Wurth Solar, Solibro, Miasole, Nanosolar, Shellsolar, Avancis, Solar Frontier and Honda Soltec). Currently, CIS and CIGS PV cells efficiency ranges from 7% to 16%.

Third Generation Solar Cells

Now a day's, third generation (3G) solar cell technology is an emerging technology and still in research phase. The 3G PV solar cell includes nanostructured solar cells (i.e. organic photovoltaic (OPV), dye-sensitized cell (DSSC), ETA solar cell, quantum dot sensitize solar cell (QDSSC) and organic-inorganic hybrid solar cell etc.) While, these cells working on same p-n junction solar cell phenomenon but having separately photoengraved and charge carriers that will helps tofaster recombination in devices and this will ultimately increase the efficiencies of the cell. These types of PV cells are far behind, when compared with the efficiency point of view to the conventional PV cell have number of advantages over 1G and 2G PV cells. It is consider that 3G solar cells are potential to overcome the Shockely-Queisser limit of 31-41% power efficiency of the single band gap material solar cell devices.

A. Dye sensitized solar cells (DSSC)

In 1991, Professor Michael Gratzel at EPFL in Switzerland first demonstrated the DSSC efficiently by using TiO_2 and ruthenium metal dyes and with 11% efficiency. This is the mildstone in 3G PV research. DSSC were synthesized between two glass substrates in sandwich type structure, but thereafter it was also reported on flexible substrates. The DSSC works on photoelectrochemical(PEC) principle. In DSSC high surface area TiO_2 plays dual role 1) act as window layer for visible light; which further absorbed by dye molecules and 2) receives photo generated electron from the dye molecules and holes are passed to the other side of the dye. Then the circuit is completed by redox couple in electrolyte, which can be liquid or solid. The last 20 years research and development effort lead to develop commercial devices by Dyesol, EPFL, G24i, Mitsubishi and Peccell. DSSC has many advantages over conventional PV cells as it is colorful, low processing cost and can be synthesized on flexible substrates. However, the major disadvantage is that dyes in these cells can be degrade under heat and UV light, furthermore solvent evaporation is difficult to avoid due to improper sealing.

B. Organic photovoltaic (OPV) solar cells

This is one of the alternative technology immerging in recent years than the conventional PV cells. The solar cells are constructed by using organic or polymer materials. Organic cells are constructed on variety of substrates irrespective of their shape and size and by low cost synthesis technique (i.e. printing and coating). OPV cells are lightweight; flexible which makes them ideal for mobile applications. Furthermore, it will be fitted on a variety of uneven surfaces. This makes them useful for portable applications. The leading developers in OPV technology industries such as Konarka and Plextronics are developed and make it commercially available in the market.

C. Nanostructured solar cells

Now days, nanostructured PV cells are immerging as an alternative to conventional Silicon solar cell technology. These types of devicestructures are under research and development and which arerely on use of composite/heterostructure materials such as quantum dots/wires, quantum wells, ETA solar cells, inorganic organic hybrid structures etc.These solar cells are working on the similar principle that of DSSC. Nanostructured wide band gap metal oxide (MO) plays dual role in device structure; first to provide high surface area for the growth of a light absorber materials in layer structure, also absorbs UV part of incident light which may harm the absorber layer and second, receives the photo-generated electron from the absorber materials and finally execution of circuit completion by redox couple either organic or inorganic materials like liquid or solid. These are most advantageous PV cell technology in future, because; 1) to overcome the Shockely-Queisser limit of 31-41% power efficiency of conventional technology, 2) the inorganic light absorber materials are more stable, cheaper, colorful and tune their prperties according to their size and shape, 3) the devices can be synthesized by low cost wet chemical deposition techniques which may reduce the processing cost.

Conclusion

In last few decades, the research in PV technologies have been concentrated onto search a new efficient device; that can be convert maximum sunlight into electricity. The outcome of these efforts is focusing us to transformed interest towards utilization ofnanocrystalline materials for solar cell application;due to their unique structural, optical and electrical properties depending on their size and shape. Application of these features in photovoltaic device has led to develop novel solar cell structure. DSSC is one of the devices investigated much in last few decades and consider asan alternative to conventional solar cell. These devices are working on PEC principle, but have their own limitations; those forces to search new photovoltaic materials and devices. The nanostructured solar cellis working on the similar principle of DSSC. This overcomes the problems of DSSC and replace unstable dye layer by stable inorganic metal chalcogenides nanoparticles layer in the device structure.

As a consequence of the problems faced by the DSSC, the ETA solar cell structure has potential to overcome it. The ETA solar cell structure was developed in the late 1990's and use the concepts from both DSSC and thin film solar cells. The foundation of nanostructured solar cells concept is the establishment of a layerheterostructure between large internal surface area of wide band gap MO and extremely thin film absorber layer consisting of nanoparticles of a narrow band gap metal chalcogenides in the solar cell to improve light harvesting and stability as compared to DSSC.

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References

1. http://www.algore.com/
2. J. Hansen, M. Sato, R. Ruedy, K. Lo, D. W. Lea, M. M. Elizade, PANS (2006) 103, 39, 14288.
3. J. Hansen, R. Ruedy, M. Sato, K. Lo, Rev. Geophys. (2010) 48, RG404.
4. http://www.rrecl.com/PDF/Success%20in%20Scaling-up%20Solar%20Energy%20in%20Rajasthan,%20India.pdf
5. Szokolay, S.V.Solar Energy and Building, New zokolay, S.V.Solar Energy and Building, New York: John Wiley and Sons, Inc.1975.
6. Anderson, B.The Solar Home Book, Harrisville: Cheshire Books, 1976.
7. S.K. Patra and P.P. Datta. 'Renewable sources of energy potential and achievements', Technical digest, Issue-6.
8. Peter Meisen. 'Overview of sustainable renewable energy potential in India.' Geni, Jan 2010.
9. Rose, Harvey, "Solar Energy Now" (Ann Arbor Science).
10. http://www.konarka.com/index.php/technology/our-evolution/

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Thin Film Characterization Techniques --------A Theoretical Background

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Abstract:

The advancement of science and technology in the recent years has replaced the traditional and laborious experimental techniques of analysis by sophisticated instrumental techniques of analysis, which give more accurate and reproducible results. This paper describes various experimental techniques used for the characterization of thin films.

Introduction:

The experimental details pertains to the evaluation of various properties using analytical techniques viz. X-ray diffraction (XRD), energy dispersive analysis by X-rays (EDAX), scanning electron microscopy (SEM), transmission electron microscope (TEM), optical absorption, Fourier transform infrared spectrophotometer (FTIR) and various aspects concerning with new devices formation.

Discussions:

Structural Studies (XRD): X-ray diffraction (XRD) is an important technique for material characterization. XRD enables information to be obtained on atomic scale from both crystalline and non crystalline materials. This technique was also used to determine crystal structure of metals and alloys, minerals, ceramics, semiconductors, inorganic compounds, polymers and organic materials. X-ray diffraction (XRD) technique is used for the realization of structural property and can be employed exclusively to categorize the crystalline phase in the sample. This technique is suitable for both form of samples i.e. thin film as well as bulk and can yield the information regarding the crystallinity of the material, nature of the phase present, lattice parameter, grain size out of plane orientation. In case of thin film, the change in lattice parameter with respect to the bulk gives the idea of nature of strain present in the film.

X-ray diffraction method is specially used for the investigation of the internal structures. It is now known that this internal structure consists of a regular arrangement of atoms, which follow certain laws of symmetry. Bragg's explains the fundamental of XRD equation, which places the condition for the constructive interference for the scattered X-ray from the successive atomic planes, formed by the crystal lattice of the material. The Bragg's condition is formulated by

$$2d\sin\theta = n\lambda$$

where, λ is the wavelength of the incident X-ray, d is the interplaner distance, θ is the scattering angle and n is an integer for the order of diffraction.

The full width at half maximum (FWHM) of the plot estimates the size of the grains in the film with respect to the sample normal. A given substance always produces a characteristic diffraction pattern, whether that substance is present in the pure state or as one constituent of a mixture of substances. The powder pattern of a substance is characteristic of that substance and form a sort of fingerprint by which the substance may be identified. Any one powder pattern is characterized by a set of line position 2θ and a set of relative line intensities. But the angular positions of the lines depend on the wavelength used, and a more fundamental quantity is the spacing d of the lattice planes forming each line.

Scanning Electron Microscope (SEM)

Scanning electron microscope is an indispensable tool for research and development, which uses a beam of electrons to examine specimens to explain the phenomena occurring on micrometer (μm) or sub-micrometer scales. The types of signals produced when the electron beam impinges a specimen surface include secondary electrons, back-scattered electrons, auger electrons, characteristic X-rays and photons of various energies. These signals are obtained from specific emission volumes within the samples and are used to examine many characteristics of the sample composition, surface morphology, and surface topography.

The sharpness and contrast of SEM micrograph and depth of field in images are dependent upon three major electron beam parameters. (1) electron probe size (2) electron probe current and (3) electron probe convergence angle. For the highest resolution image, electron probe size must be as small as possible. For the best depth where a large range of heights on the specimen appear in focus at the same time, convergence angle must be made as small as possible. However, probe current will be inescapably reduced when probe size and angle of convergence are made very small. Small beam angle can be achieved by using a small objective lens aperture, a long working distance or both. Therefore, these parameters must be selected intelligently to obtain appropriate imaging conditions in each situation. Since the image is formed by secondary emission of electrons, the samples should be conducting. However, the surface of non-conducting can also be studied after coating the samples with a gold film. The thickness of the gold coating is usually 500 to 1000 Å.

Transmission Electron Microscope (TEM)

The ability of a transmission electron microscope (TEM) is to provide high resolution images and crystallographic information from a selected area of a specimen and its lateral spatial resolution of the order of nanometer are valuable from the view point of the material characterization applications. TEM has become an essential instrument for the microstructural studies of metals, alloys, ceramics, composites and organic materials. Now a days, transmission electron microscopy (TEM) is used as characterization technique to study the material characteristics such as, structure, texture, shape, and size as smaller as single column of atomic. TEM catch thousand time smaller image than the smallest resolution object in light microscopy . While, TEM operates on the similar principle as the light microscope and detect image using transmitted beam.

In TEM, a sample of a thin foil is irradiated by electron having high energy instead of light source. TEM forms two dimensional black and white images, from the interaction of the electrons transmitted through the specimen; the image is magnified and focused onto an imaging device, such as a fluorescent screen, on a layer of photographic film, or to be detected by a sensor such as a CCD camera. The typical TEM instrument consists of, electron source, thermionic gun, electron beam, electromagnetic lenses, vacuum chamber, two condensers, sample stage, phosphor or fluorescent screen and linked computer.

In TEM, the image is carried by only one beam (transmitted) and high-resolution electron microscopy (HR-TEM) uses phase contrast resulting from an interference of several beams. Very often HR-TEM works close to the resolution limit and gives 3-D image. At this smaller magnification, crystal defects, structure, exact shape, size of the individual atom can be studied.

Energy Dispersive X- ray Analysis (EDAX)

Energy dispersive X-ray analysis is a powerful technique for the compositional analysis of the thin film samples. As the electron beam scans the surface, the emerging X-rays are fed into the X-ray analyzer, which has been set for the element of interest. Whenever X-ray of that energy is detected, a dot is brightened at the corresponding point in the display tube of the SEM. By positioning the SEM electron beam on a spot of interest, a simultaneous semi quantitative analysis of all elements can be performed by plotting counts versus energy (keV). The heights of the peaks are not an exact measure of concentration because not all elements are excited with the same efficiency. For a more quantitative measurement, known elemental standards must be employed. However, the modern equipment's having computer interfacing is capable of determining the sample composition very accurately using the software with stored element standards.

Fourier Transform Infrared (FTIR) Spectroscope:

Fourier Transform Infrared (FTIR) spectroscopy has wide applications in industries, especially in chemical factories. Infrared spectra give information about the presence of specific functional group; absorbs specific frequency radiations, due to which amplitude of vibrations is increased and there by absorption band at different frequencies are recorded. Therefore, the presence of functional groups, water molecules, nature of bonding and forces working between atoms can be predicted, and hence infrared spectra gives information about the structural formula. Infrared radiation refers broadly to that part of the electromagnetic spectrum between the visible and microwave regions of greatest practical use to the organic chemist is the limited portion between 4000 cm^{-1} and 666 cm^{-1}(2.5-15.0 μm). Recently there has been increasing interest in the near infrared region, 14,290-4000 cm^{-1} (0.7-2.5 μm) and the far infrared region, 700-200 cm^{-1}(14.3 μm). Although the infrared spectrum is characteristic of the entire molecule, it turns out that certain groups of atoms give rise to bands at or near the same frequency regardless of the structure of the rest of the molecule. It is the persistence of these characteristic bands that permits the chemist to obtain useful structural information by simple inspection and reference to generalized charts of characteristic group frequencies.

Stretching: In which the distances between the two atoms increases or decreases, but the atoms remain in the same bond axis. Stretching vibrations are found to occur in the order of bond strength.

Bending: In which the position of the atoms changes relative to the original bond axis. Bending vibrations generally requires less energy and occur at longer wavelength. Band intensities in IR spectrum may be expressed either as Transmittance (T) or Absorbance (A).

Transmittance: It is defined as the ratio of radiant power transmitted by a sample to the radiant power incident on the sample.

UV-Visible spectrophotometer

UV-Vis spectrophotometer is used to determine the absorption or transmission of UV/Vis light (200 to 700 nm) by a sample. It can also be used to measure concentrations of absorbing materials based on developed calibration curves of the material. A spectrophotometer is employed to measure the amount of light that a sample absorbs. The instrument operates by passing a beam of light through a sample and measuring the intensity of light reaching a detector. The beam of light consists of a stream of photons. When a photon encounters an analytic molecule (the analytic is the molecule being studied), there is a chance the analytic will absorb the photon. This absorption reduces the number of photons in the beam of light, thereby reducing the intensity of the light beam. The equilibrium situation in semiconductor can be disturbed by generation of carriers due to optical absorption. Optical photon incident on any material may be reflected, transmitted or absorbed. The phenomena of radiation absorption in a material is considered to be due to (1) inner shell electron, (2) valance band electron, (3) free carriers including holes as well as electrons, and (4) electron bound to localized impurity centers or defects of some type.

References:

1. B.D. Cullity, 'Elements of X-ray Diffraction' Addison Wesley Publ. Co. (1978).
2. W.L. Bragg, Proc. Cambridge Phil. Soc. 17 (1913) 43.
3. Maurice J. Simott, 'Thin Solid State for Engineers', Jhon Wiley and Sons, 1958.
4. J.D. Hanawatt, H.W. Rinn and L.K. Frevel, Ind. Eng. Chem. Anal. Ed. 8 (1936) 244.
5. J.D. Hanawatt, H.W. Rinn and L.K. Frevel, Ind. Eng. Chem. Anal. Ed.10 (1938) 457.
6. Joint Committee on Powder Diffraction Standards, 1601, Park lane,Swarthmore, Pa,19081.
7. Cecil E. Hall 'Introduction to Electron Microscopy', McGraw Hill Book Co., New York, 1966.
8. Douglas M. Considine and Glenn D. Considine (Eds) 'Van Nostrand's Scientific Encyclopedia', (7th Edition), Van Nostrand Reinhold, New York, 1989.
9. D.B. William, D.T. Carpenter and V.J. Keast, Asia/Pacific Microscopy and Microanalysis, (Sept.1999).
10. P. Koshy, 'XXVI Annual Conf. of EMSI on Electron Microscopy and Applied field', (Feb.2001).
11. Ludwing Reimer, 'Scanning Electron Microscopy (Physics of image formation and microanalysis)', Springer series in optical science, (1978).
12. D.B. Williams, C.B. Carter, "Transmission Electron Microscopy", Plenum Press, New York, 1996.
13. Encyclopedia of semiconductor Technology, John Wiley and Sons. Inc. 1984.
14. H. Stanley, Pine Organic chemistry, fifth Ed., McGraw Hill Book Co, 1987.

Growth and Characterization of Barium Oxalate Crystals by Single Diffusion Gel Method

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ABSTRACT

Barium oxalate crystals were grown by agar-agar gel through the single diffusion technique. The tendency of barium oxalate crystals to cylindrical growth was demonstrated. The optimum growth conditions barium oxalate was achieved by controlling the parameters like, concentration of gel, concentration of reactants, aging period and reversing of reactants. The crystal structure of grown material was determined by X-ray diffraction technique and was found to be monoclinic with lattice parameters 'a' = 6.6562 Å, b = 8.0464 Å, c = 2.8090 Å, β= 96.832°, and V = 149.38 $Å^3$. The FTIR spectrum indicates OH and carbonyl group along with the presence of metal-oxygen bond. Morphology of grown crystals, investigated by scanning electron microscopy, exhibited compact grains including small and large sizes. Since the grown crystals are transparent, they show strong absorption in the ultra violet region above 290 nm wavelength.

Keywords: Crystal growth, Barium oxalate, X-ray spectroscopy, FTIR, and SEM.

1. Introduction

A solid which consist of atoms or other microscopic particles arranged in a periodic manner in all directions is called as a crystal. The strong influence of single crystals in the present day technology is evident from the recent advancements ultra-small electronic gadgets. Crystals of different materials have several applications such as they are used in semiconductor devices like electrical diodes, photodiodes, transistors, integrated circuits, magnetic devices like tape heads, transformer cores, superconductors, optoelectronics, quantum electronics, quantum and nonlinear optics, telecommunication etc. hence today's demand is to grow large crystals with good quality, high purity and symmetry. With this demanding requirement it is important to study the growth of single crystals and hence, investigation of their physical properties towards the fulfillment of device fabrication is crucial for both academic as well as applied research. Therefore, enormous amount of toil and treasure has been lavished on the development of crystal growth techniques. The in-depth explanation of various techniques can be obtained in the literature [1-6]. There are three major stages involved in this research. The first is the production of pure materials and improved equipment's associated with the preparation of these materials.

Second one is the production of single crystals first in the laboratory and then extending it to commercial level. The third is the characterization and utilization of these crystals in devices.

In present study, we have adopted the agar-agar gel technique to grow the barium oxalate single crystals. We have successfully grown the cylindrical transparent barium oxalate single crystals and studied their physical properties.

2. Experimental

In the present work, barium oxalate crystals were grown by single diffusion technique. The growth of barium oxalate crystals was carried out in agar-agar gel by adopting the similar technique as reported (Dalal and Saraf 2009) [10]. Barium chloride ($BaCl_2$, 99.9%), oxalic acid ($H_2C_2O_4$, 99%), Agar-Agar powder ($C_{14} H_{24} O_9$) were used as the starting materials. All chemicals were of AR grade. The borosilicate glass tubes were used as crystallization apparatus. The glass tubes used for single diffusion were of 25 cm in length having outer diameter of 2.5cm outer diameter and 250ml beaker. The solution of 0.5, 1.0, 1.2, 1.5, and 2M concentrations were prepared and stored in clean glassware. Agar-agar gel was prepared by mixing (0.5 to 2.0gm) of agar powder in 100ml double distilled water at boiling temperature. Barium chloride of concentration 0.5 to 2M and oxalic acid of concentration 0.5 to 2M were used as reactants.

The prepared solution of oxalic acid were transferred into the test tube followed by addition of appropriate volume of agar gel and then kept undisturbed for aging period of few days. After setting and aging over the set-gel, the solution of barium chloride (desire volume and molarity) which is the reactant, was poured gently along the wall and allowed to diffuse into the gel medium. The open end of test tube was closed with cotton plug to protect from dust particles and kept undisturbed at room temperature.

We keenly observed the reaction and noticed that a thin precipitation layer was formed on the surface of the gel. This precipitate band increased gradually and diffusion proceeded into the gel. After 5 to 6 days nucleation process observed at the interstitial sides inside the test tube and then some transparent, star, platy shapes crystals were noticed. The crystals were harvested by washing them carefully with acetone. Prismatic, opaque, and platy shaped crystals were obtained with maximum size of a $3 \times 4 \times 2\ mm^3$.

The reaction which leads to the growth of crystals is expressed as

$$\mathbf{BaCl_2 + H_2C_2O_4 \longrightarrow BaC_2O_4 + 2HCl}$$

The optimum conditions for growing a well-defined crystals are given in table 1.

Table 1. The optimum condition established for growth of barium oxalate crystals

Sr. No	Conditions	Single Diffusion
1	Percentage of gel	1%
2	Con. of Barium Chloride	1M
3	Volume of Barium Chloride	5 ml
4	Con. of Oxalic acid	1M
5	Volume of oxalic acid	10 ml
6	Gel setting period	24 hours
7	Gel aging period	32 days
8	Temperature	Room temperature
9	Quality	Star shaped, Needle shaped, Platy shaped
10	Size	1 to 5 cubic mm

3. Growth kinetics

The growth of barium chloride was observed while growing in a test tube and effect of various parameters such as percentage of gel, concentration of first and second reactants, reversing and aging periods were studied.

3.1 Effect of aging period

To observe the effect of aging period on the growth of barium oxalate crystals. The aging period changes from 24 to 48 hours, while other parameters kept constant. We have found 24 hours aging period indicating the fast growth rate.

3.2 Effect of percentage of gel

To observe the effect of percentage of gel on the growth of crystals, all other parameters were kept constant except the percentage of the gel. It was found that for lower percentage (0.5%) of gel, the growth was slow and form small particles which were in large in number. When percentage of gel increased from 1.0 to 1.5% dendrite shaped crystals growth was observed. The size and appearance of growing crystals found more precise for 1.0% of gel as compare to other percentage of gel. As shown in Fig.1 (a)–(e) good, transparent crystals of barium oxalate having cubic to cylindrical shaped crystals were obtained.

Fig1 (a)

Fig1 (b)

Fig1 (c)

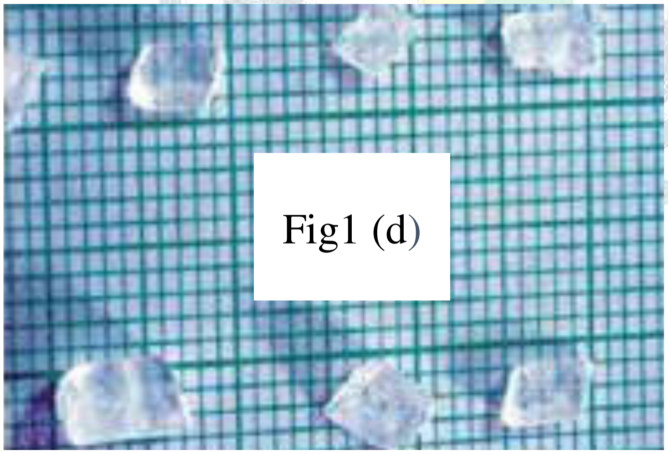

Fig1 (d)

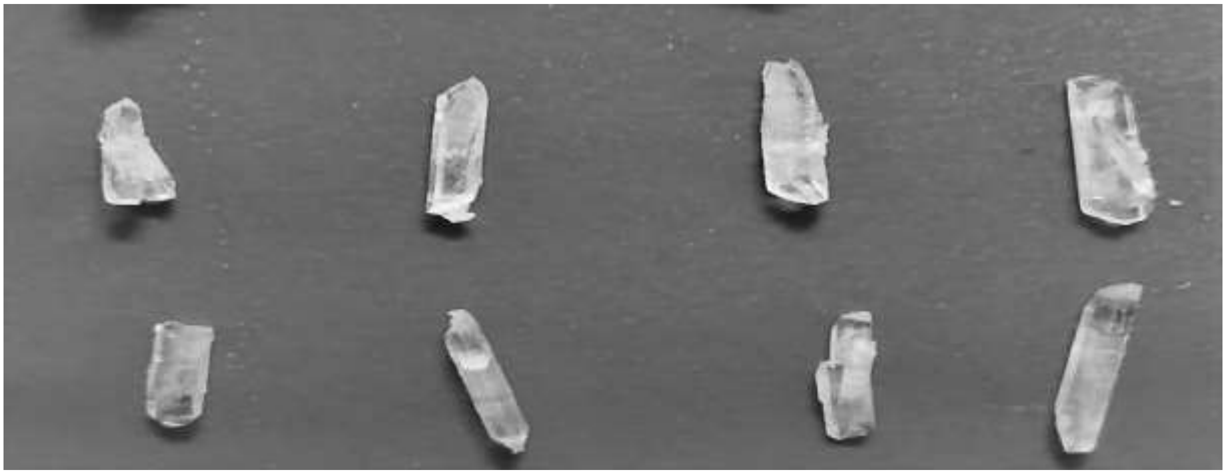

Fig 1(e)

Figure 1 (a-e): Photographs of barium oxalate grown crystals.

4. Result and discussion

4.1 X-ray diffraction studies

X-ray diffractogram is useful method to analyze the crystal structure of unknown material. X-ray diffractogram of gel grown barium oxalate crystals was recorded using powder rotation photograph method on Minislex Regaku X-ray diffract meter at Dept. of Physics at Shivaji University Kolhapur. The sample was rotated in the range 10^0 -80^0 (2θ), scanning speed was kept 2^0/ min and chart speed was 2 cm/ min. X-ray diffractogram of barium oxalate is shown in fig. 2.

From the diffraction pattern, “d” values and (h, k, l) planes were computed. Calculated “d” values are well matched with the reported ones. The unit cell parameters and system calculated by the computed program are given in table 2. These parameters satisfy the conditions for monoclinic system. i.e. $a \neq b \neq c$ & $\alpha \neq \beta \neq \gamma$.

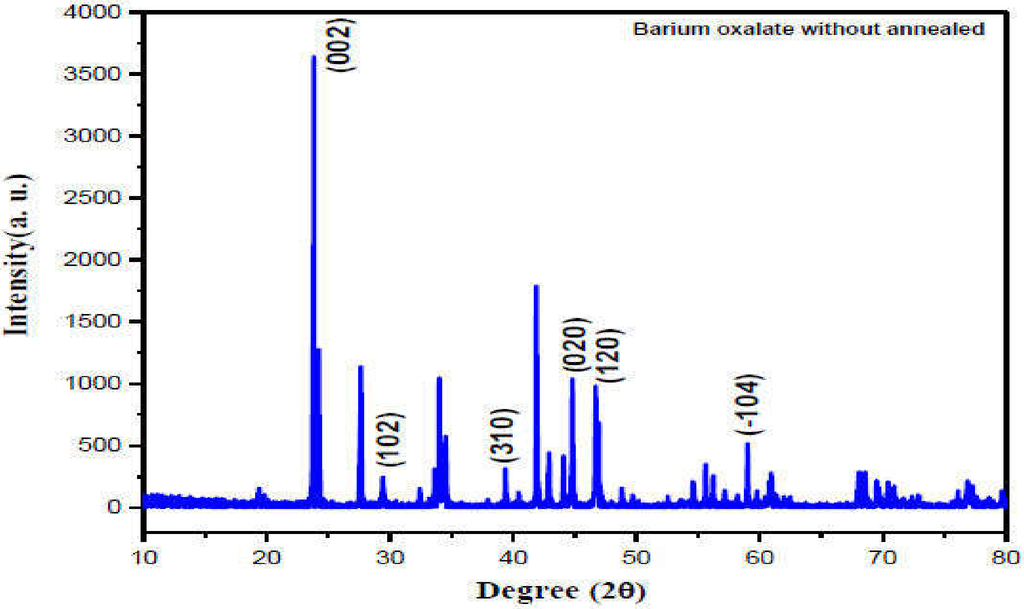

Figure 2: X-ray diffraction pattern of as grown barium oxalate single crystal.

4.2 Fourier transform infrared (FTIR)

The Fourier transform infrared (FT-IR) spectrum of barium oxalate was recorded at room temperature in the spectral range of 500 – 4500 cm^{-1} by KBr pellet method using SHIMADZU spectrophotometer at the department of Physics, Shivaji University Kolhapur. Figure 3 shows the FTIR spectrum of barium oxalate. A few of the prominent vibrational modes are empirically assigned here. The bands around 2950 to 3650cm^{-1} are attributed to asymmetric and symmetric –OH stretching of water. The – OH stretching frequency of barium oxalate appeared at 2923cm^{-1}. The moderate absorption around the 3500 to 3200cm^{-1} is probably due to stretching of alcohol group. The fundamental FT-IR frequencies observed in all barium oxalate crystals [11]. Table 3 shows FTIR spectral and vibrational assignments of barium oxalate.

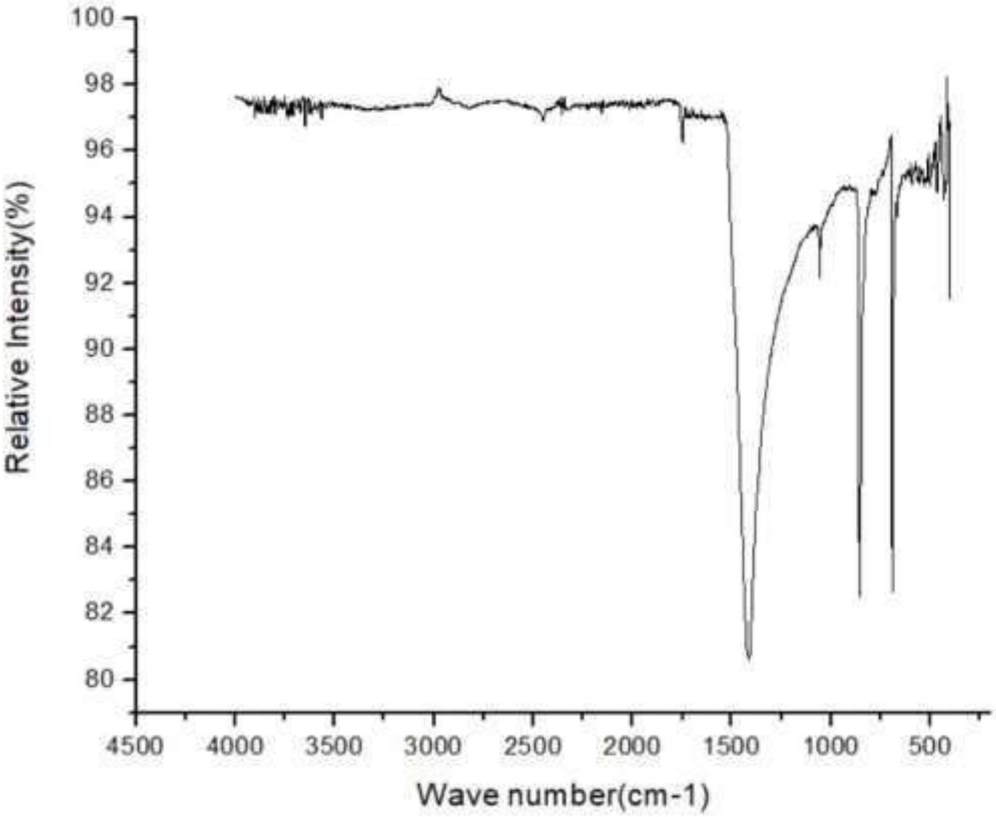

Figure 3. FTIR of Barium oxalate crystal

Table 3. FT – IR spectral and vibrational assignments of barium oxalate.

Wave number cm^{-1}	Intensity	Assignments
3640 - 3610	S,sh	O – H Stretch
3500 – 3200	S,b	O–H Stretch
3330 - 3270	n,s	C=C -H Stretch
3300 – 2500	m	O –H Stretch
3000 - 2850	m	H-C = O Stretch
1710 - 1665	s	C = O stretch
1370 -1350	s	C – H rock
1000 -650	m	= C- H bend
700 - 610	b	C –H bend

m= medium, W = weak, S = strong, B = broad, Sh = sharp, n = normal.

Scanning Electron Microscopy (SEM)

In the present work powdered sample of barium oxalate crystals was examined by using SEM technique at the Dept. of Physics Shivaji University Kolhapur. The study of the surface of the crystal gives valuable information about its internal structure. Figure 4 (a) illustrates SEM photographs of single crystals of barium oxalate crystal. High resolution SEM image is shown in Figure 4 (b). It is observed that due to growth conditions voids are created at the grain boundary. SEM images revealed that the growth of barium oxalate crystals consist of flat layered particles as well as spherical small grains. The individual flat grains possessed sharp edge [13].

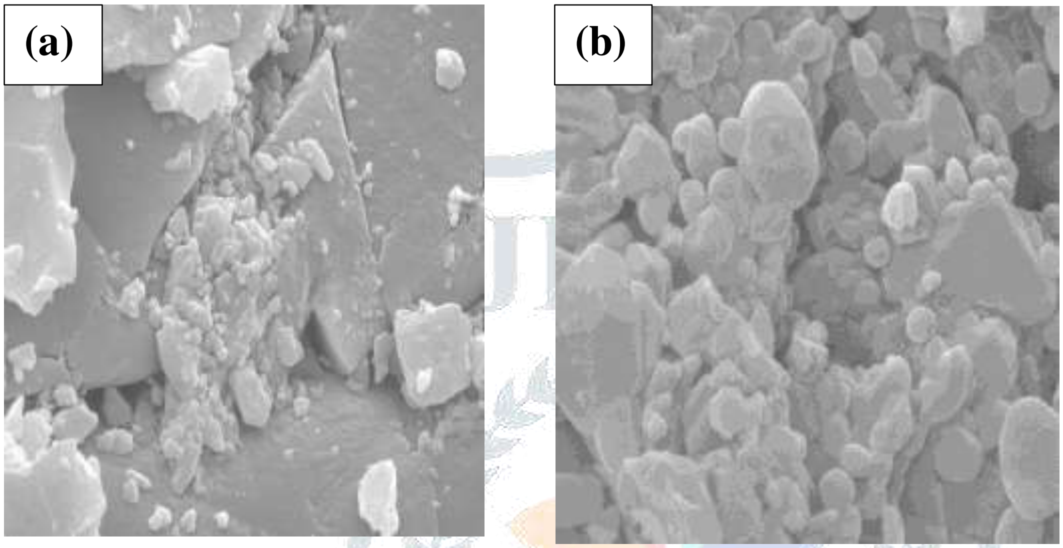

Figure 4: SEM images of as grown (a) barium oxalate crystal and (b) high resolution image.

UV-Vis Absorption spectroscopy

Absorption spectrum of barium oxalate crystals was obtained by a SHIMADZU UV-2450, UV- Vis spectrophotometer at the Dept. of Physics Shivaji University Kolhapur. Figure 5 shows UV-Vis absorption spectrum of barium oxalate crystal. Spectrum shows that the barium oxalate crystal allows to pass the entire visible and IR wavelengths and absorbs only ultra-violate wavelengths and therefore, the absorption coefficient is high at low wavelengths and high at short wavelengths. Since it is transparent crystal for wide range of wavelength (350-900 nm), the barium oxalate crystals can be used for second and third harmonic generations of the 1064 nm radiation [14-15]. Optical band gap energy of the as-grown barium oxalate crystals is calculated using the following simple conversion equation;

Band gap energy (ev) = $\frac{1240}{\lambda\,(nm)}$

The band gap energy of barium oxalate crystal is found to be 4.06ev and tabulated in table 4.

Table 4: the band gap energy of Barium oxalate crystals.

Crystal	Λ(nm)	Band gap Energy(ev)
Barium oxalate	305.00	4.06

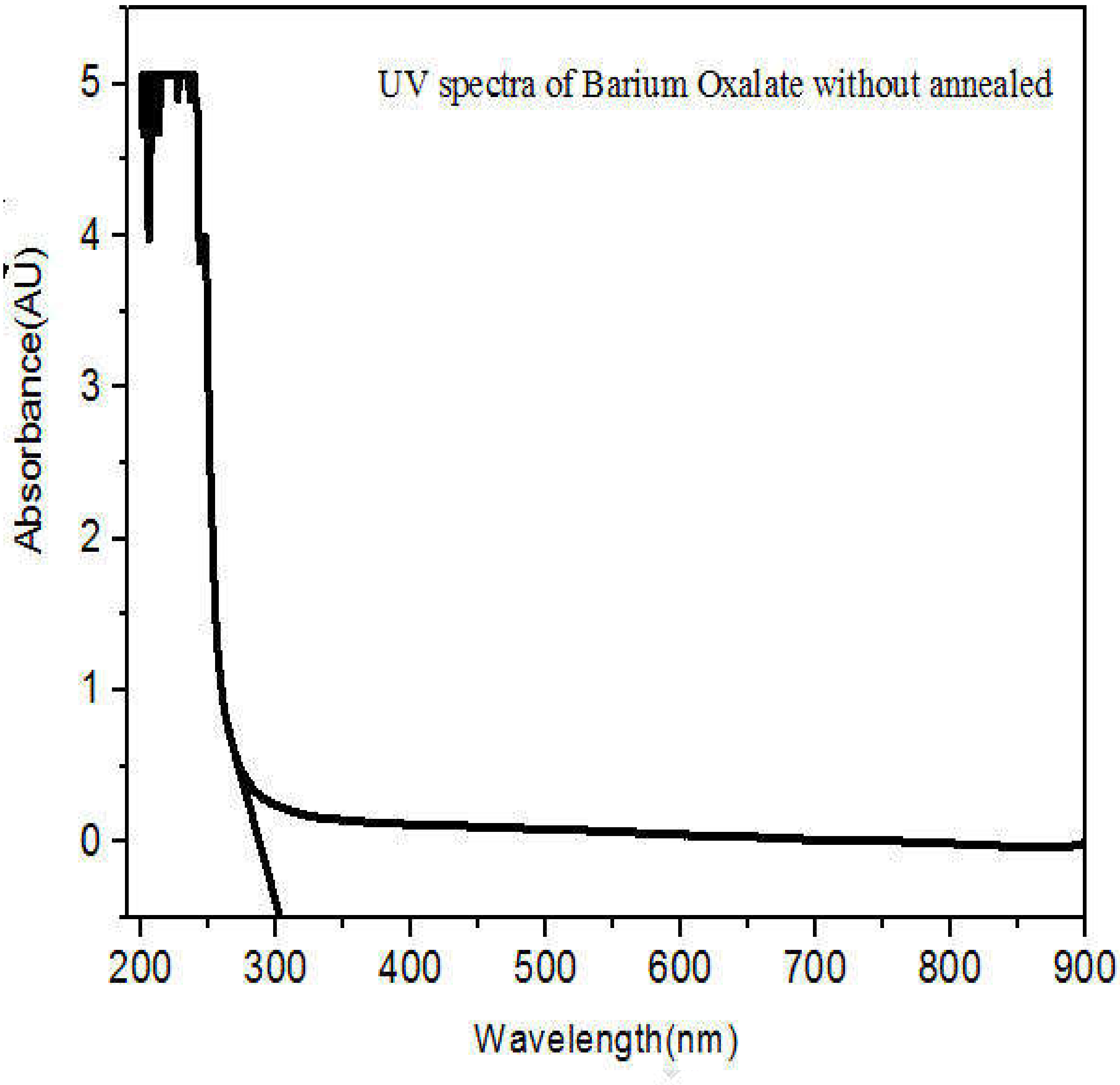

Figure 5: Optical absorption spectra of as-grown barium oxalate crystal.

5 Conclusions

From systematic investigation on the single diffusion gel growth of the barium oxalate crystals. Best conditions have been established to get good crystals.

1) Gel method is found suitable for growing barium oxalate crystals.

2) The growth of barium oxalate crystals was accomplished by allowing diffusion of barium chloride solution through ager-ager gel impregnated with oxalic acid in single diffusion gel tube system, with all growth conditions. Barium oxalate crystals possessed cubic and cylindrical shapes
3) The crystals obtained in ager-ager gel with average size of $3 \times 4 \times 2$ mm^3 in single diffusion.
4) Different habits of barium oxalate crystals can be obtained by changing parameters like gel density, gel aging pH of gel, concentration of reactant etc.
5) The 'd' values of grown material obtained from the XRD are well matches with POWD Programmed.
6) The FTIR, studies suggested different characteristics features and morphology of grown crystals.
7) UV-Vis absorption spectra of barium oxalate crystal showed 4.06 eV optical band gap energy.

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References

[1] H.K. Henisch; In crystal growth in gels, Pennsylvania state university press. **20**(1973).

[2] H.K. Henisch; In crystals in gel and lies gang rings, Cambridge university press, Cambridge ;(1988).

[3] H. W. Liaw, J. W. Faust; Jr. In American conference on crystal growth, Gaithersburg, Maryland (1969).

[4] H.W.Liaw,J.W.Faust;Jr. J. Cryst. Growth 13-**14,** 471(1972).

[5] A.R.Patel and A.V.Rao; J.Cryst.Growth **43,** 351(1978).

[6] K.V.Kurian and M.A.Ittyachen; J. Mater, Sci. **15,** 1724(1980).

[7] K.Suryanarayana and S.M.Dharamaprakash; Mater.Chem.Phys.**42,** 92(2000).

[8] S.K.Arora; Advanced in gel growth,A review progress in crystal growth and characterization of materials **4**, 345(1981).

[9] S.K. Arora, Vipul Patel,Kothari and Brijesh Amin; Crystal growth and design **343-349**,4(2004).

[10] S.A. Firdous, I. Quasim,M.M.Ahmad and P.N.Kotru;Bull.Mater.Sci.**377 – 382**,33 (2010).

[11] K. Nakamoto 1970 'Infrared Spectra of inorganic and co-ordination Compounds' (New York;Johm wiley and sons Inc) 2nd edn..

[12] S.J.Nandre, S.J.Shitole and R.R.Ahire, Archives of Physics Research, 2012, 3(1) PP70-77.

[13] S.J.Nandre, S.J.Shitole, S.S.Sonawane and R.R.Ahire, International Journal of Basic and Applied Research, special issue 2012, 125-128.

[14] Nisha Santha kumaria, P. Kalainathan, S. Cryst.Res. Technol.4 (2008)317.

[15] Kalaisevi. D., Mohan Kumar. R, and R Jayavel, Cryst.Res.Technol.8 (2008)851.

Physical and Morphological Study of Barium Oxalate Crystals Grown by Agar-Agar Gel Method

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ABSTRACT

Barium oxalate crystals were grown by agar-agar gel through the single diffusion technique. The tendency of barium oxalate crystals to cylindrical growth was demonstrated. The optimum growth conditions barium oxalate was achieved by controlling the parameters like, concentration of gel, concentration of reactants, aging period and reversing of reactants. The crystal structure of grown material was determined by TGA, DTA, DSC and EDAX.

Keywords: Crystal growth, Barium oxalate, TGA, DTA, DSC, and EDAX.

Introduction

The growth of crystal occurs not only in the crust of Earth or in laboratory but also in a living body. Many crystals, particularly, bio-materials and proteins, cause various ailments and health related problems. The urinary stones are usually composed of either pure or mixed crystals of calcium oxalate, brushite, struvite, and hydroxyapatite and carbonate apatite [1]. Arthropathies, i.e., bone and joint diseases, are caused by crystals such as hydroxyapatite, calcium pyrophosphate and monosodium urate monohydrate [2]. There are other crystals which play important role in various ailments, for instance, f.c.c. type ferritin crystals in development of cataract [3] and cholesterol crystals for cardiovascular diseases and gall stones [4]. This bio-crystallization occurring in human body causes suffering and it is not desirable to occur. This has been discussed in detail by the predecessors of the present author [5-7]. There are several micro-organisms which synthesize crystals, for example, magneto-tactic bacteria synthesizing magnetite [8], chrysophytes [9] diatoms and act in opoda synthesizing siliconous materials and S. layer bacteria synthesizing gypsum and calcium carbonate surface layers [10]. Calcite crystals are found in mollusk shells [11] and as a component in gall stones [12]. The earlier crystal growth study was divided into two parts :(1) The study of the equilibrium between the crystal and surrounding medium(2) The study of the kinetics of growth.

Experimental

Experimental procedure 5 gm of agar-agar powder was dissolved in to hot double distilled water mixed with 0.5 M to 1 M barium chloride solution was incorporated then again the mixture was stirred to make homogenous mixture. The crystallizing vessel were used essentially consist of standard glass tube having inner diameter 2.5 cm and the length 25 cm. Gelling mixture poured in glass test tubes. These tubes were hermitically sealed to prevent evaporation and contamination of the exposed surface by dust particles of atmosphere or atmospheric impurities and were kept undisturbed. Usually in 3 to 4 days the gel was to be set which depends on the environmental temperature. It was observed that the mixture in a glass tube was initially transparent and slowly turned light white. The water slowly evaporated and gel was completely set. After ensuring firm gel setting, it was kept for aging for 3 to 4 days. After that 0.5 M to 1 M solution of oxalic acid was added as a supernatant over the set get. Nucleation was observed after 5 to 6 days and crystals started to grow. White color, larger size, transparent and shining crystals were obtained in the gel, as shown in fig.1, Optimum condition tabulated in table 1, [13].

Table 1 Optimum conditions for barium oxalate crystal grown by agar-agar gel method

Concentration of agar-agar gel	5 %
Concentration of reactant, strontium chloride	1M
Concentration of supernatant, oxalic acid	1 M
Room temperature	27^0C
Gel aging period	4 days
Growth period	25 - 40 days
Quality of crystals	White colour, larger size (1mm × 1mm) transparent, shining crystals

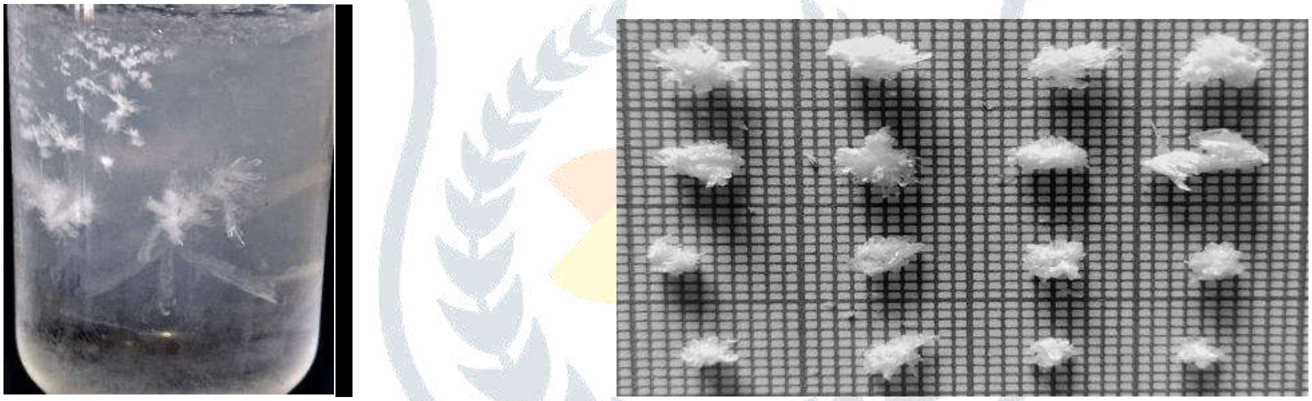

Fig.1 (a) Barium crystal inside the test tube (b) Opaque and shiny crystals

Result and Discussion-

Thermo-Gravimetric Analysis (TGA)

TGA was carried out at Department of Physics, Shivaji University Kolhapur, TGA curve for barium oxalate is shown in figuer.2. From the thermo gram of barium oxalate one can observe that

i) The compound is stable up to 50^0C.

ii) 5.165% weight loss in temperature range 50^0C. To 172^0C may be due to dehydration of water molecule and up to 172^0C there is no further loss of weight.

iii) 25.68% weight loss in temperature range 172^0C to 277^0C from the dehydrated compound corresponds to loss of CO.

iv) 36.68% weight loss in temperature range 277^0C to 435^0C corresponds to loss of CO_2.

v) 13.45% weight loss in temperature range 435^0C to 478^0C.

v) The residue remains stable from 478^0C and decompose the material. [14-16].

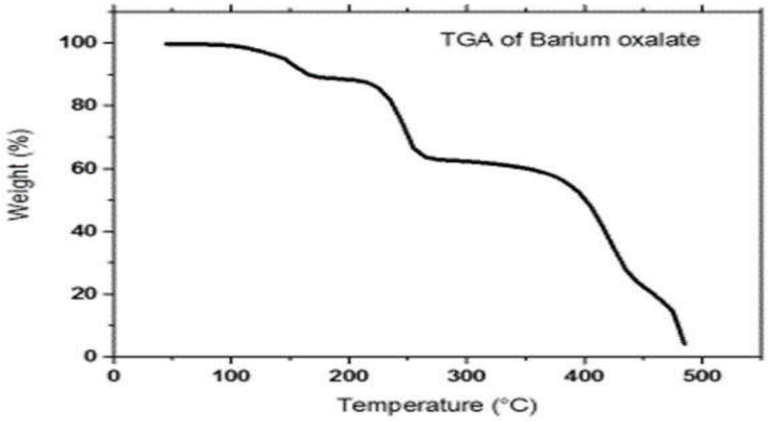

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Figure 2 TGA of Barium oxalate crystal grown by agar-agar gel

TGA data indicates that the grown crystals contains water molecule,

Table 2 TGA Data of Barium oxalate

Stage	**Temperature range**	**Observed % weight loss**	**Calculated % weight loss**	**Loss of molecule in stage**
I	50^0C-172^0C	5.165%	5.045%	H_2O
II	172^0C-277^0C	25.68%	25.8%	It may be CO
III	277^0C-435^0C	36.68%	35.99%	CO_2
IV	435^0C-478^0C	13.45%	13.56%	-

Differential Thermal Analysis (DTA)

DTA was carried out at Department of Physics, Shivaji University Kolhapur.DTA curve for barium oxalate is shown in figure3. From the thermo gram of barium oxalate one can observe that.

In DTA curve of barium oxalate by agar-agar gel at 37.51^0C an endothermic peak is observed due to the loss of bulk of water of crystallization. The decomposition of oxalate is observed at the onset due to complete dehydration. In DTA curve the exothermic peaks at $153.^0$C to 154.54^0C shows the decomposition of oxalate. Loss of weight at the temperature range $153.^0$C relates to the loss of water of crystallization which is endothermic in character.

Loss of weight at the temperature 250.07^0C endothermic peak is observed that means the weight loss with respect to temperature of the grown crystals was further supported by

DTA results. DTA data is shown in table- 3

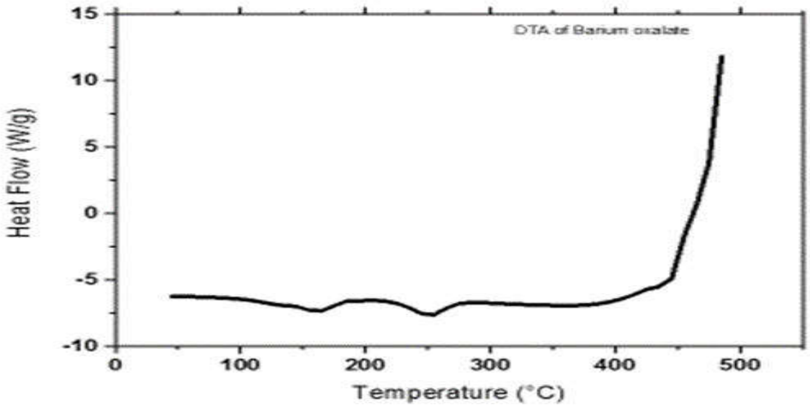


Figure 3 DTA of Barium oxalate

Table no.3 DTA data of barium oxalate

Peak recorded	Peak height	Nature	ΔH(J/gm)
37.51^{0}C	-0.600	Endothermic	-0.6406
154.54^{0}c	-0.5	Exothermic	-0.5344
250.07^{0}c	-0.4	Endothermic	-0.4613

Differential Scanning Calorimeter (DSC)

DSC was carried out at Department of Physics, Shivaji University Kolhapur, The DSC thermogram was recorded in the temperature range from 25^{0}C to 450^{0}C.Microcrystalline (powdered) samples of barium oxalate crystals were taken for DSC studies and the weight of the sample 8.5230mg.The sample was hold for 10 min in air to evaporate water due to moisture and then heated from 25^{0}C to 450^{0}C.at the rate 10c/min in Air .After reaching the temperature of 450^{0}C,the sample was hold for I minute at 450^{0}C and then again cooled from 450^{0}C to 25^{0}C at the rate of 10C/min in Air.

The DSC curve for barium oxalate gel grown crystal shown in figure 4. And the DSC data collected from this curve is tabulated in the table 4.

Step-I

i) The initiation temperature is 225^{0}C and equilibrium temperature 277^{0}C.At 225^{0}C (initiation temperature) initiation of phase change start & is completed at peak endo-down temperature of 250.07^{0}C(transition temperature).The temperature at which the sample and the reference come to the thermal equilibrium by thermal diffusion appears to be at 277^{0}C.The peak appeared in the DSC curve at 154.54^{0}C indicates the phase transformation due to loss of water molecules and formation of stable anhydrous barium oxalate. This is the good agreement with the TGA curve,

ii) Area under the curve is 5707.384 mJ.

iii) Heat of transisiton ΔH i.e. enthalpy change of transisiton 517.56 J/g which 0.51756kJ/mole. Since molecular weight is 1g/mole, ΔHtr = ΔHf i.e. heat of phase transformation is also 0.5756 kJ/mole, where ΔHf is enthalpy change of new phase transformation or it is called heat of phase formation.

Step-II

i) The initiation temperature is 430^{0}C and equilibrium temperature is 450^{0}C.At 430^{0}C (initiation temperature) initiation of phase change starts and is completed at peak endo- down temperature of 438.76^{0}C (transition temperature).The temperature at which the sample and the reference come to the thermal equilibrium diffusion appears to be 450^{0}C.The further phase transition occurs at temperature 438.76^{0}C due to the loss of carbon and H_2O and formation of stable barium oxalate. This is good agreement with TGA Curve.

ii) Area under the curve is 232.43mJ.

iii) Heat of transition ΔH i.e. enthalpy change of transition 21.99J/g which is 0.02199KJ/mole. Since molecular weight is 1 g/mole, Hence ΔHtr = ΔHf i.e. heat of phase transformation is also 0.02199KJ/mole. Where ΔHf enthalpy change of new phase transformation or it is called heat of phase formation. DSC data is shown in table- 4.

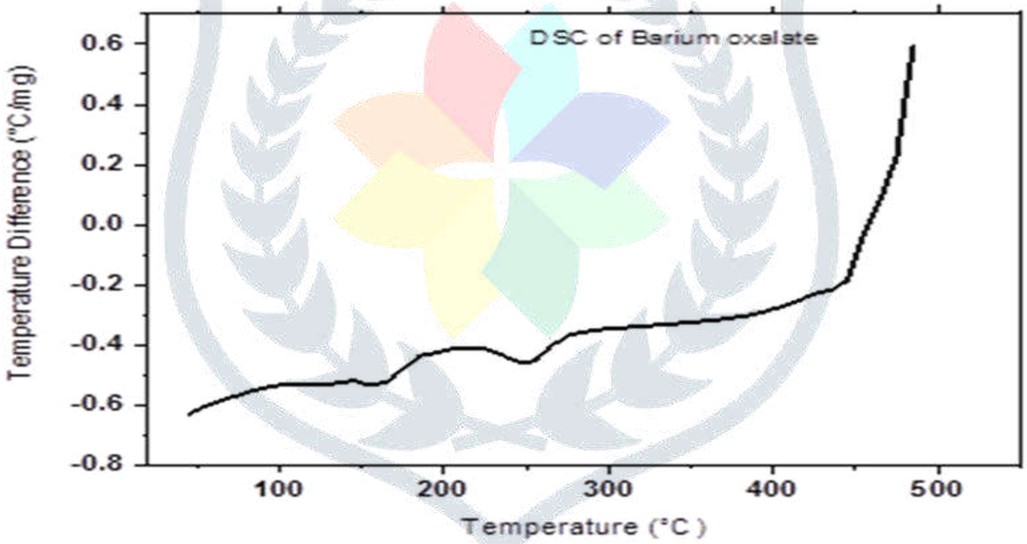


Figure 4 DSC curve for Barium oxalate

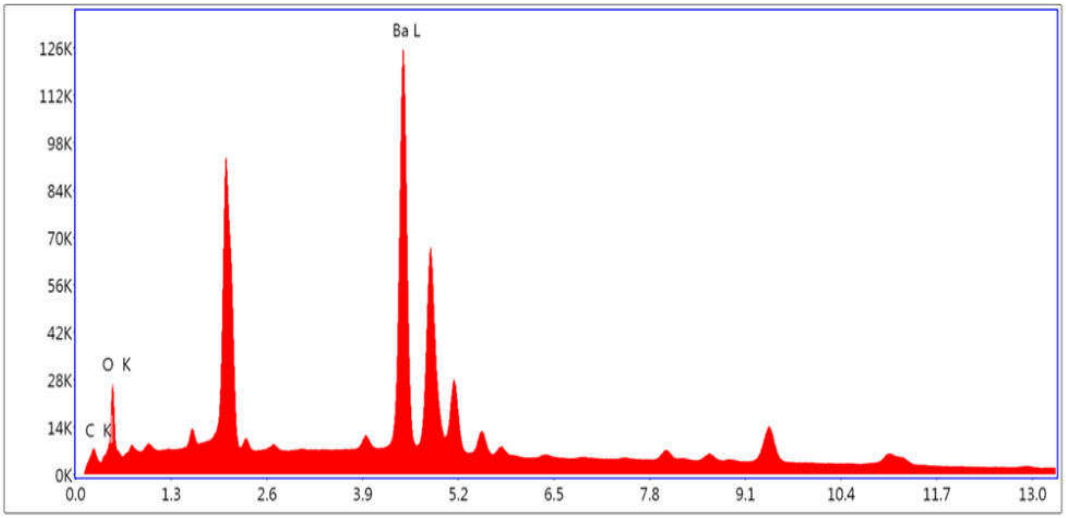
DSC data is shown in table- 4

Sample	Weight of the sample	Stage	Change in the enthalpy(ΔH)	Transition temperature (Tr)
Barium oxalate	0.8523gm	I	0.51756KJ/mole	250.07^{0}C
		II	0.02199KJ/mole	438.76^{0}C

Energy Dispersive Analysis by X-rays (EDAX) –

Energy Dispersive analysis by X-ray (EDAX) is used for the quantitative analysis of barium oxalate and is also called as elemental analysis. Fig 5& Table No 5 shows, in present work elemental analysis of gel grown barium oxalate crystals was Department of Physics, Shivaji University Kolhapur. It conclude that the (weight

& atomic %) of copper (Cu) in the grown crystal measured by EDAX are very close with the values calculated from the molecular formula.[17-20]



eZAF smaryt quant Results

Element	Weight%	Atomic%	Net.Int	Error	%	K ratio	Z	R	A	F
Ck	7.36	34.64	443.18	7.82	0.05	0.05	1.47	0.75	0.47	1.00
Ok	8.71	30.80	991.30	7.87	0.05	0.05	1.42	0.77	0.39	1.00
Barium	83.93	34.56	5594.20	2.05	0.80	0.80	0.91	1.07	1.03	1.03

Conclusions –

The present work reports the growth and characterization of barium oxalate single crystals. We have demonstrated the formation of barium oxalate single crystals in agar-agar gels. Barium oxalates exhibits micro-rod-like and spherulites growth (flower) shape are observed. Further to obtain good quality single crystals of barium oxalate, both reactants –barium chloride and oxalic acid were interchanged. With barium chloride incorporated gels result only fibers. These facts have been explained by taking in account the interaction of the reactants ions with the sodium and silica ions. The effect of temperature on growth of barium oxalate crystals showed that there is a decrease in nucleation density at higher temperature which is due to the increases of the aqueous solubility of barium oxalate.

References

[1] M. Menon, B. G. Parulkar and G. W. Drach; Campbell's Urology, W. B. Saunders, New York, 9th Edition,3 (1998) 2662-2676.

[2] S. J. Gupta; J. Indian Rheumatol Assoc., 10(2002) 5-13.

[3] D. G. Brooks, K. Manova-Todorova, J. Farmer, L. Lobmayr, R. B. Wilson, R. C. Eagle, Jr., T. G. St. Pierre and D. Stambolian; Invest. Ophthalmol. Vis. Sci., 43(2002)1121.

[4] S. P. Wrenn; "Engineering Approaches to Cholesterol-Linked Diseases", (2001).

[5] V. S. Joshi; Ph. D. Thesis, Saurashtra University, Rajkot (2001).

[6] K. C. Joseph; Ph.D. Thesis, Saurashtra University, Rajkot, (2005).

[7] B. B. Parekh; Ph. D. Thesis, Saurashtra University, Rajkot (2006).

[8] R. B. Frankel and R. P. Blakemore; "Eds in Iron Biominerals, Plenum",New York, (1991).

[9] J. Kristiansen and R. A. Andersen; "Eds in Chrysophytes Aspects and Priblems",Cambridge University Press, Cambridge (1986).

[10] M. Sarikaya; Proc. Natl. Acad. Sci. USA,B96(1999) 14183.

[11] C. E. Bowen and H. Tang; Comp. Biochem. Physiol., 115A(4)(1996)269.

[12] D. S. June and E.S. Weley; Science, 159 (1968)1113.

[13] P.V.Dalal and K.B.Saraf ,:"Bull.Mater.Sci" Vol.29 N0.5,2006 421-425.

[14] K.S.Raju,Johan Varughese and M.A.Ittyachen; " Bull. Mater.Sci." 21(1998)375.

[15] D.K.Sawant,H.E.Patil.D.S.Bhavsar,K.D.Girase and J.H.Patil; "Journal of Thermal Analysis and Calorimetry," 107 (2012)3.

[16]N. S. Patil, P. A. Savale. S. K. Bachhav and S. T. Pawar ; ' Archive of physics research', Vol2(1), (2011). 39-47,

[17]D. K. Sawant., H. M. Patil and D. S. Bhavsar., 'Pelagia research Library, DCS' Vol2(3), (2011) 63,

[18]D. K. Sawant., H. M. Patil and D. S. Bhavsar., 'Scholars Research Library Archives of Physics Research', Vol2(2), (2011). 67.

[19] S.J.Nandre,S.J.Shitole and R.R.Ahire; "Journal of Nano and Electronic Physics"Vol.4,4,(2012)4013.

[20] M.Selvapandiyan, S. Sudhakar and M.Prasath; "Int. Journal of Engineering Research and Application", Vol. 7,8,(3) (2017), 65-72.

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Nanonecklace of CdO through simple solution chemistry

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ABSTRACT

CdO nanonecklace like structure with interconnected nanobeads were produced by air annealed $Cd(OH)_2$ nanowire structure thin film at 290 °C. Simple and low cost chemical route has been successfully employed for the synthesis of $Cd(OH)_2$ nanowires on fluorine doped tin oxide (FTO) coated glass substrates at room temperature (27 °C). Structural analysis confirmed the conversion of hydroxide phase to the oxide phase by annealing which also leads to change in optical band gap from 3.5 to 2.34 eV. The necklace like nanostructure represent unique surface morphology which can be emerged as a potential candidate towards wide range of applications in different fields of nanotechnology such as solar cell, gas sensor, supercapacitor and photo-catalyst.

1. Introduction

Now a day's nanostructures were attracted wide research interest because of their novel properties and potential technological applications. They are also predicted to play important role in optoelectronic, electrochemical devices and gas sensors [1]. Wide efforts have been taken towards the synthesis of semiconducting nanomaterials with different structures such as nanorods, nanowires, nanocrystals, nanobeads [2–7] etc. because of their size and dimensionality dependence of functional properties. Cadmium oxide (CdO) is one of the most promising n-type semiconductor with a direct optical band gap of 2.5 eV and an indirect band gap of 1.98 eV [8] which have wide applications like photocatalysts, transparent conducting oxide, and solar cells [9–12]. Various attempts have been reported for the synthesis of CdO thin films by using different synthesis methods such as spray pyrolysis, pulse laser deposition, electrochemical deposition, successive ionic layer adsorption and reaction (SILAR), and chemical bath deposition [13–18]. Among which chemical bath deposition is very simple, low cost method and operated at room temperature.

Present investigation has been focused on nanonecklace-type morphology of CdO obtained by using $Cd(OH)_2$ nanowires as intermediate step synthesized by simple, and low cost wet chemical route onto fluorine doped tin oxide (FTO) coated glass substrates at room temperature (27 °C) followed by heat treatment. Structural, surface morphological and chemical bond formation analysis was performed to characterize the samples and obtained results are discussed herein.

2. Experimental details

Initially, $Cd(OH)_2$ thin film consisting of nanowires was synthesized at room temperature (27 °C) by using chemical method; similarly as reported earlier [19,20]. Specifically, 100 mM (50 ml) $CdCl_2$ was complexed by addition of ammonia. The dropwise addition of ammonia (up to 10 ml) in the solution bath leads to the formation of clear solution with resultant pH ~12 (i.e. basic bath), which is the basic requirement for the formation of $Cd(OH)_2$ film on the substrate surface. The solution was stirred for few seconds and then gently immersed the pre cleaned FTO substrates vertically in a solution along the wall of the beaker at room temperature. After 21 h, the white $Cd(OH)_2$ film was deposited on the substrate surface. Then, substrate was taken out from the solution, rinsed with double distilled water and dried in air followed by annealing at optimized temperature of 290 °C for 1 h in order to get CdO film.

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1369-8001/

3. Results and discussion

Structural properties of the films were measured by X-ray diffractometer (XRD) (D8 Advance, Bruker) with Cuk$_\alpha$ radiations ($\lambda = 1.5406$ Å) in the 2θ range from 20° to 80° is shown in Fig. 1. The diffraction peaks at (100), (200), (231), (202) and (051) planes were indexed to monoclinic crystal structure for $Cd(OH)_2$ (Fig. 1(a)) which is good agreement with standard JCPDS data (Card no. 88-1594). Fig. 1(b) shows the complete conversion of $Cd(OH)_2$ into CdO phase after heat treatment. The characteristic diffraction peaks at (111), (200), (220), (311) and (222) planes confirms the formation cubic crystal structure of CdO and is in well agreement with standard JCPDS data (Card no. 05-0640).

Fig. 2 shows the variation of absorbance with wavelength in the range of 300–800 nm using UV–vis (Shimadzu, model no.: UV 1601) spectrophotometer. At shorter wavelength, absorption coefficient of $Cd(OH)_2$ is lower to that of CdO. Absorption edge of $Cd(OH)_2$ shifts towards longer wavelength after its conversion into CdO. The optical band gap values were calculated by plotting the graph of $(\alpha h\nu)^2$ versus $h\nu$ (Fig. 2 inset). The extrapolation of the straight line at $(\alpha h\nu)^2 = 0$ gives the value of band gap energy and were obtained as 3.5 eV and 2.34 eV for as-deposited $Cd(OH)_2$ and annealed CdO, respectively. CdO with nanostructured morphology can have diverse applications like photoanode for the formation of solar cells with high surface area [21], as a sensor for detection of hazardous gases [22], interconnected nanostructure with high surface area towards energy storage application like supercapacitor [23] and photo-catalyst for water treatment [24].

Fig. 3(a) illustrates a probable schematic representation for the formation of CdO nanobeads resulting to nanonecklace. During annealing, the bundles of $Cd(OH)_2$ nanowires were separate out by evolution of water molecule and try to assembles into spherical nanodroplets (beads) of CdO to minimize its surface energy. Fig. 3 (b and c) shows the surface morphology of the nanostructures using high resolution field emission scanning electron microscopy (FE-SEM, JEOL 6360 A). The clear appearance of $Cd(OH)_2$ in the form of nanowires having porous structure with diameter in the range of 50–100 nm is seen from Fig. 3(b). The individual wires merge together resulting bundles formation. Fig. 3(c) shows the FE-SEM image of annealed sample; exhibit a clear alteration in the morphology. The diameter of nanobeads becomes heterogeneous with particle size in between 20 and 50 nm. These nanobeads are interconnected with each other along their length leading to form 'nanonecklace' like morphology. The random distribution of CdO nanonecklace spread on FTO substrate with enough porous surface area is observed. The formation of this structure is attributed to the natural oxidation of the $Cd(OH)_2$ nanowire surface when exposed to air annealing at optimized temperature of 290 °C.

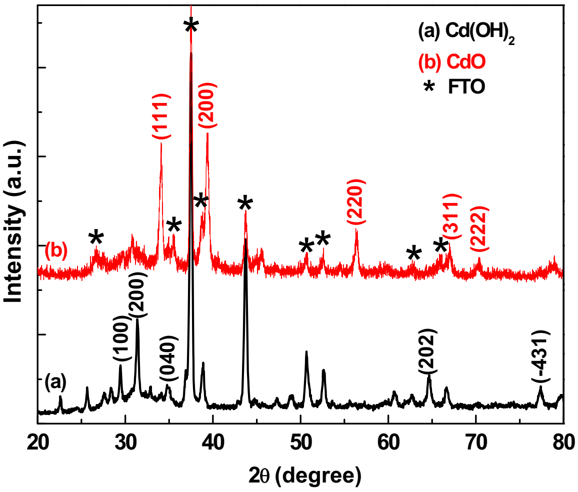

Fig. 1. X-ray diffraction patterns (a) $Cd(OH)_2$ nanowires and (b) CdO nanonecklace.

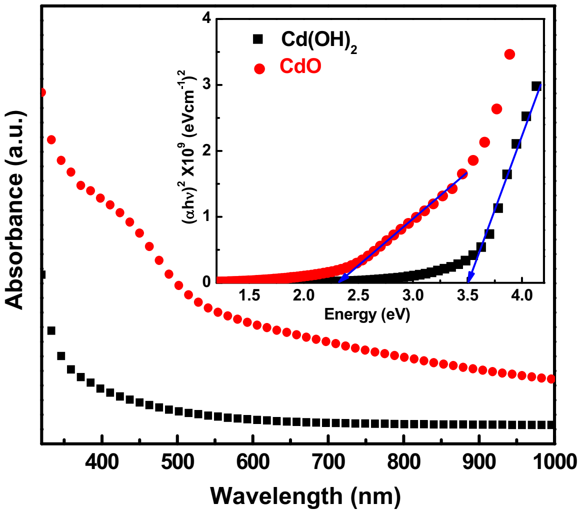

Fig. 2. Optical absorption spectra of as-deposited $Cd(OH)_2$ and annealed CdO. Inset depicts the plots of $(\alpha h\upsilon)^2$ versus $h\upsilon$ for $Cd(OH)_2$ and CdO.

Due to more negative solubility product (k_{sp}) value of $Cd(OH)_2$ (2×10^{-14}) than $[Cd^{2+}][OH^{2-}]$, stable cadmium hydroxide phase can be formed as

$$CdCl_2 + NH_3 + 2H_2O \rightarrow Cd(OH)_2 + NH_4Cl + HCl \quad (1)$$

The CdO film was obtained by annealing of $Cd(OH)_2$ film at 290 °C for 1 h in air as

$$Cd(OH)_2 \xrightarrow[290^0C]{} CdO + H_2O\uparrow \quad (2)$$

In this process, whitish $Cd(OH)_2$ nanowires film was changed to brown CdO film with the formation of necklace like nanostructure.

Fig. 4 shows the FTIR studies of $Cd(OH)_2$ and CdO powder samples using RX-1 Perkin Elmer, IR spectrometer. For $Cd(OH)_2$ sample (Fig. 4(a)), the peak at 3510 cm^{-1} can be attributed to stretching vibrations of hydroxyl group attributed to contain of $Cd(OH)_2$ [25]. The peaks 3346 cm^{-1}, 3251 cm^{-1} may be assigned to H-bonded O-H stretching which can be assigned to stretching vibrations of H_2O molecules. The peaks at 729 cm^{-1} attributed to presence of C=C bond of aromatic hydrocarbon. The broadening of IR bands is observed for annealed sample (Fig. 4(b)). Peaks at 3346 cm^{-1}, 3251 cm^{-1} and 2461 cm^{-1} are seen to be completely disappeared and with poor resolved shoulders attributed to presence of CdO.

4. Conclusions

Chemical bath deposition method was used to form $Cd(OH)_2$ nonowires thin film on FTO coated glass substrates at room temperature. A clear alteration in morphology of CdO was observed by air annealing of $Cd(OH)_2$ film at optimized temperature (290 °C, 1 h). The nanobeads were interconnected with each other along their length leading to the formation of 'nanonecklace' like morphology. XRD and FTIR analysis confirm complete conversion of hydroxyl phase to oxide phase. Due to annealing, the absorption edge was clearly shifted to longer wavelength which is a consequence of the conversion of $Cd(OH)_2$ to CdO with optical band gap reduction from 3.5 to 2.34 eV. Such unique morphology can find potential applications in nanotechnology such as solar cells, supercapacitor gas sensors and photo-catalyst.

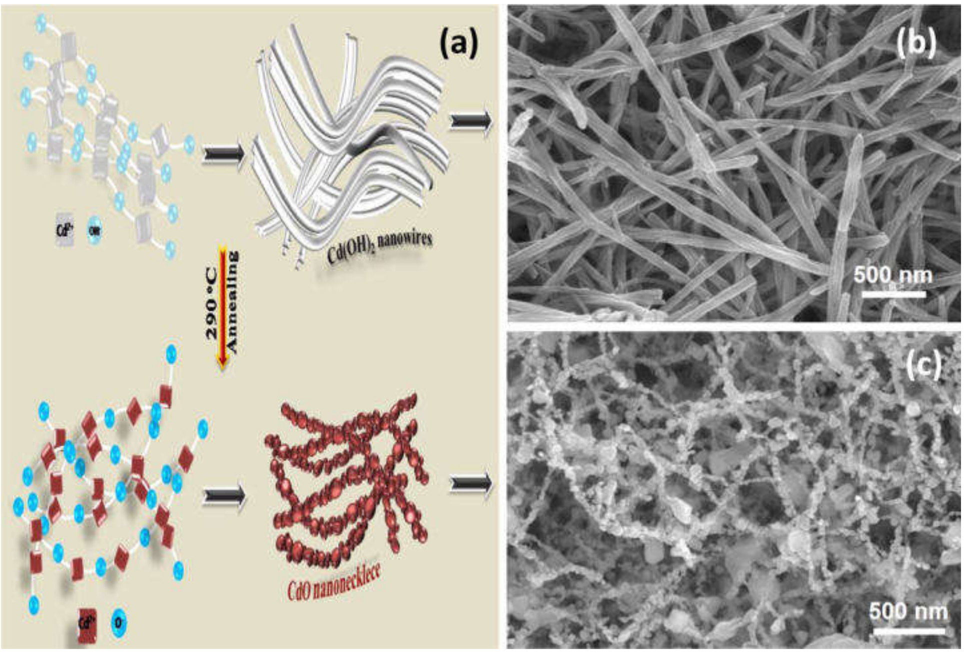

Fig. 3. (a) Schematic representation for the formation of CdO nanobeads resulting to nanonecklace (b) Scanning electron micrographs of $Cd(OH)_2$ nanowires and (c) CdO nanonecklace.

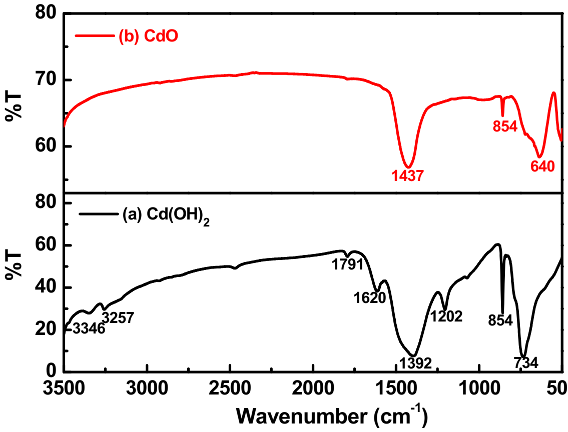

Fig. 4. FTIR spectra of (a) as-deposited $Cd(OH)_2$ nanowires and (b) annealed CdO nanonecklace.

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References

[1] Y.N. Xia, P.D. Yang, F. Kim, H.Q. Yan, Adv. Mater. 15 (2003) 353–389.
[2] G. Nagaraju, S. Ashoka, P. Chithaiah, C.N. Tharamani, G.T. Chandrappa, Mater. Sci. Semicond. Process. 13 (2010) 21–28.
[3] P.R. Nikam, P.K. Baviskar, J.V. Sali, K.V. Gurav, J.H. Kim, B.R. Sankapal, Ceram. Int. 41 (2015) 10394–10399.
[4] D.S. Dhawale, A.M. More, S.S. Latthe, K.Y. Rajpure, C.D. Lokhande, Appl. Surf. Sci. 254 (2008) 3269–3273.
[5] P.K. Baviskar, P.R. Nikam, S.S. Gargote, A. Ennaoui, B.R. Sankapal, J. Alloy. Compd. 551 (2013) 233–242.
[6] G. Singh, I.P.S. Kapoor, R. Dubey, P. Srivastava, Mater. Sci. Eng. B 176 (2011) 121–126.
[7] P.K. Baviskar, J.B. Zhang, V. Gupta, S. Chand, B.R. Sankapal, J. Alloy. Compd. 510 (2012) 33–37.
[8] Y.C. Zhang, G.L. Wang, Mater. Lett. 62 (2008) 673–675.
[9] S. Millesi, M. Schiliro, F. Greco, I. Crupi, G. Impellizzeri, F. Priolo, R.G. Egdell, A. Gulino, Mater. Sci. Semicond. Process. 42 (2016) 85–88.
[10] S. Calnan, A.N. Tiwari, Thin Solid Films 518 (2010) 1839–1849.
[11] R.R. Salunkhe, V.R. Shinde, C.D. Lokhande, Sens. Actuators B Chem. 133 (2008) 296–301.
[12] S.B. Jambure, C.D. Lokhande, Mater. Lett. 106 (2013) 133–136.
[13] M.A. Rahman, M.K.R. Khan, Mater. Sci. Semicond. Process. 24 (2014) 26–33.
[14] R.R. Salunkhe, D.S. Dhawale, D.P. Dubal, C.D. Lokhande, Sens. Actuators B Chem. 140 (2009) 86–91.
[15] T. Singh, D.K. Pandya, R. Singh, Mater. Sci. Eng. B 176 (2011) 945–949.
[16] B. Sahin, F. Bayansal, M. Yuksel, H.A. Cetinkara, Mater. Sci. Semicond. Process. 18 (2014) 135–140.
[17] M.A. Yildirim, A. Ates, Sens. Actuators Phys. 155 (2009) 272–277.
[18] H. Khallaf, C.T. Chen, L.B. Chang, O. Lupan, A. Dutta, H. Heinrich, A. Shenouda, L. Chow, Appl. Surf. Sci. 257 (2011) 9237–9242.
[19] B.R. Sankapal, R.D. Ladhe, D.B. Salunkhe, P.K. Baviskar, V. Gupta, S. Chand, J. Alloy. Compd. 509 (2011) 10066–10069.
[20] V.S. Bagal, G.P. Patil, A.B. Deore, P.K. Baviskar, S.R. Suryawanshi, M.A. Morec, P. G. Chavan, Chem. Phys. Lett. 650 (2016) 7–10.
[21] R.S. Mane, H.M. Pathan, C.D. Lokhande, S.H. Han, Sol. Energy 80 (2006) 185–190.
[22] R.N. Bulakhe, C.D. Lokhande, Sens. Actuators B Chem. 200 (2014) 245–250.
[23] S.P. Mundinamani, M.K. Rabinal, Mater. Res. Express 2 (2015) 116401.
[24] S. Millesi, M. Schiliro, F. Greco, I. Crupi, G. Impellizzeri, F. Priolo, R.G. Egdell, A. Gulino, Mater. Sci. Semicond. Process. 42 (2016) 85–88.
[25] M. Ristic, S. Popvic, S. Music, Mater. Lett. 58 (2004) 2494–2499.

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CdO necklace like nanobeads decorated with PbS nanoparticles: Room temperature LPG sensor

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HIGHLIGHTS

- Conversion of $Cd(OH)_2$ nanowires to CdO nanonecklace by air annealing at 290 °C.
- Decoration of PbS nanoparticles over CdO nanobeads by SILAR method.
- Formation of n-CdO/p-PbS nano-heterojunction as room temperature LPG sensor.
- Maximum gas response of 51.10% with 94.54% stability.

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ABSTRACT

Simple chemical route has been employed to grow interconnected nanobeads of CdO having necklace like structure through air annealing of cadmium hydroxide nanowires. This nanobeads of n-CdO with high surface area has been decorated with p-PbS nanoparticles resulting in the formation of nano-heterojunction which has been utilized effectively as room temperature liquefied petroleum gas (LPG) sensor. The room temperature gas response towards C_2H_5OH, Cl_2, NH_3, CO_2 and LPG was investigated, among which LPG exhibits significant response. The maximum gas response of 51.10% is achieved with 94.54% stability upon exposure of 1176 ppm concentration of LPG at room temperature (27 °C). The resulting parameters like gas response, response and recovery time along with stability studies has been studied and results are discussed herein.

1. Introduction

Recently, nanomaterials with diverse nanostructure surface architecture such as nanoparticles, nanowires, nanotubes and quantum dots has gain enormous interest due to their different surface architectures in numerous applications for the variety of device developments such as photovoltaics [1], gas sensors [2], supercapacitors [3] and solar cells [4]. Direct fabrication of device by using the nanostructure architectures towards sensor development is a challenging task. Furthermore, development of gas sensors to monitor combustible gases is becoming very imperative for safety requirements in homes and industries. Among all, liquefied petroleum gas (LPG) is one of the extensively used in very household but potentially hazardous gases. The explosion may be caused when LPG leaks accidentally or by mistake and hence, there is prevailing need to detect LPG leakage at lower limit. In last few decades, metal oxide semiconducting materials have extensively used as gas sensor [5–7] but they suffer poor sensitivity along with high operating temperatures. To overcome these limitations, the fabrication of heterojunctions has gained essence importance. Many reports are available on the fabrication of heterojunctions by using physical or chemical methods [8–12]. The heterojunctions show some interesting properties that have been widely studied. For instance, Lee et al. reported that a TiO_2/water solid-liquid heterojunction behaves similar to a Schottky diode and works as a self-

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powered UV detector with excellent performance [13]. Zhang et al. reported that a heterojunction of Bi_2MoO_6/TiO_2 can effectively separate photo-generated carriers by the photo-induced potential at the interface of Bi_2MoO_6/TiO_2 heterojunction [14]. ZnO/Cu_2O heterojunction shows good current rectifying behaviour reported by Zhang et al. [15]. Therefore, more studies in fabricating devices based on heterojunctions are necessary, especially in nanostructure systems.

Present investigation focuses the synthesis of controlled morphology of n-type nanobeads of CdO through room temperature chemical bath deposited cadmium hydroxide $[Cd(OH)_2]$ nanowires with post thermal treatment on to fluorine doped tin oxide (FTO) coated glass substrates. Anchoring of p-PbS nanoparticles has been performed to form n-CdO/p-PbS nano-heterojunction in thin film form towards the detection of LPG at room temperature (27 °C).

2. Experimental details

2.1. Materials

Cadmium chloride ($CdCl_2$), lead nitrate ($Pb(NO_3)_3$) and sodium sulphide flakes (Na_2S) were purchased from Loba Chem., India with analytical grade and used as received. Fluorine doped tin oxide (FTO) coated glass was used as substrate (Sigma-Aldrich Glass, thickness: 2 mm, sheet resistance: ~15 Ω/□). FTO were cleaned by adopting the following process: FTO were initially rinsed in dilute HCl for 5 s, ultrasonically cleaned with soap solution followed by rinsing with ethanol for 5 min. and then finally rinsed with double distilled water.

2.2. Synthesis of CdO nanostructure

Initially, $Cd(OH)_2$ nanowires were synthesized at room temperature by using chemical method. In detail, 0.1 M (50 ml) solution of $CdCl_2$ was complexed by drop wise addition of aqueous ammonia (10 ml) with the resultant pH ~12. The solution was stirred for few seconds and gently, FTO coated glass substrate was vertically immersed along the wall of the beaker kept room temperature. After 21 h, the white $Cd(OH)_2$ film was deposited on the substrate surface. Then, the substrate was taken out from the solution, rinsed with double distilled water and dried in dry air. CdO necklace like nanostructure film was obtained by air annealing $Cd(OH)_2$ film at optimized temperature of 290 °C for two hours and the complete growth with reaction mechanism is reported elsewhere [16].

2.3. Coating of PbS nanoparticles on CdO nanostructure

The successive ionic layer adsorption and reaction (SILAR) method was employed to anchor PbS nanoparticles onto CdO nanonecklace at room temperature (27 °C). Lead nitrate $[(PbNO_3)_3]$ with concentration of 8 mM was used as a cationic precursor with pH 9. Sodium sulphide (Na_2S) solution (5 mM) was used as an anionic precursor with pH 11. The immersion time in anionic and cationic precursors was 20 s with rinsing time of 10 s in double distilled water. The 10 immersion SILAR cycles were optimized to get the complete coverage of PbS nanoparticles over CdO necklace type nanostructure to form nano-heterojunction towards enhanced gas sensing performance.

2.4. Experimental setup for LPG measurement

The setup consists of a 27 L closed glass dome, an air tight glass bottle, half filled with double distilled water, an LPG cylinder, a liquid level monitor for gas volume measurement and a vacuum pump as per our earlier report [17]. The sample with the dimensions 1 cm^2 was kept inside the dome duly contacted with silver paste over the PbS as a front contact and the FTO coated glass substrate as a back contact. These two contacts were connected to a Potentiostat/Galvanostat model Super 1000S (SAP Instruments Pvt. Ltd, India) for the current–voltage measurements.

2.5. Characterizations

The structural properties of the films were measured by using X-ray diffractometer (XRD) (D8 Advance, Bruker AXS) with Cuk$_\alpha$ radiations (λ = 1.5406 Å) in the 2θ range from 10 to 80°. A high resolution field emission scanning electron microscopy (FE-SEM, JEOL 6360A) coupled with an energy-dispersive X-ray spectrometer (EDX) was employed to analyze the surface morphologies and chemical composition of samples. The gas sensing properties of n-CdO/p-PbS were studied under forward biases condition, between 0 and 2 V to obtain the current density versus voltage (J-V) characteristics curves for the formed sensor at room temperature.

3. Results and discussion

3.1. Structural studies

The CdO nanonecklace were obtained simply by calcinations of the $Cd(OH)_2$ nanowires at 290 °C in air for two hours. Fig. 1(a) show X-ray diffraction (XRD) patterns of CdO and PbS decorated CdO samples. The peaks marked by stars (*) are contributed from FTO substrates. The peaks corresponding to CdO (111), (200), (220), (311), and (222) have been detected. The result shows that the CdO has a pure cubic phase with space group Fm3m (225) and calculated lattice constant of a = 4.73 Å (JCPDS Card no. 00-005-0640). The peaks corresponding to PbS (006), (008), (116), (204), and (422) gives better support towards the formation of PbS nanoparticles over CdO nanonecklace (JCPDS Card no.01-080-1144) whereas (111), (200), (220), (222), and (311) in the same XRD patterns supports the existence of CdO material below PbS nanoparticles.

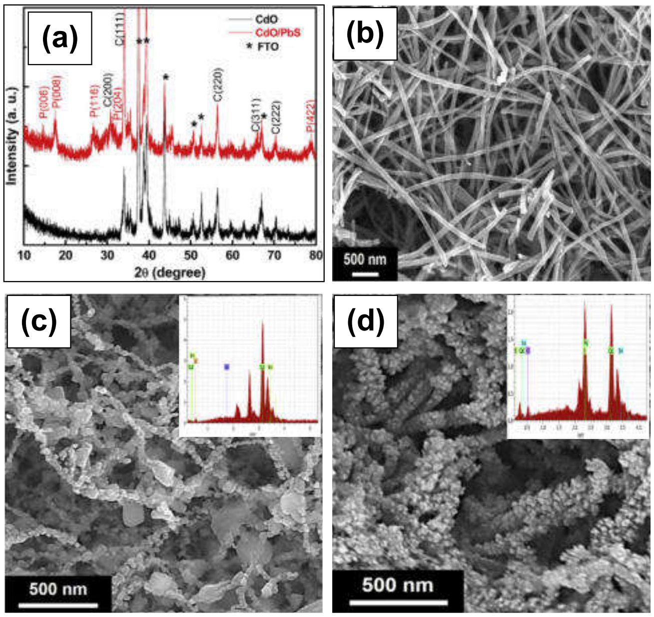

Fig. 1. (a) X-ray diffraction spectrum of CdO and PbS deposited over CdO. Scanning electron micrographs of (b) $Cd(OH)_2$, (c) CdO, (d) CdO/PbS on FTO coated glass substrate. Inset shows the EDX patterns of CdO and PbS decorated CdO on FTO substrate.

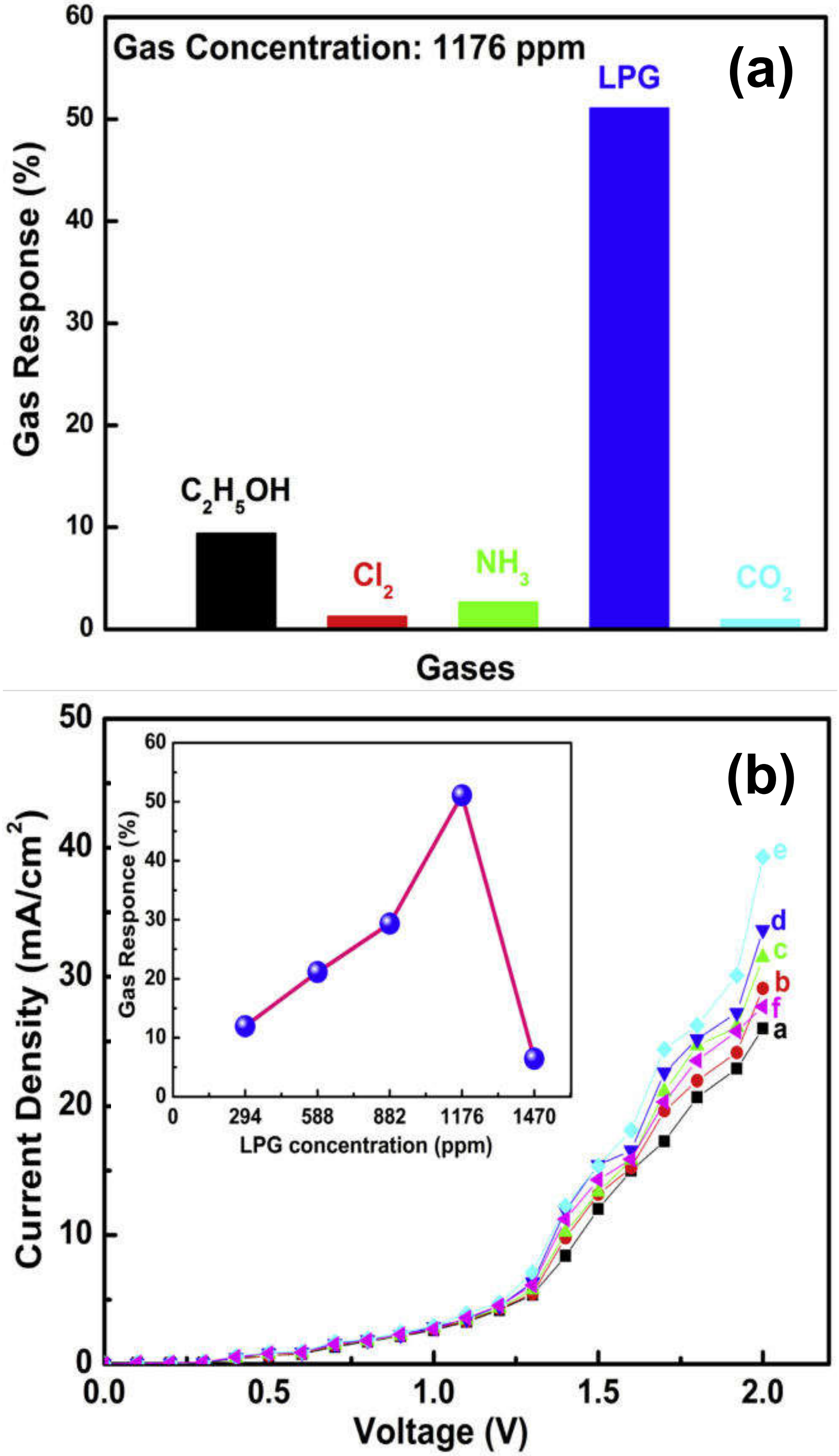

Fig. 2. (a) Gas response (%) of n-CdO/p-PbS nano- heterojunction with different gases at room temperature. (b) Forward biased current density-voltage (J–V) characteristics of FTO/n-CdO/p-PbS nanonecklace type heterojunction in air and at various concentrations of LPG as curve (a) 0 ppm (air), (b) 294 ppm, (c) 588 ppm, (d) 882 ppm, (e) 1170 ppm, and (f) 1470 ppm. Inset shows variation in gas response (%) vs. LPG concentration (ppm) of n-CdO/p-PbS heterojunction at 2 V.

3.2. Surface morphological studies and elemental analysis

The SEM images of $Cd(OH)_2$, CdO and CdO/PbS thin films are as shown in Fig. 1(b), (c) and (d), respectively. Fig. 1(b) clearly depicts the formation of bundles consisting of nanowires for $Cd(OH)_2$. The novel necklace like CdO nanostructure with interconnected small beads is observed in Fig. 1(c). It is seen that the hydroxide part was removed during air annealing leading to the formation of CdO by quenching its diametric area which leads to the formation of interconnected nanobeads whereas small nanoparticles with size ranges from 50 to 100 nm of PbS seems to be decorated on nanobeads of CdO (Fig. 1(d)). The uniform deposition of p-type PbS over n-type CdO necklace results in the formation of high surface area p–n junction at the nano level and hence, the formation of nanoheterojunction (NHJ). Small agglomeration of PbS nanoparticles is also observed at the interconnections of network structures. The observed structure is porous with interconnected network having high surface area which is beneficia towards gas sensing application as it enables gas species to enter easily through porous structure which adsorb-desorb gas molecules easily at nanoheterojunction interface.

The energy-dispersive X-ray spectrum (EDX) of CdO and CdO/PbS nanonecklace on FTO substrates are shown as insets of Fig. 1(c and d). The elemental analysis confirms the formation of CdO on FTO reflecting the presence of Cd, and O peaks. The inclusion of Sn and Si is from FTO coated glass substrate whereas presence of Au is from coating of Gold (Au) over sample. Elemental analysis from Fig. 1(d) inset confirms the formation of PbS over CdO showing the presence of Cd, O, Pb and S peaks, which supports well with the structural analysis.

3.3. Selectivity measurement

The gas sensing response values of nano-heterojunction device at room-temperature are shown in Fig. 2(a). As results, the response values of device for C_2H_5OH, Cl_2, NH_3, LPG, and CO_2 under the same test conditions with gas concentration of 1176 ppm at room temperature are 9.42, 1.25, 2.65, 51.1, and 0.95%, respectively. It demonstrates that the device has an excellent selectivity for LPG.

3.4. LPG sensing properties of n-CdO/p-PbS nano-heterojunction

The heterojunction formed between CdO and PbS was tested by coating silver (Ag) paste over PbS layer. The complete device FTO/n-CdO/p-PbS/Ag layer is designed and current density – voltage (J-V) curves for the devices were measured. The forward biased current density–voltage (J–V) characteristics of the n-CdO/p-PbS nanoheterojunction in air and under various concentrations of LPG is as shown in Fig. 2(b). The formed n-CdO/p-PbS NHJ was tested as a sensor towards liquefied petroleum gas (LPG) at room temperature (27 °C). The current density of heterojunction in air (J_a) and in the presence of LPG (J_g) were measured at a fixed voltage and following equation was used to calculate the gas response.

$$S\% = \frac{J_g - J_a}{J_a} \times 100 = \frac{\Delta J}{J_a} \times 100$$

Fig. 2(b), curve (a) depicts J-V characteristics of n-CdO/p-PbS nano-heterojunction in air as a reference and under the various concentrations of LPG from 294–1470 ppm (curve (b-f)). After exposure of LPG towards the junction, the forward current density enhances with LPG concentration. The maximum change in the current density was observed for 1176 ppm concentration of LPG at 2 V.

The gas response at various concentrations of LPG was calculated at a fixed voltage of 2 V and is shown in inset of Fig. 2(b). The gas response increases from 11.76% to 51.10% with increase in LPG concentration and attained maximum 51.10% at 1176 ppm. This is due to unimolecular layer of gas molecules would be expected to form on the interface, which would interact with the interface more actively, giving rise to higher response. Above 1176 ppm, a decrease in response value was observed at 1470 ppm which is due to formation of multilayer of gas molecules at the interface of the junction; the potential barrier height may increase at the interface or may be due to recombination of charge carriers [11,18–20].

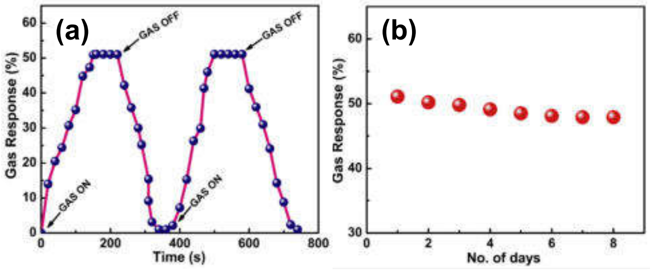

Fig. 3. (a) Shows gas response (%) vs. time (s) for n-CdO/p-PbS heterojunction at fixed voltage of 2 V at 1176 ppm of LPG concentration and (b) shows the variation of gas response (%) vs. time in number of days for n-CdO/p-PbS heterojunction at fixed voltage of 2 V at 1176 ppm of LPG concentration.

The response transient curves for first two exposures to LPG at fixed voltage of 2 V and 1176 ppm of LPG are as shown in Fig. 3(a). The n-CdO/p-PbS heterojunction shows good reversibility to LPG that has shown maximum response of 51.10%. The response transient curve provides information of response and recovery times of heterojunction. Upon exposure to LPG, the sensor reaches the maximum response of 51.10% with response time 150 s. Further when sensor exposed to fresh air, sensor shows recovery time 134 s. The repeatability test was performed by exposing the junction to fresh air followed by exposure to LPG. The device resulted into good reversibility with response and recovery times of 148 s and 142 s, respectively.

3.5. Stability studies

The stability study of NHJ is very important in order to design and manufacture the long term stable gas sensor device for domestic as well as industrial applications. The stability study for n-CdO/p-PbS nanonecklace type heterojunction was carried out over 8 days. Fig. 3(b) shows the variation of gas response against the number of days. It is clearly observed that the gas response falls from 51.10% to 48.31% that means response value decreases up to 2.79% of its maximum value (51.10%) in 6 days and remains stable even after 6 days which shows 94.54% stability. From all above characteristics, it is cleared that the present inorganic/inorganic (n-CdO/p-PbS) heterojunction is more stable and suitable for device fabrication towards commercialization. On other hand, the organic partner used in the fabrication of inorganic/organic heterojunction for LPG detection is hygroscopic in nature and decomposes with time and hence shows the less stability and repeatability of device.

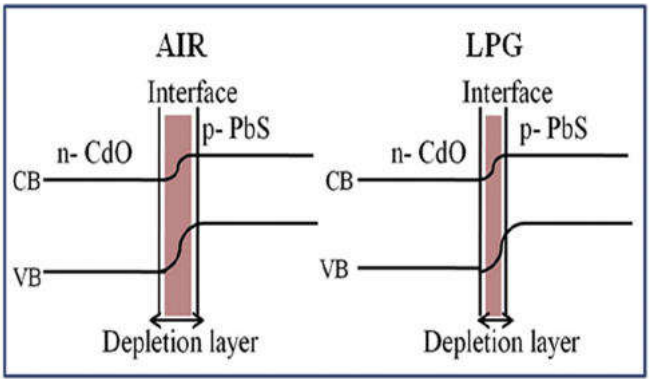

Fig. 4. The schematic representation of energy band diagram of n-CdO/p-PbS heterojunction.

3.6. LPG sensing mechanism of nano-heterojunction

When n-CdO/p-PbS heterojunction is exposed to LPG, due to reducing nature of the interacting species, the resistance of nano-heterojunction decreases and gas response is increased as LPG concentration goes on increasing. At higher concentration of LPG, the gas response may decrease due to saturation of LPG molecules at the junction. The sensing property of sensor to reducing nature of LPG, may relates surface chemical oxygen absorption of sample, also the role of chemisorptions or atmospheric oxygen adsorbs on the surface by extracting electrons from sensing material results in the reduction of barrier height, leading to decrease in resistance and increase in gas response [19]. Fig. 4 shows schematic representation of change in potential barrier height. Alternatively, upon exposure to LPG, it likely seems to be dissociation of reducing LPG at surface or interface of the junction. This leads to change in work function of p-PbS and increases the carrier concentration near the interface of nano-heterojunction. Hence in turn barrier height of the nano-heterojunction decreases. The change in potential barrier height and depletion width at the heterojunction interface is responsible for current transporting through the nano-heterojunction [21–24]. The similar behaviour for the change in barrier height was reported by S. Patil et al. [19] where they have measured the change with the aid of capacitance measurement. D. Patil et al. proposed the model based on the principle of formation of heterojunction to explain the LPG sensing behaviour of nano-composite and observed shifting in the potential barrier height with change in the resistance of heterojunction on exposer of gas [25].

4. Conclusions

Necklace like nanostructure of CdO was obtained by air annealing $Cd(OH)_2$ nanowire film at 290 °C resulting into the formation of interconnected nanobeads with necklace like porous structure. p-PbS nanoparticles were successfully decorated on to n-CdO by using successive ionic layer adsorption and reaction (SILAR) method at room temperature (27 °C). Such nanostructures having unique surface morphology may be potential candidates towards gas sensing application. The n-CdO/p-PbS nano-heterojunction was successfully used as liquefied petroleum gas (LPG) sensor at room temperature (27 °C) with the maximum response of 51.10% under exposure of 1176 ppm concentration of LPG at operating voltage of 2 V with low response and recovery times.

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References

[1] A.A. Hussain, A.R. Pa, R. Kar, H. Bailung, J. Chutia, D.S. Patil, Comparative study of nanocomposites prepared by pulsed and dc sputtering combined with plasma polymerization suitable for photovoltaic device applications, Mater. Chem. Phys. 148 (2014) 540–547.

[2] A.K. Jaiswal, S. Singh, A. Singh, R.R. Yadav, P. Tandon, B.C. Yadav, Fabrication of Cu/Pd bimetallic nanostructures with high gas sorption ability towards development of LPG sensor, Mater. Chem. Phys. 154 (2015) 16–21.

[3] B.R. Sankapal, H.B. Gajare, D.P. Dubal, R.B. Gore, R.R. Salunkhe, H. Ahn, Presenting highest supercapacitance for TiO_2/MWNTs nanocomposites: novel method, Chem. Eng. J. 247 (2014) 103–110.

[4] P. Baviskar, R. Gore, A. Ennaoui, B. Sankapal, Cactus architecture of ZnO nanoparticles network through simple wet chemistry: efficient dye sensitized solar cells, Mater. Lett. 116 (2014) 91–93.

[5] A. Srivastava, K. Jain, Rashmi, A.K. Srivastava, S.T. Lakshmikuma, Study of structural and microstructural properties of SnO_2 powder for LPG and CNG gas sensors, Mater. Chem. Phys. 97 (2006) 85–90.

[6] R.J. Wu, Y.L. Sun, C.C. Lin, H.W. Chen, M. Chavali, Composite of TiO_2 nanowires and Nafion as humidity sensor material, Sens. Actuator. B Chem. 115 (2006) 198–204.

[7] G.K. Mani, J.B.B. Rayappan, ZnO nanoarchitectures: ultrahigh sensitive room temperature acetaldehyde sensor, Sens. Actuator. B Chem. 223 (2016) 343–351.

[8] F. Du, H. Zhang, X. Du, J. Zhu, X. Zhong, Controllable synthesis and optical properties of CdS/CdSe hetero-nanostructures with various dimensionalities, Mater. Chem. Phys. 148 (2010) 118–124.

[9] P.R. Nikam, P.K. Baviskar, J.V. Sali, K.V. Gurav, J.H. Kim, B.R. Sankapal, SILAR coated Bi_2S_3 nanoparticles on vertically aligned ZnO nanorods: synthesis and characterizations, Ceram. Int. 41 (2015) 10394–10399.

[10] K. Lokesh, G. Kavitha, E. Manikandan, G.K. Mani, K. Kaviyarasu, J.B.B. Rayappan, R. Ladchumananandasivam, J.S. Aanand, M. Jayachandran, M. Maaza, Effective ammonia detection using n-ZnO/p-NiO heterostructured nanofibers, IEEE Sens. J. 16 (2016) 2477–2483.

[11] D.S. Dhawale, D.P. Dubal, A.M. More, T.P. Gujar, C.D. Lokhande, Room temperature liquefied petroleum gas (LPG) sensor, Sens. Actuator. B Chem. 147 (2010) 488–494.

[12] N. Thovhogi, E. Park, E. Manikandan, M. Maaza, A. Gurib-Fakim, Physical properties of CdO nanoparticles synthesized by green chemistry via Hibiscus Sabdariffa flower extract, J. Alloy. Compd. 655 (2016) 314–320.

[13] W.J. Lee, M.H. Hon, An ultraviolet photo-detector based on TiO_2/water solid-liquid heterojunction, Appl. Phys. Lett. 99 (2011) 251102.

[14] M. Zhang, C. Shao, J. Mu, Z. Zhang, Z. Guo, P. Zhang, Y. Lin, One-dimensional Bi_2MoO_6/TiO_2 hierarchical heterostructures with enhanced photocatalytic activity, Cryst. Eng. Comm. 14 (2012) 605–612.

[15] P.W. Zheng, L. Lin, F. Peng, Z. Huang, F. Lai, *I-V* characteristics of ZnO/Cu_2O thin film n-i-p heterojunction, Phys. B Condens. Matter 406 (2011) 1253–1257.

[16] N.B. Sonawane, P.K. Baviskar, R.R. Ahire, V.H. Ojha, B.R. Sankapal, Anonecklace of CdO through simple solution chemistry, Mater. Sci. Semicond. Process 49 (2016) 81–83.

[17] R.D. Ladhe, K.V. Gurav, S.M. Pawar, J.H. Kim, B.R. Sankapal, p-PEDOT as a heterojunction partner with n-ZnO for the detection of LPG at room temperature, J. Alloys Compd. 515 (2012) 80–85.

[18] R.D. Ladhe, P.K. Baviskar, B.R. Sankapal, LPG sensor based on complete inorganic n-Bi_2S_3-p-CuSCN heterojunction synthesized by a simple chemical route, J. Phys. Appl. Phys. 43 (2010) 245302.

[19] S.V. Patil, R.N. Bulakhe, P.R. Deshmukh, N.M. Shinde, C.D. Lokhande, LPG sensing by p-polyaniline/n-PbS heterojunction junction capacitance structure, Sens. Actuator. A Phys. 201 (2013) 387–394.

[20] D.S. Dhawale, D.P. Dubal, V.S. Jamadade, R.R. Salunkhe, S.S. Joshi, C.D. Lokhande, Room temperature LPG sensor based on n-CdS/p-polyaniline heterojunction, Sens. Actuator. B Chem. 145 (2009) 205–210.

[21] Z. Ling, C. Leach, The effect of relative humidity on the NO_2 sensitivity of a SnO_2/WO_3 heterojunction gas sensor, Sens. Actuator. B Chem. 102 (2004) 102–106.

[22] H. Tai, Y. Jiang, G. Xie, J. Yu, X. Chen, Fabrication and gas sensitivity of polyaniline-titanium dioxide nanocomposite thin film, Sens. Actuator. B Chem. 125 (2007) 644–650.

[23] Z. Ling, C. Leach, R. Freer, Heterojunction gas sensors for environmental NO_2 and CO_2 monitoring, J. Euro. Ceram. Soc. 21 (2001) 1977–1980.

[24] S.S. Joshi, C.D. Lokhande, S.H. Han, A room temperature liquefied petroleum gas sensor based on all-electrodeposited n-CdSe/p-polyaniline junction, Sens. Actuator. B Chem. 123 (2007) 240–245.

[25] D. Patil, K. Kolhe, H.S. Potdar, P. Patil, Investigation of poly(o-anisidine)-SnO_2 nanocomposites for fabrication of low temperature operative liquefied petroleum gas sensor, J. Appl. Phys. 110 (2011) 124501.

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Influence of Mn^{2+} Magnetic Ions on the Properties of $Cd_{1-x}Mn_xS$ Thin Films Synthesized by Chemical Bath Deposition

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II-VI semiconductor based ternary CdMnS compound material has received more attention due to its wide area of applications in semiconductor technology. $Cd_{1-x}Mn_xS$ ($x = 0$, 0.2, 0.4, 0.6, 0.8 and 1.0) thin films were successfully prepared by chemical bath deposition technique on non-conducting glass substrates. Thin films were deposited at a bath temperature of 80 °C and pH = 11 by using the chemical bath reaction of cadmium chloride ($CdCl_2$) and manganese chloride ($MnCl_2$) with thiourea $(NH_4)_2S$ in an aqueous solution. Further, the prepared samples were characterized by UV-visible spectroscopy, photoluminescence, XRD, SEM and EDAX to study the optical, structural, surface, and chemical properties. Effect of Mn^{2+} ions on the film thickness of $Cd_{1-x}Mn_xS$ films was investigated using weight difference technique. The film thickness of $Cd_{1-x}Mn_xS$ films decreases as Mn^{2+} ions increase in the bath solution. The polycrystalline nature with hexagonal and cubic structures of the as-deposited films was confirmed by XRD. The band gap value of the deposited films was observed to increase with increasing Mn^{2+} ion concentration, this might be ascribed to the fact that Cd atom was substituted by Mn atom in the CdS structure. EDAX analysis confirmed the deposition of Cd, Mn and S elements in the films. Photoluminescence spectra of $Cd_{1-x}Mn_xS$ with different values of the composition parameter x exhibited two emission peaks with different intensities. The measurement of the electrical resistivity of $Cd_{1-x}Mn_xS$ films was performed at room temperature using two probe methods. The variation in electrical resistivity values with compositional parameters was discussed based on deposition parameters. The investigated polycrystalline $Cd_{1-x}Mn_xS$ thin films show promising technological applications in semiconductor industry.

Keywords: CdMnS films, Optical properties, Electrical properties, Chemical bath deposition, Mn^{2+} ion.

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1. INTRODUCTION

The n-type CdS [1] (band gap ~ 2.42 eV) and p-type MnS [2] (band gap ~ 3.88 eV) are important materials of group II-VI semiconductors and they have potential application prospect in electronics and optoelectronic devices, sensors, lasers and thin film based devices in semiconductor industries [3]. The CdS structure has high electrical resistivity values and the energy gap of CdS is narrow [4]. Hence, the use of CdS alone is not enough for future hopes. To do this, unlike earlier reports, we have incorporated here Mn^{2+} ions into the CdS structure to produce CdMnS thin films in a wide range of composition ($x = 0.0$ to 1.0). Doping of CdS with Mn^{2+} ions has been made to achieve improved structural, electrical and optical properties. Most of the research done so far has focused extensively on structural, optical and electrical properties of $Cd_{1-x}Mn_xS$ thin films. However, the study of the influence of Mn^{2+} ions on various properties of $Cd_{1-x}Mn_xS$ thin films is rare in the literature.

A variety of techniques like spray pyrolysis, thermal evaporation, molecular beam epitaxy, sputtering, chemical vapor deposition, pulsed laser deposition, chemical bath deposition (CBD) etc. have been used in the synthesis of CdMnS thin films [5, 6]. Among these, CBD is one of the important techniques. CBD can provide simplicity, cost effectiveness, ease of handling and requires low cost equipment. It can be performed using a range of precursors and synthesis conditions like temperature, time, concentration of reactants etc. The technique is simple, inexpensive and has a high yield, reproducible on large-area thin films [7, 8].

This paper attempts to use a CBD technique for the deposition of $Cd_{1-x}Mn_xS$ thin films for different values of the composition x and systematic study of the influence of Mn^{2+} ions on various characterization properties of $Cd_{1-x}Mn_xS$ thin films.

2. EXPERIMENTAL DETAILS

$Cd_{1-x}Mn_xS$ thin films were deposited using CBD technique. Cadmium chloride ($CdCl_2$), manganese chloride ($MnCl_2$) and thiourea (CH_4N_2S) were used as Cd^{2+}, Mn^{2+} and S^{2-} ion sources, respectively. The stock solutions of $CdCl_2$ (1 M), $MnCl_2$ (1 M) and thiourea (1 M) all of AR grade were prepared using distilled water. The experimental solutions of $CdCl_2$ and $MnCl_2$ were dissolved in high purity DI water in 50 ml glass beaker. Subsequently, thiourea was added dropwise to the solution with continuous stirring until a volume of 50 ml reached. Ammonia solution was added until the pH reached 11 and stirred for few minutes. The microscopic non-conducting glass substrate was cleaned with distilled water and liquid soap, soaked in dilute HCl for one day, washed with acetone and finally with distilled water. Then the substrate was kept vertically inclined into the chemical bath. The chemical bath maintained at 80 °C for one hour. Finally, deposited samples were taken out of the solution cleaned with DI water and

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dried in air at room temperature. To study the influence of Mn^{2+} on various properties of $Cd_{1-x}Mn_xS$ thin films, the CBD parameters, such as complexing agent, deposition time, temperature and pH of the solution were firstly optimized in the present procedure to achieve good quality films. Fig. 1 shows the schematic sketches of the sample preparation process.

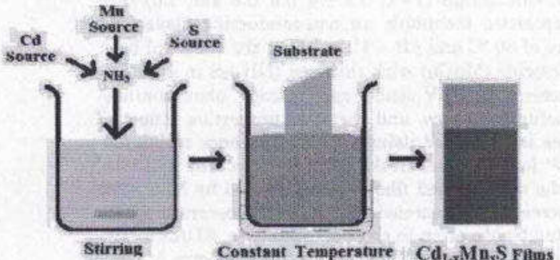

Fig. 1 – Process flow for deposition of $Cd_{1-x}Mn_xS$ films

The deposited CdMnS thin film exhibits yellowish to yellow brownish color with variation in Mn^{2+} ion concentration.

The chemical reaction for the deposition of CdMnS by CBD is as shown below

$$NH_3 + H_2O \leftrightarrow NH_4 + OH^-$$
$$SC(NH_2)_2 + 3OH^- \leftrightarrow 2NH_3 + CO_3^{2-} + HS^-$$
$$HS^- + OH^- \leftrightarrow H_2O + S^{2-}$$
$$Cd^{2+} + 4NH_3 \leftrightarrow [Cd(NH_3)_4]^{2+}$$
$$Mn^{2+} + 4NH_3 \leftrightarrow [Mn(NH_3)_4]^{2+}$$
$$[Cd(NH_3)_4]^{2+} + [Mn(NH_3)_4]^{2+} + S^{2-} \leftrightarrow$$
$$CdMnS + by\text{-}product$$

3. RESULTS AND DISCUSSION

The as-deposited films were characterized by different techniques. The film thickness was measured using gravimetric weight difference method. The XRD of the films was recorded using Bruker AXS D8 advance spectrophotometer. The surface morphology of the CdMnS films was analyzed by FESEM (SEM Hitachi S-47009). The compositional purity of the films was confirmed by EDAX analysis. The UV-visible spectrum was recorded by the spectrophotometer in the wavelength range 300-900 nm. The room temperature PL spectrum was recorded by Perkin Elmer LS55 using laser source at a wavelength of 390 nm. The dc electrical transport properties have been studied at room temperature by two-probe dc electrical conductivity equipment.

3.1 Thickness Measurement

The as-deposited film thickness of $Cd_{1-x}Mn_xS$ samples was measured by gravimetric weight difference method using a high-precision electric balance. This method gives an appropriate value of the thickness of the deposited films. The thickness of the film can be determined using the equation [9]

$$t = \frac{(w_2 - w_1)}{A\bar{\rho}} \times 10^{-4}\ \mu m$$

where w_1 and w_2 are the weights of the substrate before and after film deposition in grams, A is the area of the deposited film in cm^2 and ρ is the theoretical density of the deposited material.

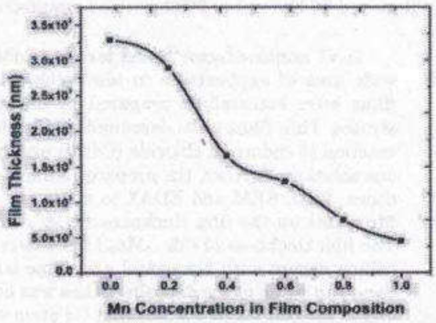

Fig. 2 – Variation in film thickness as a function of Mn concentration

Fig. 2 shows the variation in film thickness versus Mn^{2+} ion concentration in the CdS structure. It is seen that the thickness of the film decreases with the addition of Mn^{2+} ions to the CBD solution. It can be ascribed to the fact that Mn^{2+} ion has smaller atomic/ionic radius (117/80 Pm) than that of Cd^{2+} (154/97 Pm). As Mn^{2+} ion concentration in the bath solution increases, the film (Mn^{2+}) content also increases. Further, substitution of Cd^{2+} by Mn^{2+} atoms is easily possible in the chemical bath.

3.2 Characterization Using XRD

The crystal structure of the as-deposited films has been investigated by XRD patterns which are shown in Fig. 3. The diffractogram illustrated in the figure clearly shows that the as-deposited films are polycrystalline in nature. The analysis of these diffractograms was done and the corresponding data (interplanar distance d, hkl planes, grain size etc.) were determined. There are six prominent reflections at d values equal to 3.577 Å, 3.351 Å, 3.164 Å, 2.066 Å, 1.890 Å and 1.760 Å that correspond to the (100), (002), (101) (110), (103) and (200) reflections, respectively. XRD pattern of the films indicates that they are polycrystalline with both the hexagonal wurtzite type structure (JCPDS card No. 772306 for CdS and card No. 894953 for MnS) and cubic structure with preferential growth along the (002) direction. The addition of Mn^{2+} to the CdS matrix showed the formation of a solid solution up to $x = 0.8$. The further incorporation of Mn^{2+} resulted in phase separation of both CdS and MnS.

The average grain size enhanced with the addition of Mn^{2+} ions into the bath solution. A plot showing grain size versus concentration is represented in Fig. 4. When Mn^{2+} ions are added to the host lattice of CdS, Mn atoms substitutionally occupy Cd atom sites instead of forming a separate MnS phase. The effect of Mn^{2+} ions on grain size of the obtained films is shown in Fig. 4.

This caused improved crystallinity, especially for $x = 0.2$. Above the composition $x = 0.4$, phase separation started resulting in deterioration of crystallinity for films with $x = 0.6$ and $x = 0.8$. Films with $x = 1.0$ represent amorphous nature with dominant MnS phase [10].

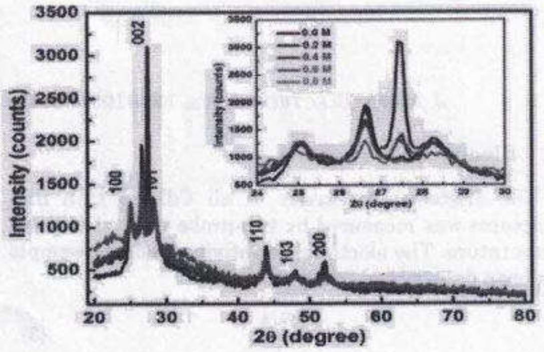

Fig. 3 – X-ray diffraction spectra of CdMnS films. The inset shows intense peaks

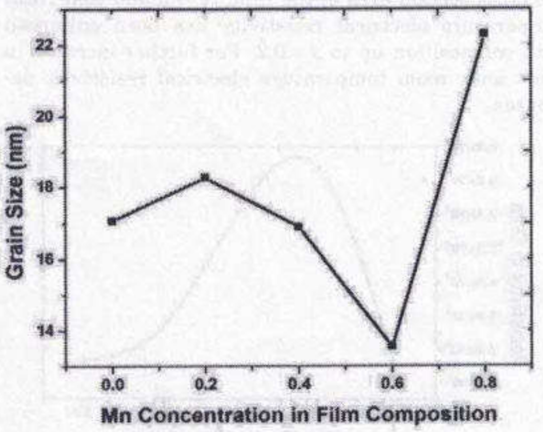

Fig. 4 – Effect of Mn concentration in the film composition on grain size

Table 1 – Observed and standard 2θ and d values for respective *hkl* planes

Sr.	2θ, degrees		d, Å		Planes
No.	Observed	Standard	Observed	Standard	(*hkl*)
1	24.90	25.18	3.5775	3.5380	(100)
2	26.61	26.91	3.3514	3.3147	(002)
3	28.21	28.61	3.1648	3.1215	(101)
4	43.84	44.36	2.0660	2.0430	(110)
5	48.15	48.60	1.8906	1.8716	(103)
6	51.96	51.69	1.7606	1.7692	(200)

The XRD data are given in Table 1. The average grain size in the deposited films is estimated using Scherrer relation:

$$D = \frac{k\lambda}{\beta\cos\theta}, \qquad (2)$$

where k is the Scherrer constant, λ is the wavelength of X-rays, β is the full width at half maximum (FWHM) in radians and θ is the Bragg angle.

3.3 SEM Analysis

The surface morphology of $Cd_{1-x}Mn_xS$ thin films was investigated by FESEM. Fig. 5 shows variations in the surface morphology of $Cd_{1-x}Mn_xS$ ($x = 0.0$, 0.2, 0.4, 0.6, 0.8, 1.0) films with respect to increase in Mn^{2+} ion concentration in the coating solution. All the films were scanned at 20 K magnification.

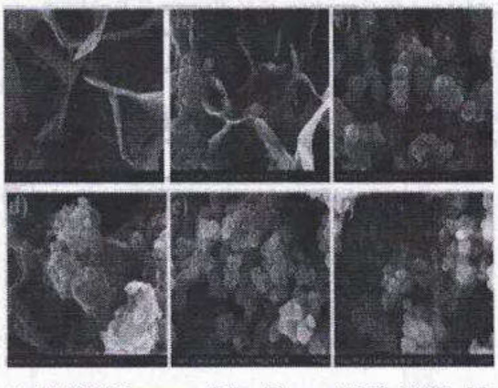

Fig. 5 – FESEM images of the films: a) CdS, b) $Cd_{0.8}Mn_{0.2}S$, c) $Cd_{0.6}Mn_{0.4}S$, d) $Cd_{0.4}Mn_{0.6}S$, e) $Cd_{0.2}Mn_{0.8}S$, f) MnS

The micrographs show the uniform deposition of $Cd_{1-x}Mn_xS$ films without any pinholes. Pure CdS has a flower-like structure and is shown in Fig. 5a. As we incorporate Mn^{2+} ions into CdS coating solution, Mn atoms interact with CdS molecules. This interaction slightly changes the film surface morphology, which is confirmed by Fig. 5b. Further increase in Mn^{2+} ion concentration in the coating solution resulted in the formation of nanocrystalline CdMnS compounds that is shown in Fig. 5c-e. When concentration of Mn^{2+} ions reaches the highest level, Cd atoms are replaced by Mn atoms and this gives us the pure form of MnS films. The nanocrystalline morphology of pure MnS films is shown in Fig. 5f.

3.4 EDAX Analysis

To confirm the elemental composition of Cd, Mn and S in CdMnS thin films, EDAX is carried out. Table 2 shows EDAX data of the deposited $Cd_{1-x}Mn_xS$ ($x = 0.4$) thin films. It also confirms the presence of Cd^{2+}, Mn^{2+} and S^{2-} in the obtained film matrix.

Table 2 – EDAX data for $Cd_{1-x}Mn_xS$ ($x = 0.4$) films

Element	Atomic number	Series	Atomic percent (%)
S	16	K-series	42.22
Mn	25	K-series	17.26
Cd	48	L-series	40.52
Total			100

3.5 UV-visible Spectrophotometer

The optical absorbance data of CdMnS thin films were recorded using UV-visible spectrophotometer. The absorbance spectra were used to estimate the energy band gap (E_g) by Tauc plot method. It is found that the optical band gap has been enhanced with composition. This is shown in Fig. 6. With an increase in Mn^{2+} ions, the strain was induced by Mn^{2+} ions, and therefore the lattice structure became highly distorted tending towards amorphisity of the material that caused the band gap to be enhanced. This enhancement in the band gap is in good agreement with previous results. The band gap values vary from 2.05 to 2.82 eV which is consistent with the values reported for thin films obtained by CBD [5, 11].

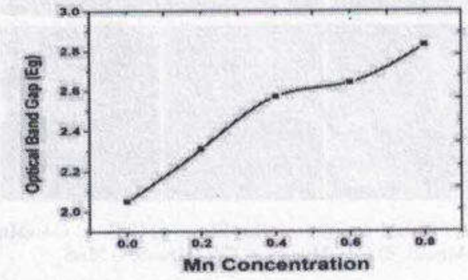

Fig. 6 – Effect of Mn concentration on band gap

The dependence of the optical band gap on the Mn^{2+} ion concentration can be attributed to Mn atoms in the CdS structure [12, 13]. The difference in the band gap values is clearly indicated by the color of the thin film, the yellow color turned to dark yellowish or orange color as Mn^{2+} ions increase.

3.6 Photoluminescence Analysis

Photoluminescence (PL) is an efficient, non-contact and non-destructive method to probe the electronic structure of different materials, which can also be used to determine the band gap, impurity levels, defects etc. Fig. 7 represents the room temperature PL spectra of $Cd_{1-x}Mn_xS$ thin films, showing two broad emission peaks at 525 and 589 nm. The emission peak at 525 nm corresponds to the green band; it is due to the donor-acceptor transition and is attributed to the radiative recombination of a hole in the valence band and of an electron in the conduction band. In addition, the unshifted peak positions indicate that the crystallite sizes are almost the same for all samples. Our XRD studies shed light on these observations. Another well-known emission peak at 589 nm (2.1 eV, red band) corresponds to the $^4T_1$-$^6A_1$ transitions of Mn^{2+} *d*-states in CdS nanocrystals.

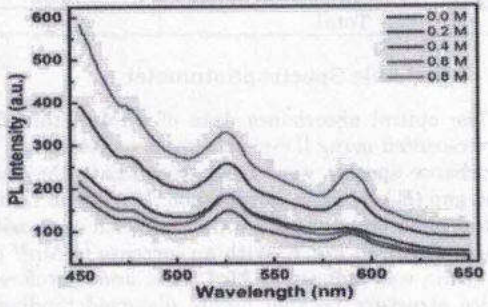

Fig. 7 – Photoluminescence spectra of CdMnS films

The vacancies created by Cd atom (surface defects) can either act as traps or as non-radiative recombination centers. Thus, PL analysis indicated that Mn^{2+} ions are distributed on the surface of the CdS lattice and fill the vacancies of Cd atoms.

3.7 Electrical Properties

The electrical resistivity of all CdMnS thin film structures was measured by two-probe method at room temperature. The electrical resistivity (ρ) of the sample has been determined using the relation

$$\rho = \frac{R A}{t} \tag{3}$$

where R is the resistance, t is the thickness, and A is the cross section area of the film. It is found that room temperature electrical resistivity has been enhanced with composition up to $x = 0.2$. For further increase in Mn^{2+} ions, room temperature electrical resistivity decreases.

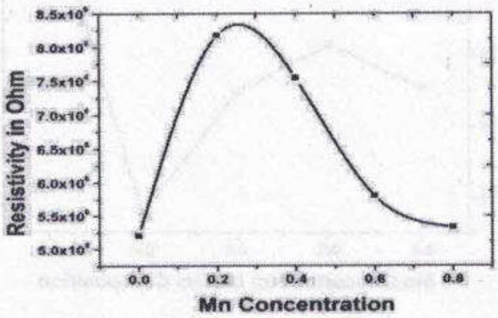

Fig. 8 – Effect of Mn concentration on resistivity of CdMnS films

This is shown in Fig. 8. The resistivity modulation by incorporation of Mn^{2+} ions into CdS lattice can be explained based on the following facts: Cd^{2+} and Mn^{2+} are co-deposited simultaneously and substitution of Cd^{2+} ions by Mn^{2+} is the predominant mechanism under this situation. The EDAX analysis of $Cd_{1-x}Mn_xS$ films also supported these observations. Also, as we add Mn^{2+} ions into CdS lattice, initially they do not react with CdS and do not form CdMnS alloy. Since the volume of Cd atom is greater than that of Mn atom, hence Mn^{2+} ions settle down at the interstitial sites of the CdS lattice. This, in turn, increases the number of scattering centers in the material, hence the resistivity. With further addition of Mn^{2+} to CdS lattice, some Mn atoms settle down at the interstitial sites of the CdS lattice, while other atoms form CdS as well as CdMnS. As a result, CdMnS dominates in the film, and hence the numbers of scattering centers reduces resulting in a decrease in resistivity. Thus, by the addition of Mn^{2+} ions into CdS films, resistivity values decrease. This property is more beneficial in designing solar cells.

4. CONCLUSIONS

The optimum condition with a bath temperature of 80 °C and pH ~ 1 yielded good quality thin films of $Cd_{1-x}Mn_xS$ using CBD technique. The effect of Mn^{2+} ion concentration on the optical, structural, morphological and electrical properties has been investigated by various analysis techniques. The structural characterization reveals the polycrystalline nature in mixed phases (hexagonal and cubic), and grain sizes are of the order of few nm. It is found that grain sizes are almost the same for all $Cd_{1-x}Mn_xS$ thin films with variation in Mn^{2+} ion concentration. The optical study reveals the increase in the band gap value with Mn^{2+} incorporation. The electrical resistivity was found to be enhanced with x up to 0.2 and then decreased with further increase in Mn^{2+} ion concentration. The photoluminescence result confirms that Mn^{2+} ions induce luminescence, exhibiting two broad peaks at 525 and 589 nm. Surface morphology also confirms almost uniform grain size of the crystals. EDAX analysis of the films shows that as Mn^{2+} ion concentration changes, the films become almost stoichiometric. Overall, the obtained $Cd_{1-x}Mn_xS$ thin films demonstrate the potential for use as a promising material for technological applications.

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AUTHOR CONTRIBUTIONS

Ashok E. Mali and Anil S. Gaikwad equally contributed in manuscript preparation, designing experimental setup, carrying out measurements and analysis part, Sanjay V. Borse and Rajendra R. Ahire contributed in composition of manuscript and result analysis.

REFERENCES

1. *Woodhead Publishing Series in Electronic and Optical Materials, Semiconductor Nanowires* (Ed. by J. Arbiol, Q. Xiong) (Woodhead Publishing: 2015).
2. C. Gümüş, C. Ulutaş, Y. Ufuktepe, *Opt. Mater.* **29** No 9, 1183 (2007).
3. R.N. Bhargava, *J. Cryst. Growth* **86**, 873 (1988).
4. L. Huang, Z.L. Wei, F.M. Zhang, X.S. Wu, *J. Alloy. Compd.* **648**, 591 (2015).
5. F. Iacomi, I. Salaoru, N. Apetroaei, A. Vasile, C.M. Teodorescu, D. Macovei, *J. Optoelectron. Adv. M.* **8**, 266 (2006).
6. H. Sekhar, G.T. Rao, P.H. Reddy, D.N. Rao, *J. Alloy. Compd.* **562**, 38 (2013).
7. J. Cheng, D. Fan, H. Wang, B. Liu, Y. Zhang, H. Yan, *Semicond. Sci. Technol.* **18 No 7**, 676 (2003).
8. D. Mugle, G. Jadhav, *AIP Conf. Proc.* **1728**, 020597 (2016).
9. C. Lai, X. Li, C. Liu, X. Guo, Z. Xiang, B. Xie, L. Zou, *Mater. Sci. Semicond. Process* **26**, 501 (2014).
10. M.P. Gonullu, S. Kose, *Metall. Mater. Trans. A* **48 No 3**, 1321 (2017).
11. S.M. Al-Jawad, *Int. J. Appl. Innov. Eng. Manag.* **3**, 329 (2014).
12. M. Ikeda K. Itoh, H. Sato, *J. Phys. Soc. Jpn.* **25**, 455 (1986).
13. C.T. Tsai, S.H. Chen, D.S. Chuu, W.C. Chou, *Phys. Rev. B* **54**, 11555 (1996).