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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

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.

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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.

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 constrains. 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-

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

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.
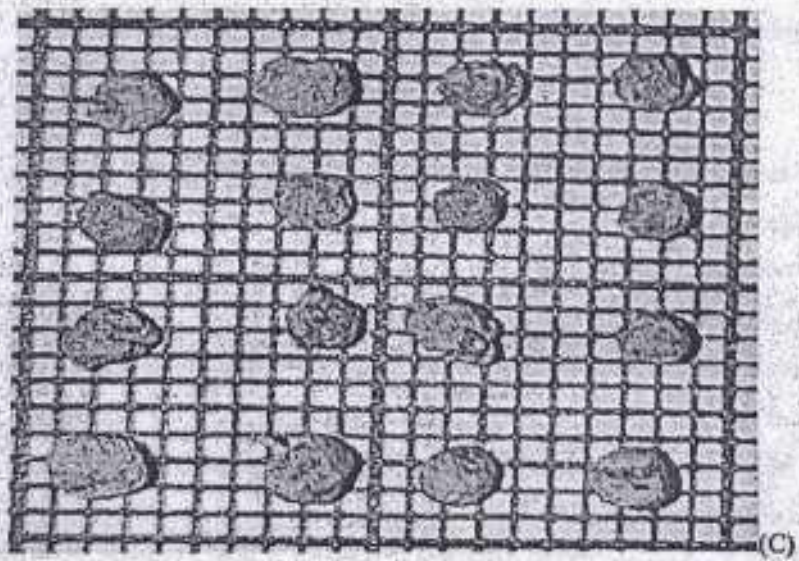
Effect of percentage of gel

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.
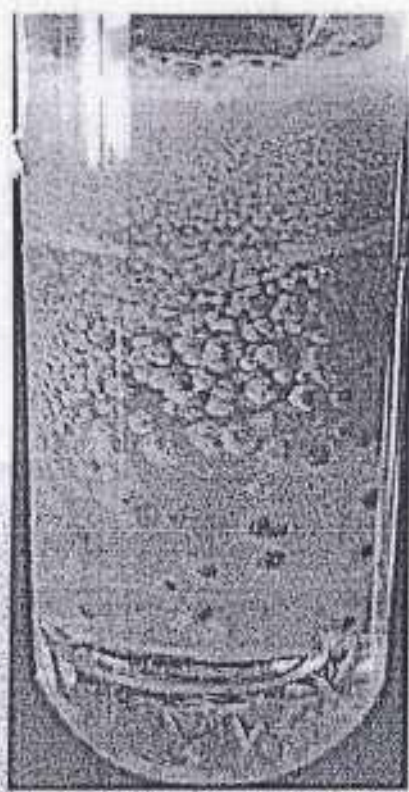
(a)
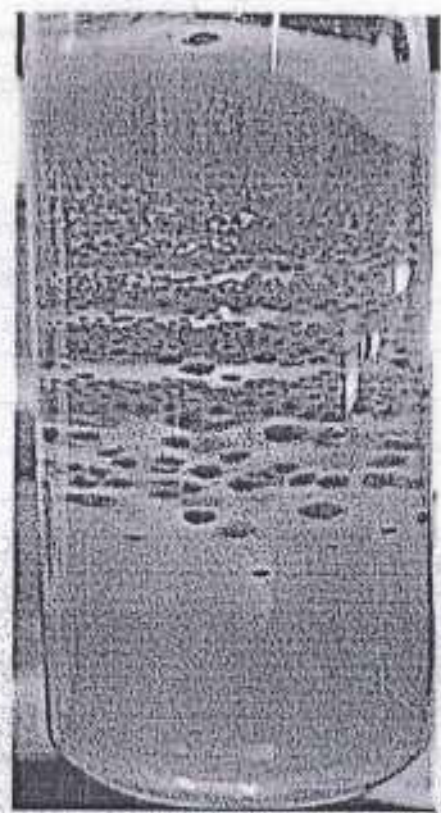
(b)

(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.

Acknowledgement:

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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:

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

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.

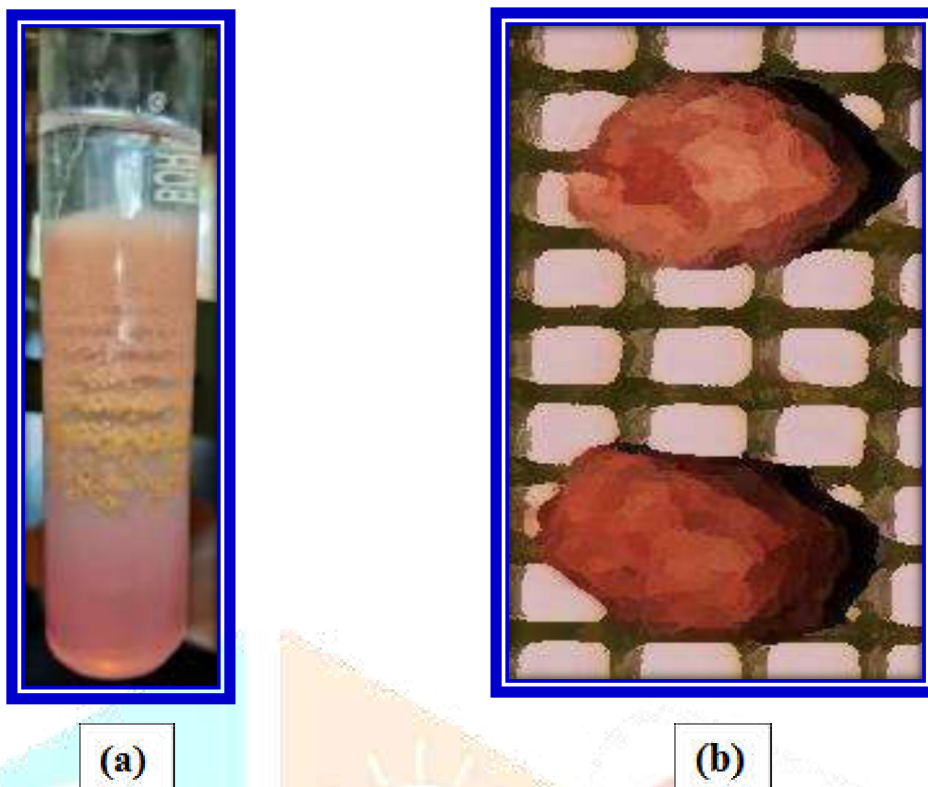| Sr.No	Condition Single Diffusion	Condition Single Diffusion
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2	Concentration of cobalt chloride	1.0M
3	Concentration of oxalic acid	1.0M
4	Volume of cobalt chloride	5.0 ml
5	Volume of oxalic acid	15 ml
6	Gel setting period	34 Hours
7	Gel aging period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

(a)   **(b)**

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.

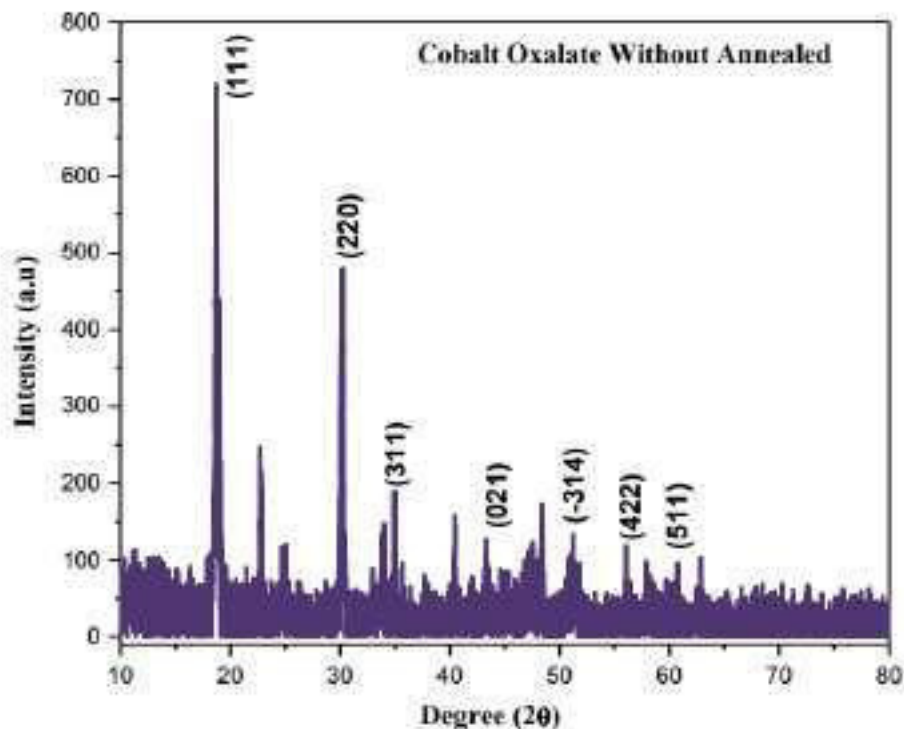| Parameters	Calculated	JCPDS data
System	Monoclinic (P)	Monoclinic
a	9·67638 Å	6·4534 Å
b	6·7156 Å	7·5009 Å
c	8·6822 Å	10·940 Å

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 $500 – 4500 cm^{-1}$ by KBr pellet method using SHIMADZU spectrophotometer at the department of Physics, Shivaji University Kolhapur. Figure 3 shows the FTIR spectrum of cobalt oxalate. The spectrum shows various frequencies of vibrational modes which confirm the presence of oxalate in the crystal.
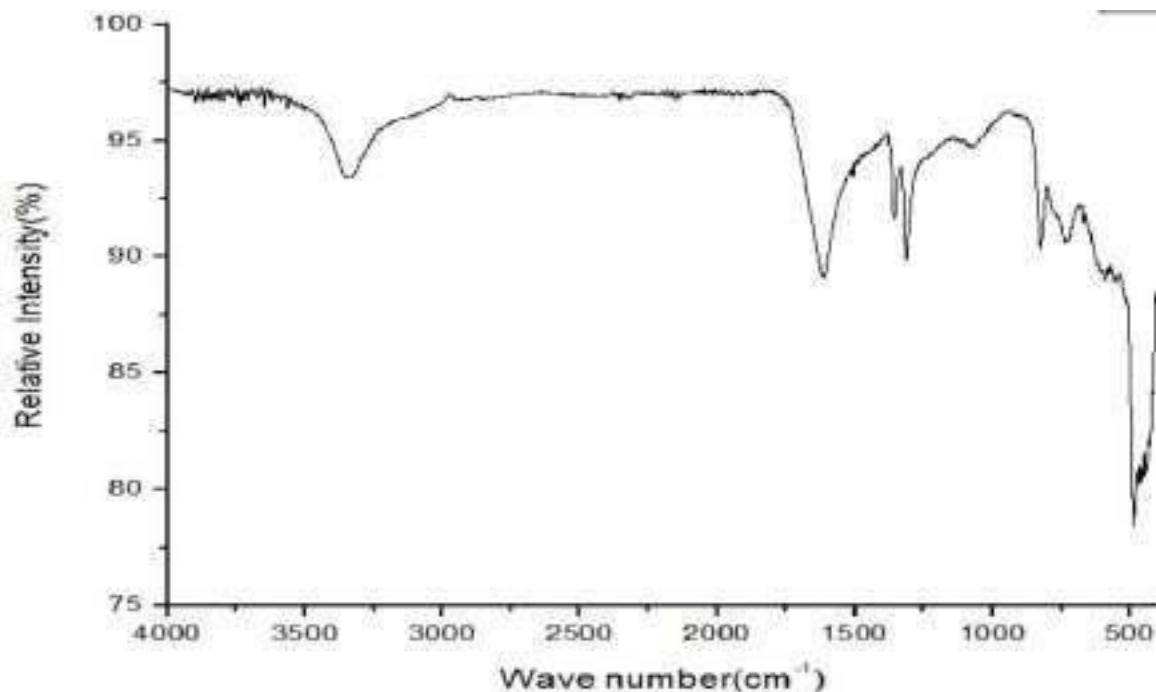
Figure 3: FTIR of Cobalt oxalate grown crystal

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.

Acknowledgements

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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

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

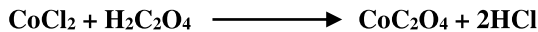$$CoCl_2 + H_2C_2O_4 \longrightarrow CoC_2O_4 + 2HCl$$

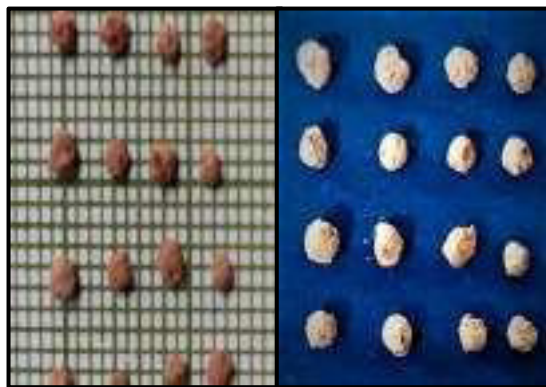Fig. 1 (a) working reaction during crystal growth in test tube

Fig. 1 (b) Harvested crystals of cobalt oxalate

III. RESULTS AND DISCUSSIONS
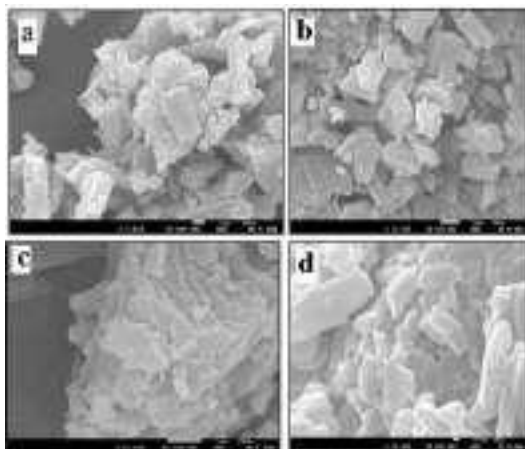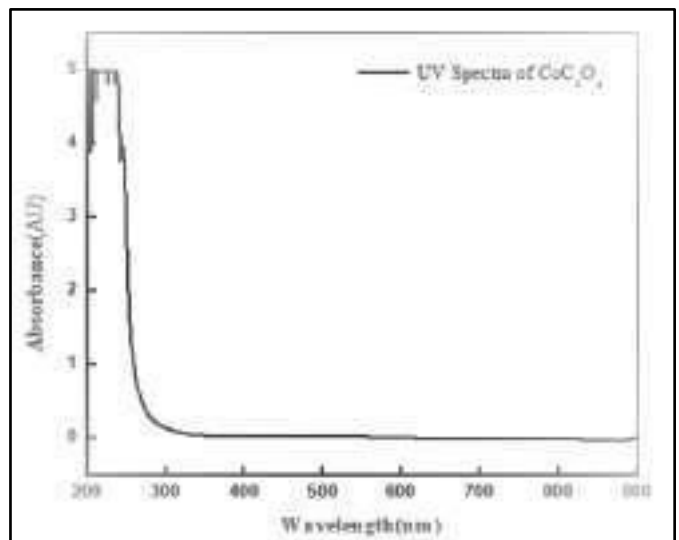
A. Scanning Electron Microscopy (SEM)

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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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 30ºC	25 to 30ºC	20 to 30ºC
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.

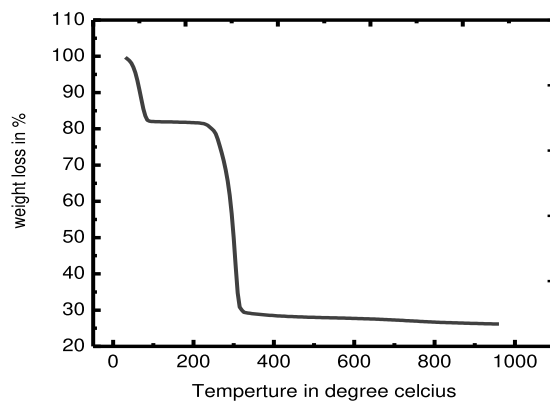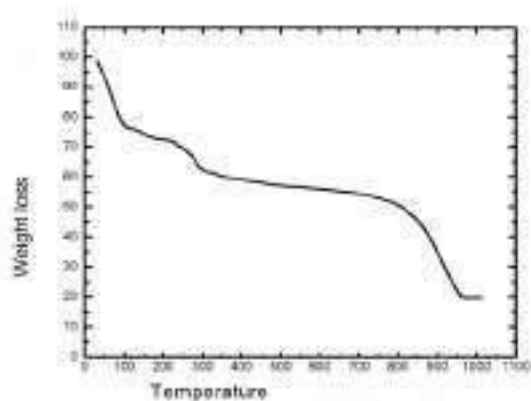| Compound	Steps	Temp. range ºC	Observed Weight loss %	Calculated weight loss %	Loss of Molecule
Lithium tartrate	I	25-95	18	18.18	2H$_2$O
	II	95-260	10	11.90	2H$_2$O
	III	260-750	15	15.50	2CO
	IV	750-950	30	32.10	2CO$_2$
Copper tartrate	I	25-210	2.15	2.50	5H$_2$O
	II	210-240	65.80	66.15	2H$_2$O
Mixed Lithium-Copper Tartrate	I	30-100	18	19.8	3H$_2$O
	II	100-210	1.5	2.0	CO
	III	210-320	49.5	50.42	CO$_2$, 2H$_2$O

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
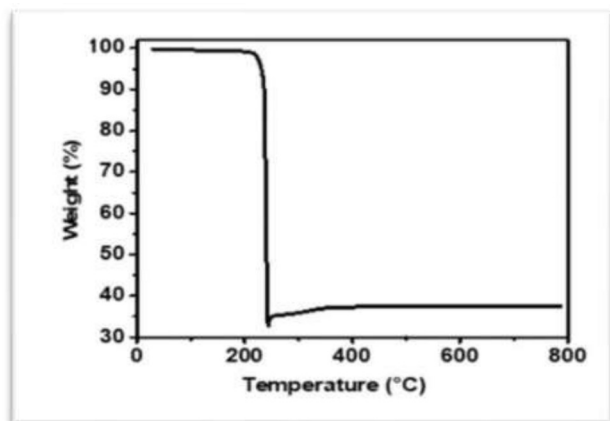

Fig. 3 TGA -DTA graph depicting the decomposition of lithium – copper tartrate crystal with respect to temperature

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.

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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

$$BaCl_2 \ + \ H_2C_2O_4 \ \longrightarrow \ BaC_2O_4 \ + \ 2HCl$$

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.
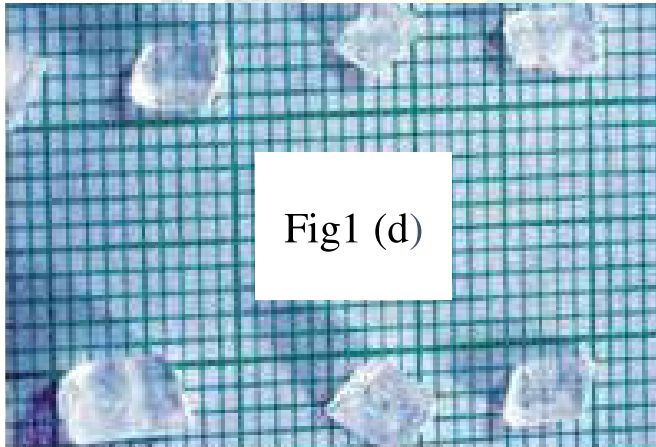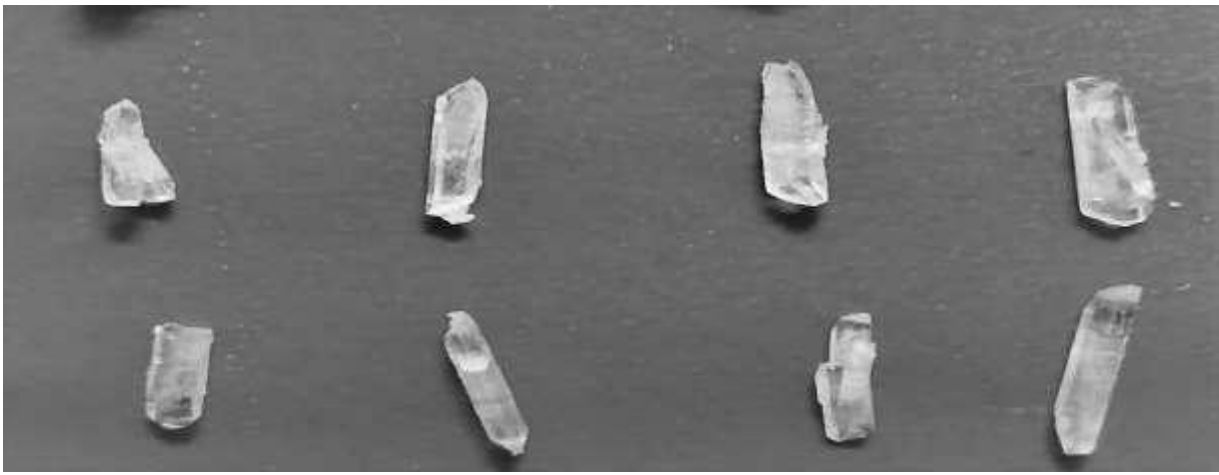
Fig1 (a)   Fig1 (b)   Fig1 (c)

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 ≠ b≠ c & α ≠ β ≠ γ.
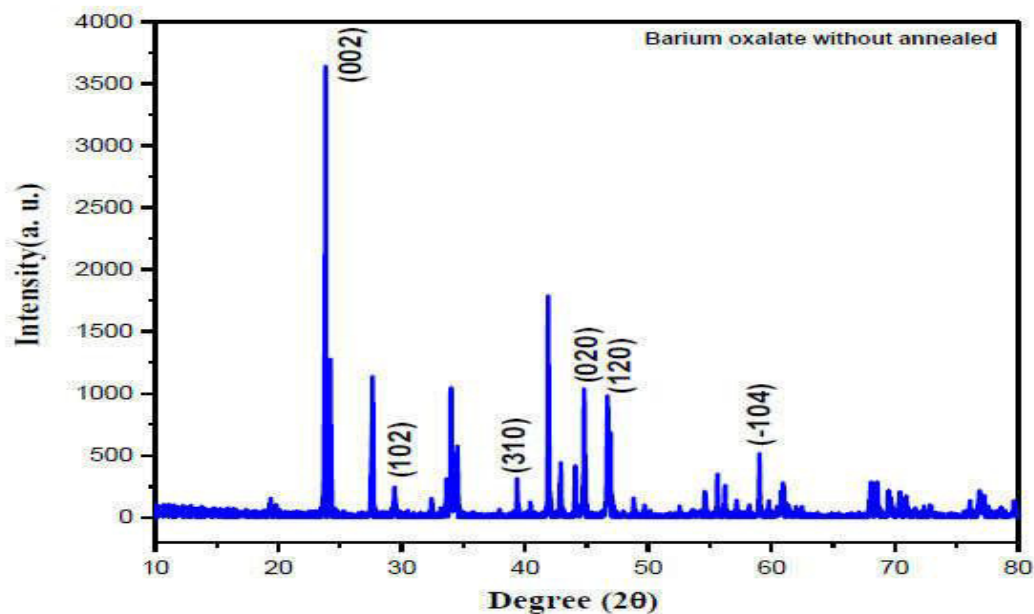

Figure 2: X-ray diffraction pattern of as grown barium oxalate single crystal.

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.
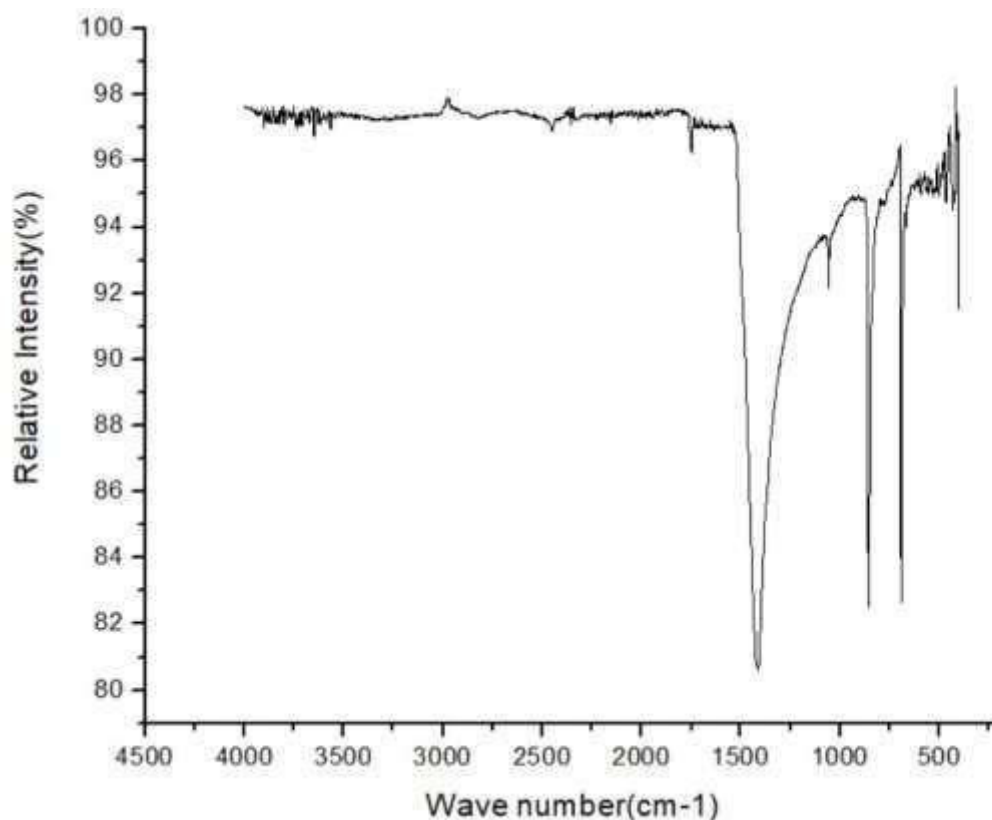

Figure 3. FTIR of Barium oxalate crystal

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].
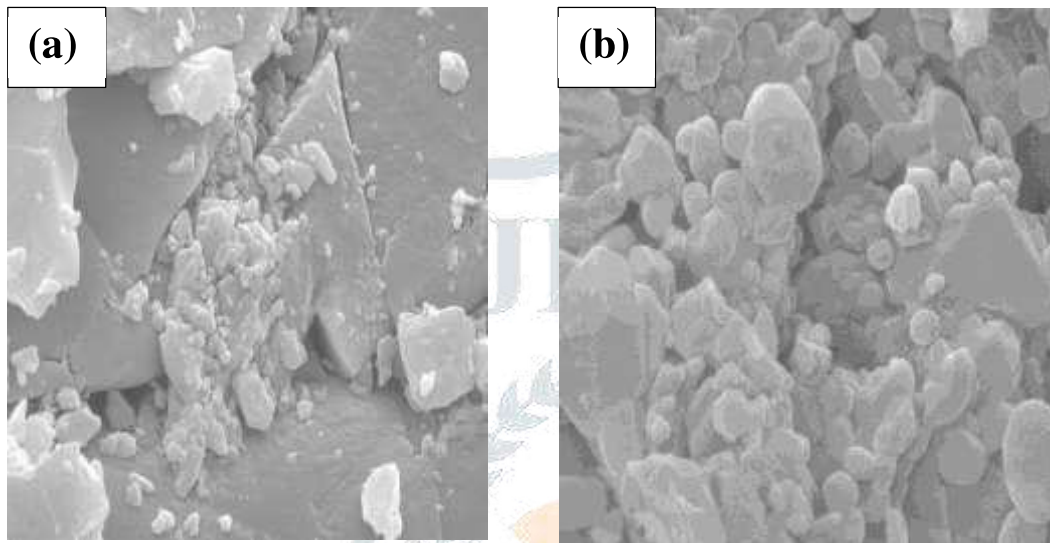

Figure 4: SEM images of as grown (a) barium oxalate crystal and (b) high resolution image.

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;

$$\text{Band gap energy (ev)} = \frac{1240}{\lambda\ (nm)}$$

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.

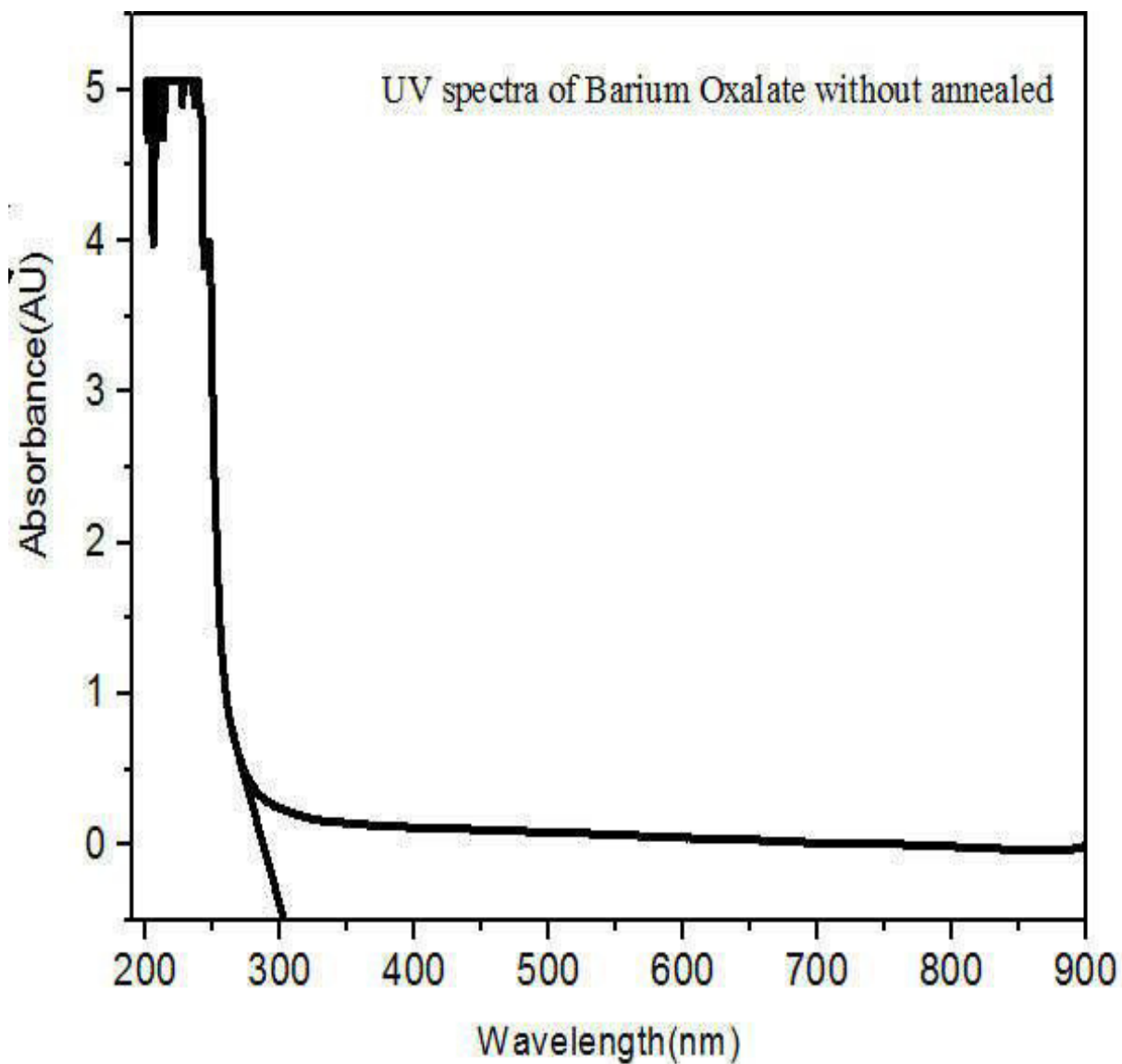| Crystal	Λ(nm)	Band gap Energy(ev)
Barium oxalate	305.00	4.06

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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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

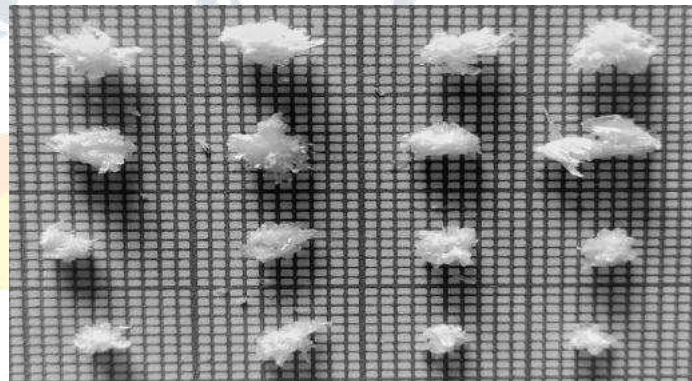|	
Concentration of agar-agar gel	5 %
Concentration of reactant, strontium chloride	1M
Concentration of supernatant, oxalic acid	1 M
Room temperature	27^0C
Gel aging period	4 days
Growth period	25 - 40 days
Quality of crystals	White colour, larger size (1mm × 1mm) transparent, shining crystals

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].
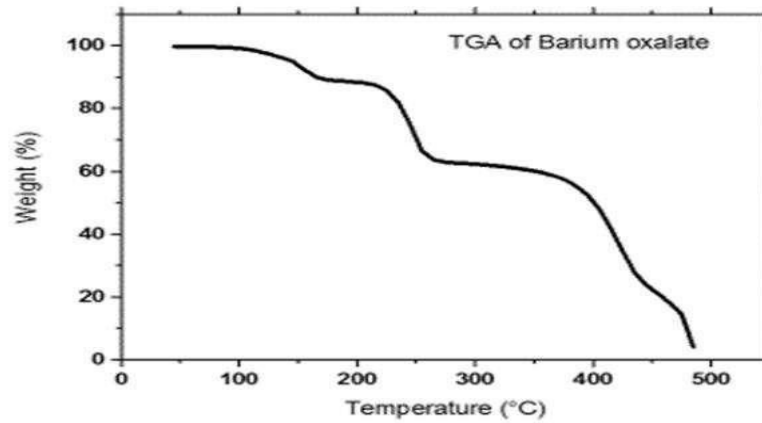
.

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 $153.^0C$ to 154.54^0C shows the decomposition of oxalate. Loss of weight at the temperature range $153.^0C$ 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
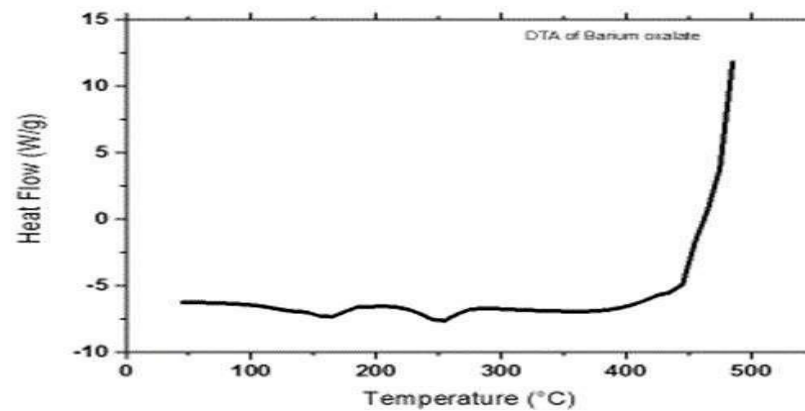
DTA results. DTA data is shown in table- 3

Figure 3 DTA of Barium oxalate

Table no.3 DTA data of barium oxalate

Peak recorded	Peak height	Nature	ΔH(J/gm)
37.51^0C	-0.600	Endothermic	-0.6406
154.54^0c	-0.5	Exothermic	-0.5344
250.07^0c	-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 25^0C to 450^0C.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 25^0C to 450^0C.at the rate 10c/min in Air .After reaching the temperature of 450^0C,the sample was hold for I minute at 450^0C and then again cooled from 450^0C to 25^0C 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 225^0C and equilibrium temperature 277^0C.At 225^0C (initiation temperature) initiation of phase change start & is completed at peak endo-down temperature of 250.07^0C(transition temperature).The temperature at which the sample and the reference come to the thermal equilibrium by thermal diffusion appears to be at 277^0C.The peak appeared in the DSC curve at 154.54^0C 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 430^0C and equilibrium temperature is 450^0C. At 430^0C (initiation temperature) initiation of phase change starts and is completed at peak endo- down temperature of 438.76^0C (transition temperature). The temperature at which the sample and the reference come to the thermal equilibrium diffusion appears to be 450^0C. The further phase transition occurs at temperature 438.76^0C 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.
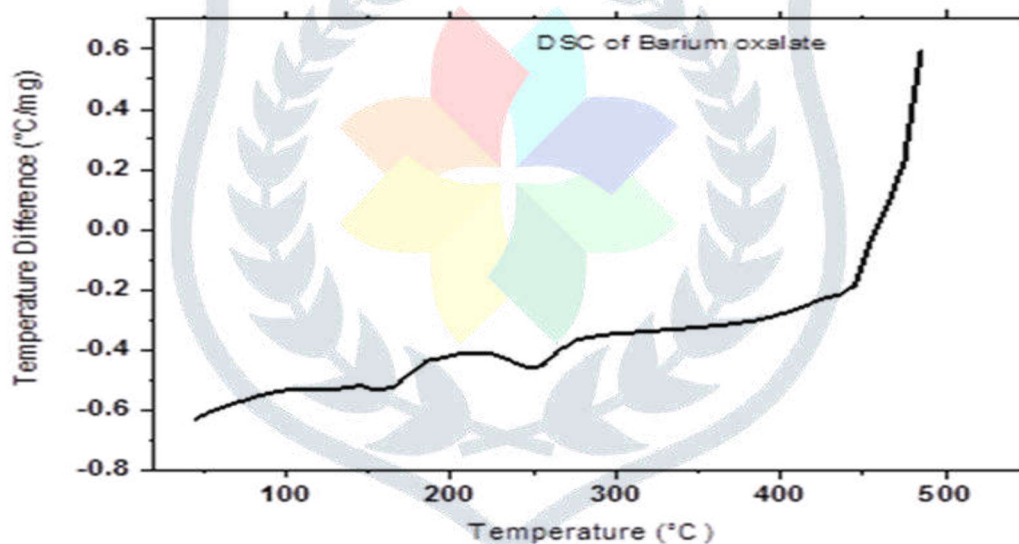

Figure 4 DSC curve for Barium oxalate

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	250.07^0C
		II	0.02199KJ/mole	438.76^0C

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]
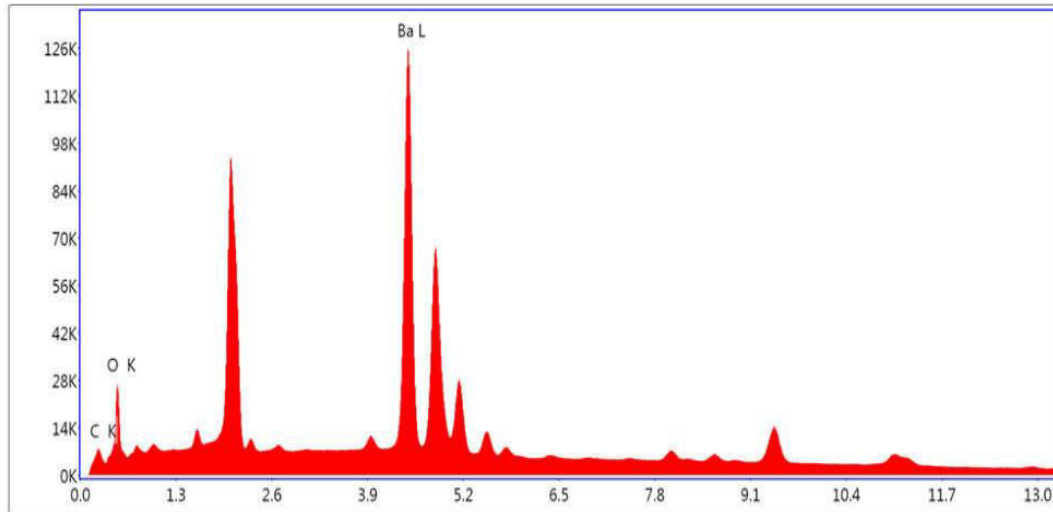
eZAF smaryt quant Results

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.

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Influence of Mn²⁺ Magnetic Ions on the Properties of Cd₁₋ₓMnₓS 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. Cd₁₋ₓMnₓS ($x = 0$, 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 (CdCl₂) and manganese chloride (MnCl₂) with thiourea (NH₄)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 Mn²⁺ ions on the film thickness of Cd₁₋ₓMnₓS films was investigated using weight difference technique. The film thickness of Cd₁₋ₓMnₓS films decreases as Mn²⁺ 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 Mn²⁺ 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 Cd₁₋ₓMnₓS with different values of the composition parameter x exhibited two emission peaks with different intensities. The measurement of the electrical resistivity of Cd₁₋ₓMnₓS 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 Cd₁₋ₓMnₓS thin films show promising technological applications in semiconductor industry.

Keywords: CdMnS films, Optical properties, Electrical properties, Chemical bath deposition, Mn²⁺ ion.

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 Mn²⁺ 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 Mn²⁺ 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 Cd₁₋ₓMnₓS thin films. However, the study of the influence of Mn²⁺ ions on various properties of Cd₁₋ₓMnₓS 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 Cd₁₋ₓMnₓS thin films for different values of the composition x and systematic study of the influence of Mn²⁺ ions on various characterization properties of Cd₁₋ₓMnₓS thin films.

2. EXPERIMENTAL DETAILS

Cd₁₋ₓMnₓS thin films were deposited using CBD technique. Cadmium chloride (CdCl₂), manganese chloride (MnCl₂) and thiourea (CH₄N₂S) were used as Cd²⁺, Mn²⁺ and S²⁻ ion sources, respectively. The stock solutions of CdCl₂ (1 M), MnCl₂ (1 M) and thiourea (1 M) all of AR grade were prepared using distilled water. The experimental solutions of CdCl₂ and MnCl₂ 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.
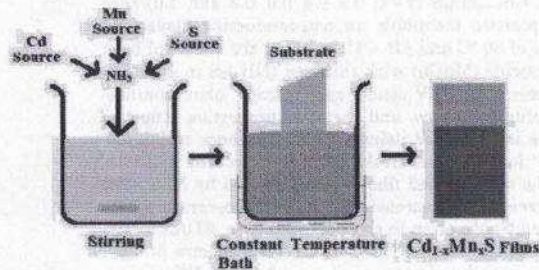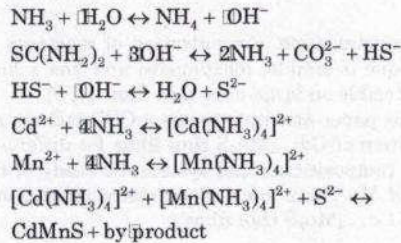

Fig. 1 – Process flow for deposition of $Cd_{1-x}Mn_xS$ films

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

$$NH_3 + H_2O \leftrightarrow NH_4 + OH^-$$
$$SC(NH_2)_2 + 3OH^- \leftrightarrow 2NH_3 + CO_3^{2-} + HS^-$$
$$HS^- + OH^- \leftrightarrow H_2O + S^{2-}$$
$$Cd^{2+} + 4NH_3 \leftrightarrow [Cd(NH_3)_4]^{2+}$$
$$Mn^{2+} + 4NH_3 \leftrightarrow [Mn(NH_3)_4]^{2+}$$
$$[Cd(NH_3)_4]^{2+} + [Mn(NH_3)_4]^{2+} + S^{2-} \leftrightarrow$$
$$CdMnS + by\ product$$

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.
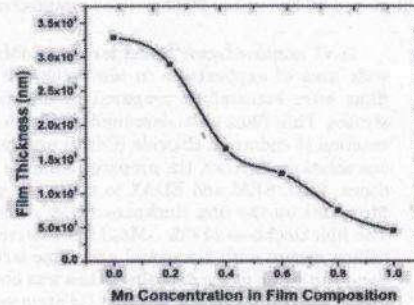

Fig. 2 – Variation in film thickness as a function of Mn concentration

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].
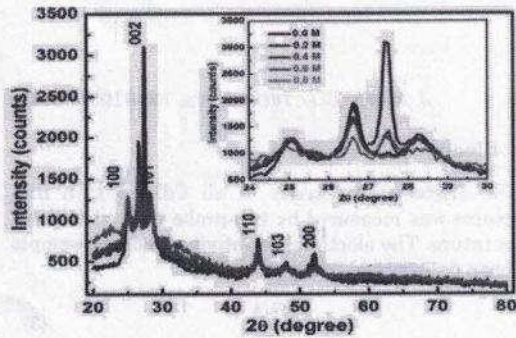
Fig. 3 – X-ray diffraction spectra of CdMnS films. The inset shows intense peaks
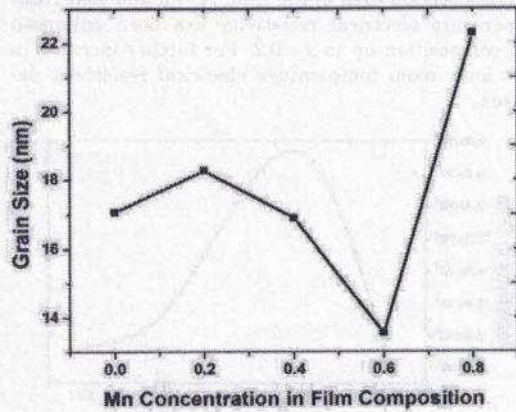

Fig. 4 – Effect of Mn concentration in the film composition on grain size

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 Mn²⁺ ion concentration in the coating solution. All the films were scanned at 20 K magnification.
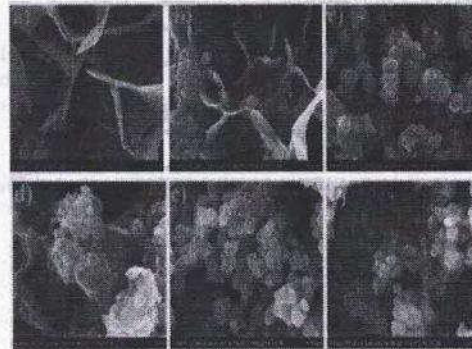

Fig. 5 – FESEM images of the films: a) CdS, b) $Cd_{0.8}Mn_{0.2}S$, c) $Cd_{0.6}Mn_{0.4}S$, d) $Cd_{0.4}Mn_{0.6}S$, e) $Cd_{0.2}Mn_{0.8}S$, f) MnS

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 Mn²⁺ 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 Mn²⁺ ion concentration in the coating solution resulted in the formation of nanocrystalline CdMnS compounds that is shown in Fig. 5c-e. When concentration of Mn²⁺ 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 Mn²⁺ ions, the strain was induced by Mn²⁺ 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].
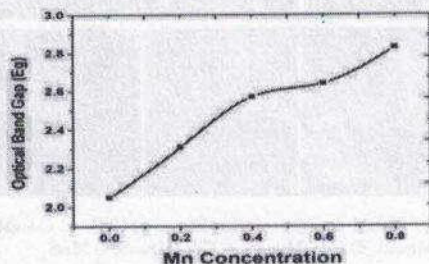

Fig. 6 – Effect of Mn concentration on band gap

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 un-shifted 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.
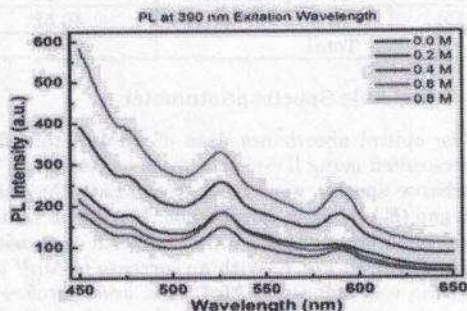

Fig. 7 – Photoluminescence spectra of CdMnS films

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

$$\rho = \frac{R \cdot A}{t} \qquad (3)$$

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.
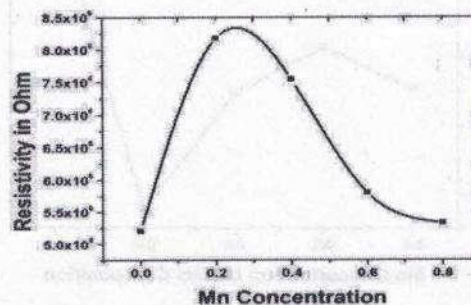

Fig. 8 – Effect of Mn concentration on resistivity of CdMnS films

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.

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