JETIR.ORG ISSN: 2349-5162 | ESTD Year : 2014 | Monthly Issue
JOURNAL OF EMERGING TECHNOLOGIES AND INNOVATIVE RESEARCH (JETIR)
An International Scholarly Open Access, Peer-reviewed, Refereed Journal

THE STUDY OF BARIUM-MAGNESIUM MIXED METAL OXALATE CRYSTALS GROWN BY AGAR-AGAR GEL TECHNIQUE

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Abstract: A new mixed-metal oxalates of barium and magnesium (BaMgO) were grown by using well known technique of crystal growth i.e gel technique. The mixed crystals were grown by single diffusion method at ambient temperature. Agar gel was used as the growth medium with test tube as crystallization container. The optimum conditions required for the growth of these crystals were worked well and grown transparent, rod-shaped barium-magnesium mixed metal oxalate crystals during a time period of 20-25 days. Fully grown crystals have size of 24 mm × 3mm × 2mm with well-defined morphology. The crystals were characterized by FTIR, XRD, TGA, and DTA analysis. The FTIR analysis exhibited presence of varied bonds related to molecular structure of BaMgO crystals. The novel metal barium which is present in the composition helps to enhance the size and transparency of the crystals. The obtained results are deliberated in details.

Index Terms **- Gel method, Agar gel, Crystal growth, Oxalates, Barium-magnesium oxalates, FTIR, XRD, TGA**

1. INTRODUCTION:

Crystals are used in a wide variety of applications, and their global requirement is continuously increasing. The crystals for these applications need certain minimum specifications in terms of purity and perfections. Naturally available crystals may not be of the required purity level. Moreover, many of the technological and commercially important crystals are all synthetic. Hence, growing crystals under controlled conditions has become a necessity [1, 2]. Numerous researchers have grown and studied characteristics of pure and mixed crystals of oxalates by gel method using silica and agar gel [3-8]. Now-a-days, hardly any solid-state investigations are made without an attempt of using well-developed crystals. Most rare earth metal oxalates and molybdates have wide applications in electro and acousto-optical devices [9, 10]. Growth from gel has proved to be very useful for materials with low solubility including oxalates [11].

The agar gel technique is an inexpensive and simple for growing single crystals and satisfies all required conditions for crystallization [4-6]. There are few efforts in the literature on the growth of oxalate by agar gel method [5, 6, 12-14]. Some of investigators have obtained crystallization of barium oxalate in agar gel and studied its characterization [6, 15]. Mixed oxalate crystal using the agar gel method has been hardly studied. The growth of barium-magnesium mixed oxalate crystals yet had not been reported. The intention of this work is to grow barium-magnesium mixed crystal using agar gel by single diffusion techniques. In this study, we have successfully grown barium-magnesium mixed oxalate using agar gel. The grown crystals were subjected to characteristic studies such as FTIR, XRD, TGA, and DTA.

2. EXPERIMENTAL:

The growth of barium-magnesium mixed oxalate (BaMgO) was carried out in agar-agar gel by single diffusion technique. In this method, glass test tubes of size 30 cm in length and 2.5 cm in diameter were used as crystallization vessels. AR-grade chemicals, oxalic acid, barium chloride and magnesium chloride were used as reactants. The gel solution was prepared by mixing agar-agar powder in double distilled water at boiling temperature [2, 16]. In the present study, the 1% Agar-agar gel is used by dissolving 1 gm of agar-agar powder in 100 ml of double distilled water at boiling temperature and cooled down slowly. The gelation takes place during cooling [1-2].

Table 1: Optimized growth parameters

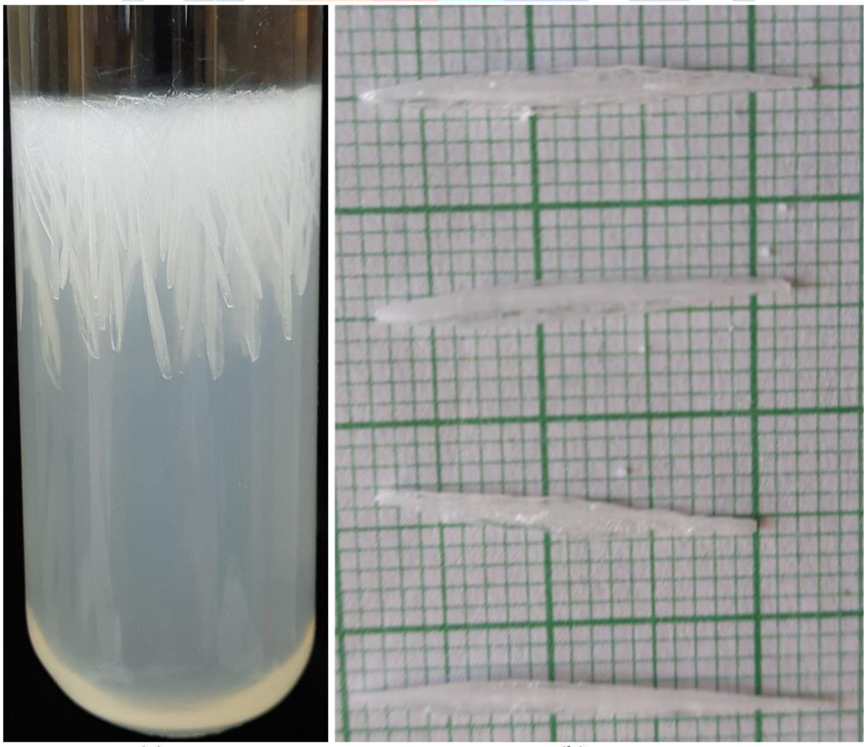
Crystallization parameter	Values
Crystallization temperature	30 - 38 °C
Molarity of barium chloride	1 M
Molarity of magnesium chloride	1 M
Molarity of oxalic acid	1 M
% of Agar gel	1 %
Agar gel setting time	1 day
Gel aging	3 days
Nucleation period	4 days
Maturity period	25 days

In single diffusion technique, the hot aqueous agar gel was mixed thoroughly with desired concentration and volume of mixture of magnesium chloride (0.5-1M, 5 mL) and barium chloride (0.5-1M, 5 mL) and kept in the test tube for setting and aging at room temperature in dust free atmosphere. After setting and aging of gel, an aqueous supernatant solution of oxalic acid (0.5-1M, 20 mL) was poured slowly over the set gel along the walls of tube with the help of pipette. We observed good quality crystals of BaMgO at 1M concentration of reactants ($MgCl_2$, $BaCl_2$ and Oxalic acid). The optimized conditions for grown crystal shown in the Table 1.

3. RESULTS AND DISCUSSION:

The set and aged gel was impregnated with supernatant solution (oxalic acid) and after 4-days nucleation observed just below the interface. It was also noted higher nucleation density at the gel-solution interface, resulting large number of crystals and less spacing between crystals which minimizes the size of the crystals. The crystal size was noted every day and it was observed that the crystal size gradually increased with time and finally the growth rate ceased after a period of 25 days. The average size of the crystals was 24 mm×3mm×2mm. The parameters such as concentration of reactants, pH of gel, impurities in the solvent, gel setting time etc., have considerable effect on growth rate. Fast growth rate in one particular direction leads to the formation of elongated crystals [17].

Figure 1(a) shows photograph of rod and needle shape BaMnO crystals in single diffusion and Fig. 1(b) shows some good quality harvested crystals.



(a) (b)

Figure 1: (a) Rod and needle shaped BaMgO crystals at the interstitial of the gel, (b) Some good quality extracted BaMgO crystals.

4. CHARACTERIZATION:

4.1 FTIR SPECTRAL ANALYSIS:

IR deals with the interaction between a molecule and radiation from the electromagnetic region and very helpful for identification of a compound. It reveals and analyses the presence of functional groups in the grown crystals [18, 19]. FT-IR spectrum of gel grown BaMgO crystal was recorded in the region 4000-400 cm^{-1} on “Agilent Cary 630 FTIR Spectrometer”. The spectrum is shown in Figure 2 and the bands assigned to the various types of vibrations are summarized in Table 2.

Table 2: Spectral assignments of IR peaks.

Wavenumber (cm^{-1})	Assignment
3563.3, 3429.2	-O-H stretching
1651.2	>C=O Stretching
865.5	-O-H plane bending
756.6, 715.5	M-O Stretching

The spectrum depicts information about the different functional groups associated with the grown crystal. The peaks at 3563.3 cm^{-1}, 3429.2 cm^{-1} were stretching vibrations of the water molecules [20]. Strong absorption occurred at 1651.2 cm^{-1} attributed to the combined effect of asymmetric stretching of >C=O function and the bending of water molecules. The absorption peaks at 865.5 cm^{-1} indicates the presence of -O-H group out of plane bending. The absorption peaks below 800 cm^{-1} are due to metal-oxygen (M-O) stretching vibrations [15, 19]. The FTIR spectrum of the BaMgO crystals grown in agar-agar gel complies with the reported IR spectrum of BaMgO in SMS gel [20].

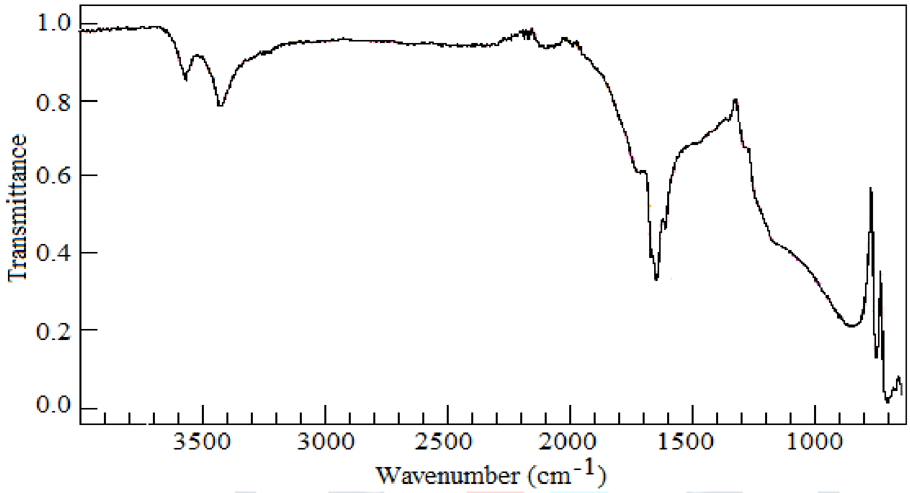


Figure 2: FTIR spectrum for BaMgO crystal.

4.2 POWDER XRD ANALYSIS:

The powder XRD pattern of BaMgO crystal is shown in Figure 3. The samples were scanned over the range of 2θ values. It was indexed using Rietveld refinement method to identify the reflecting planes. The XRD data was analyzed using FullProf Suite software and Crystallography Open Database (COD) CIF file. The existence of sharp and intense peaks at specific Bragg angles 2θ indicates the high crystalline nature of the grown crystals. The XRD peaks obtained for the BaMgO crystals are well matching with COD database. The obtained crystals of barium-magnesium oxalate are observed to be trigonal crystal system.

The 2θ values, d values and the indices of major peaks observed in the spectra of the BaMgO are given in Table 3. The obtained d-spacing and miller indices (h k l) are in good agreement with the reported values of the pure barium oxalate crystals which already have been reported [15]. From the XRD studies, the unit cell parameters have been identified and tabulated in Table 4. The mixing has brought about a change in the cell dimensions due to the change in bond lengths resulting into a change in cell volume [21].

Table 3: BaMgO XRD data

2θ	d Å	Relative Intensity (cts)	Indices
20.98	4.2293	152.74	(0 1 2)
22.94	3.8731	154.95	(0 1 4)
29.56	3.0199	196.27	(0 1 8)
33.74	2.6545	143.02	(0 1 10)
35.72	2.5111	142.52	(1 1 0)
39.34	2.2880	137.94	(1 1 6)
41.90	2.1544	140.13	(2 0 2)
48.86	1.8622	143.58	(1 1 12)

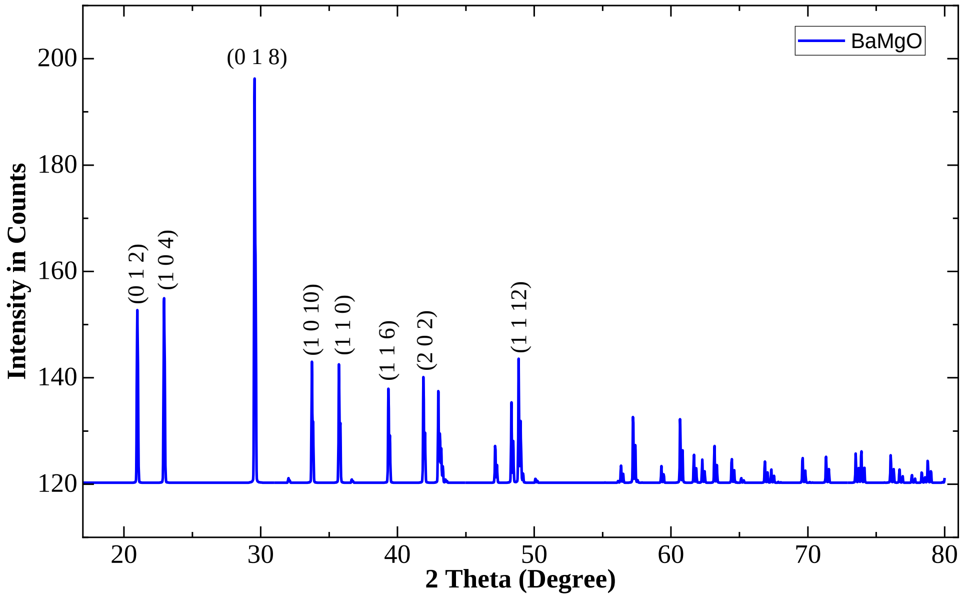


Figure 3: Powder XRD of BaMgO crystal.

Table 4: Crystal parameters of BaMgO crystals.

Crystal Parameters	a Å	b Å	c Å	α°	β°	γ°	Volume Å³	Crystal system
BaMgO	5.0083	5.0083	33.3987	90	90	120	725.50	Trigonal

4.3 THERMAL ANALYSIS (TGA AND DTA):

Thermogravimetric analysis (TGA) is a thermal analysis in which changes in physical and chemical properties of materials are being observed as a result of increase in temperature (with constant heating rate). The sample undergoes specific weight losses that are separated by enough temperature to easily identify decomposition products. Figure 4 displays the TGA and DTA curves of the BaMgO sample. Mass losses (step 1) in TG curve of the composite are observed to be 30.5% below 215 °C, this mass loss principally linked to the loss of H_2O molecule. Next comes the second step from 250 to 400 °C, shows the mass loss of 2.15%, often attributed to the loss of CO. From 450 °C, the emission of CO_2 progressively increases until 800 °C (not shown in the plot) and explains the decomposition of carbonate which leads to the formation of barium-magnesium oxide [22].

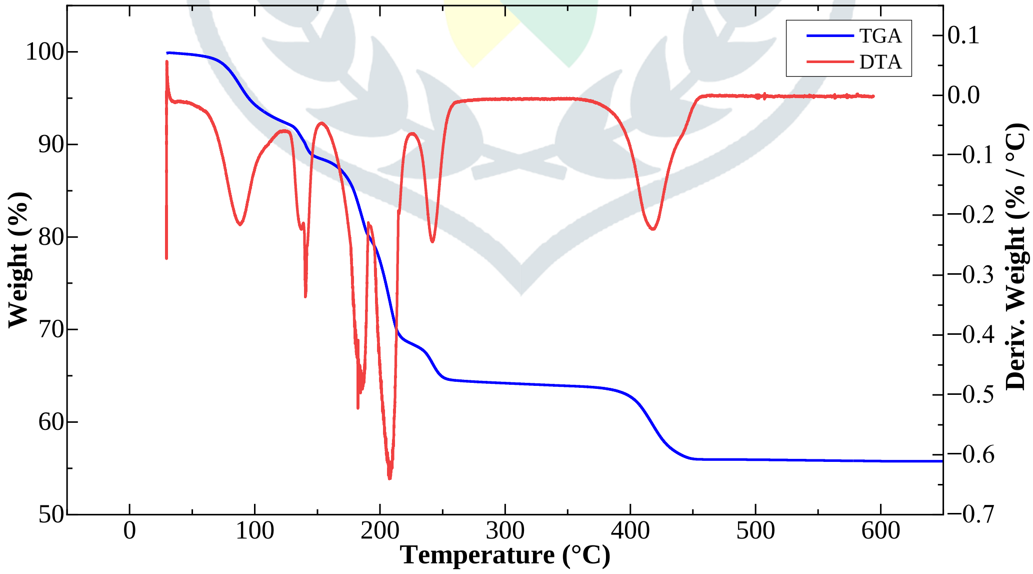


Figure 4: TGA and DTA for BaMgO crystal

5. CONCLUSIONS:

The barium-magnesium mixed metal oxalate (BaMgO) crystals were grown by single diffusion techniques using agar-agar gel as a growth medium. Different morphologies, viz., rod and needle shapes crystals in single diffusion growth were obtained. The crystal belongs to trigonal crystal system. The FTIR spectroscopic analysis confirms presence of various functional groups. X-ray diffraction spectra have confirmed the crystalline nature of grown crystals. The three oxalate decomposition stages, the dehydration, decarbonization and carbonation were found in thermogravimetric analysis.

6. ACKNOWLEDGEMENT:

The authors are grateful to Tapi Valley Education Society, Faizpur, MS, India (425503) and Dr. P. R. Chaudhari, Principal, Dhanaji Nana Mahavidyalaya, Faizpur for constant support and encouragement, and wish to thank Mr. Amol Rane, for helping in the present study.

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