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GROWTH AND CHARACTERIZATION OF BARIUM-MANGANESE OXALATE CRYSTALS GROWN IN AGAR GEL

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Abstract: Barium-manganese oxalate (BaMnO) 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 agar gel method is a low-cost and an easiest alternative to other preparation methods for the production of barium manganese oxalate crystals. The optimum conditions required for the growth of these crystals are worked out. Transparent, rod and sword shaped barium-manganese oxalate crystals were grown during a time period of 30 days. Fully grown crystals have size 28 mm× 3mm× 2mm with well-defined morphology. The grown crystals were characterized by FTIR, XRD, TGA, and DTA.

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

1. INTRODUCTION:

The crystals are supposedly to be pillars of modern technology. They have attracted human being from prehistoric times due to their beauty; however, their large-scale applications for devices have been realized from last seven decades. With the advancement of technology researchers focused on the quality of grown crystals and understanding their formation. Among the various crystallization techniques, crystallization in gels has found wide applications in the fields of technology. Also, by using this method it is possible to grow single crystals with very high perfection that are difficult to grow by other techniques [1]. This has attracted many researchers to grow single crystals of metallic ions or mixture of metallic ions by gel method. The agar-agar gel technique is an inexpensive and simple for growing single crystals and satisfies all required conditions for crystallization [2]. Agar gelation occurs only by its agarose content that is produced exclusively by hydrogen bonding. Its honeycomb structure is formed by the polymeric chain which aggregate through hydrogen bonding in aqueous medium. Due to this unique gelling property, it provides porous medium that allows only the vertical transportation of the ions. Additionally, it provides diffusional path to chemical species, invariably all over the experiment [3, 4, 5]. Metal oxalate crystals are found to be very useful in diverse and wide applications in electrical, optical devices, medical, acousto optical devices, synthesis of super-conducting compound, etc [6].

Oxalate ions $(C_2O_4)^{2-}$ are involved in building a variety of molecular structures by incorporating suitable metal ions in the crystal lattice. Growth of barium oxalate crystals in agar-agar gel has been reported [5, 6, 7]. Mixed oxalate crystal using the agar-agar gel method has been hardly studied. The growth of manganese mixed barium oxalate crystals yet had not been reported. The intention of this work is to grow manganese mixed barium crystal using agar-agar gel by single diffusion techniques. In this study, we have successfully grown barium-manganese oxalate using agar-agar gel. The grown crystals were subjected to characteristic studies such as FTIR, XRD, TGA, and DTA.

2. EXPERIMENTAL:

Barium-Manganese oxalate was grown by single diffusion method in agar-agar gel. The chemicals used in this study were oxalic acid ($C_2H_2O_4$), barium chloride ($BaCl_2.2H_2O$), manganese chloride ($MnCl_2.4H_2O$) and agar-agar gel (commercial grade). A single glass tube of the length 30 cm and diameter 2.5 cm was used as crystallizing apparatus.

$$BaCl_2.2H_2O + MnCl_2.4H_2O + 2C_2H_2O_4.H_2O \rightarrow Ba{:}Mn\ (C_2O_4)_2\ 3H_2O{+}4HCl{+}5H_2O$$

The gel solution was prepared by dissolving agar-agar powder in double distilled water at boiling temperature [1, 4, 5]. The 1% Agar-agar gel is used by dissolving 1 gm of agar-agar powder in 100 ml of double distilled water.The clear solution is boiled and cooled down slowly. The gelation takes place during cooling.

In single diffusion, hot aqueous agar gel and mixture of manganese chloride (0.5-1M, 5 mL) and barium chloride (0.5-1M, 5 mL) solutions were thoroughly mixed and kept in the test tube for setting. This highly homogeneous mixture of uniform composition was kept in dust free atmosphere at room temperature. After setting and aging the gel, 20 mL solution of oxalic acid (0.5-1M), was added.

On reversing the reactants, in single diffusion, hot aqueous agar gel and 5 mL oxalic acid (0.5-1M) solution were thoroughly mixed and kept in the test tube for setting. This highly homogeneous mixture of uniform composition was kept in dust free atmosphere at room temperature.After setting and aging, the gel, mixture of barium chloride (0.5-1M, 10 mL) and manganese chloride (0.5-1M, 10 mL) was added to the above gel.

3. RESULTS AND DISCUSSION:

In both processes, it was observed after few days that, the nucleation was seen at the interstitial and inside the gel. This nucleation was further increased and took 30 days for its complete growth. After one-month, rod and sword like shaped barium-manganese oxalate crystals were grown inside the gel as shown in Figure 1(a) and Figure 1(b) portrays some good quality transparent as well as rod and sword like shaped crystals. Different 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 like dendrite, rod [5]. From the repeated trials and measurements, optimized crystallization parameters for the growth of barium-manganese oxalate crystal are given in Table 1.

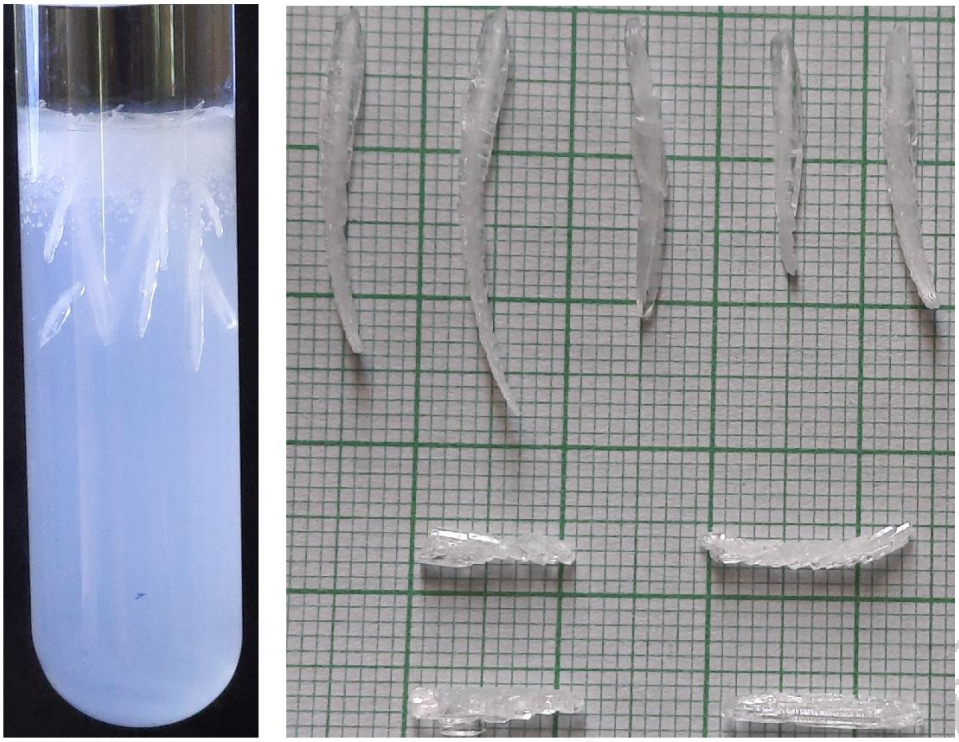

Figure 1: (a) Rod and sword like shaped BaMnO crystals at the interstitial of the gel, (b) Some good quality transparent as well as rod and sword like shaped crystals

Table 1: Optimized growth parameters

Crystallization parameter	Values
Crystallization temperature	30 - 38 ºC
Molarity of barium chloride	1 M
Molarity of manganese chloride	1 M
Molarity of oxalic acid	1 M
% of Agar gel	1 %
Agar gel setting time	1 day
Gel aging	4 days
Nucleation period	1 week
Maturity period	30 days
Shape of the crystal	Rod and Sword
Nature of the crystal	Transparent
Maximum weight and length of crystal	196 mg, 3 cm

4. CHARACTERIZATION

4.1 FTIR SPECTRAL ANALYSIS:

In the present IR study Attenuated Total Reflection (ATR) method was used. IR deals with the interaction between a molecule and radiation from the electromagnetic region and is very helpful for identification of a compound [8]. FT-IR spectrum of gel grown barium-manganese oxalate crystals was recorded in the region 4000-400 cm^{-1} on "Agilent Cary 630 FTIR Spectrometer". In this analysis, the infrared radiations induce transitions in a molecule between rotational and vibrational energy levels of the ground electronic energy state. The spectrum is shown in Figure 2 and the bands assigned to the various types of vibrations are summarized in Table 2. The strong absorption peaks in between 3000 $cm^{-1}$and 3600 cm^{-1} assigned to be due to the symmetric and asymmetric stretching modes of -O-H groups. The bands around 1623 cm^{-1} were attributed to the asymmetric stretching vibrations of >C=O groups of the $C_2O_4^{2-}$ ions together with the bending mode of water. The peaks at around 1366 cm^{-1} and 1315 cm^{-1} are assigned to >C=O group asymmetric stretching. The absorption peaks at 818 cm^{-1} indicates the presence of -O-H out of plane bending. The absorption bands below 700 cm^{-1} are due to metal-oxygen (M-O) stretching vibrations [7, 8, 9].

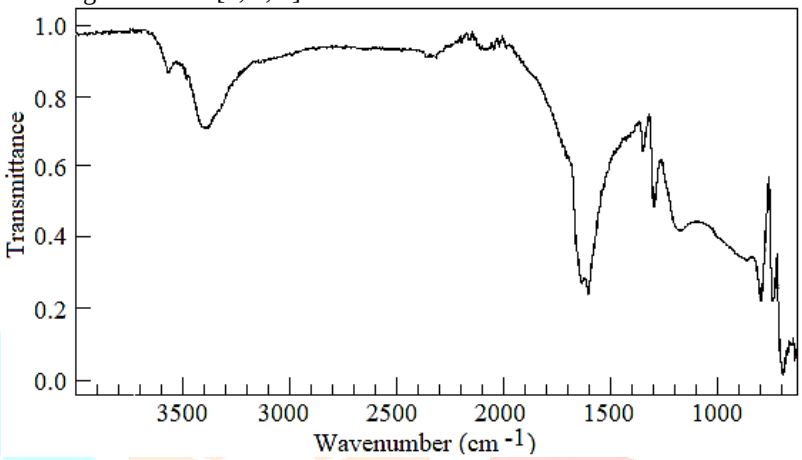

Figure 2: FTIR spectrum for BaMnO crystal

Table 2: Spectral assignments of IR peaks

Wavenumber (cm^{-1})	Assignment
3373.2	-O-H stretching
1623.3	>C=O stretch of carbonyl group
1366.1, 1315.8	>C=O Stretching
818.2 and 728.7	-O-H out of plane bending
728.7, 652.2	M-O Stretching

4.2 POWDER XRD ANALYSIS:

The powder XRD studies were carried out using Small Angle X-ray Scattering, ANTON PAAR, (SAXSPACE) with CuKα radiation (λ=1.54056 Å). The samples were scanned over the range of 2θ values (20^0 to 80^0). The powder XRD pattern of barium-manganese oxalate is shown in Figure 3. 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 (space group: R-3m) [10, 11]. The sharp and well-defined peaks at specific 2θ values testify the excellent crystalline nature and purity of the grown crystal. The 2θ values, d values and the indices of major peaks observed in the spectra of the barium-manganese oxalate 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 [6, 12, 13].

Table 3: BaMnO XRD data

2θ	d Å	Relative Intensity (cts)	Indices
24.8668	3.58	916.67	(104)
27.9476	3.19	1681.97	(015)
31.5236	2.84	2623.62	(110)
40.5645	2.22	747.22	(024)
42.6704	2.12	1042.14	(205)
54.0541	1.7	504.24	(125)
56.2194	1.63	525.93	(300)
65.9405	1.42	542.33	(220)

Calculation of cell parameters reveals that barium-manganese oxalate belong to trigonal crystal system having space group R-3m. The cell parameters of crystal are worked out using FullProf software and are a=5.6553 Å, b=5.6553 Å, c=20.8993 Å, α=90.0º, β=90.0º, γ=120.0° and unit cell volume 578.86 $Å^3$. The experimental d-values are in conformity with the calculated

ones using the above cell parameters for pure and doped crystals. Mixing has brought a change in cell dimensions due to the change in bond length [14].

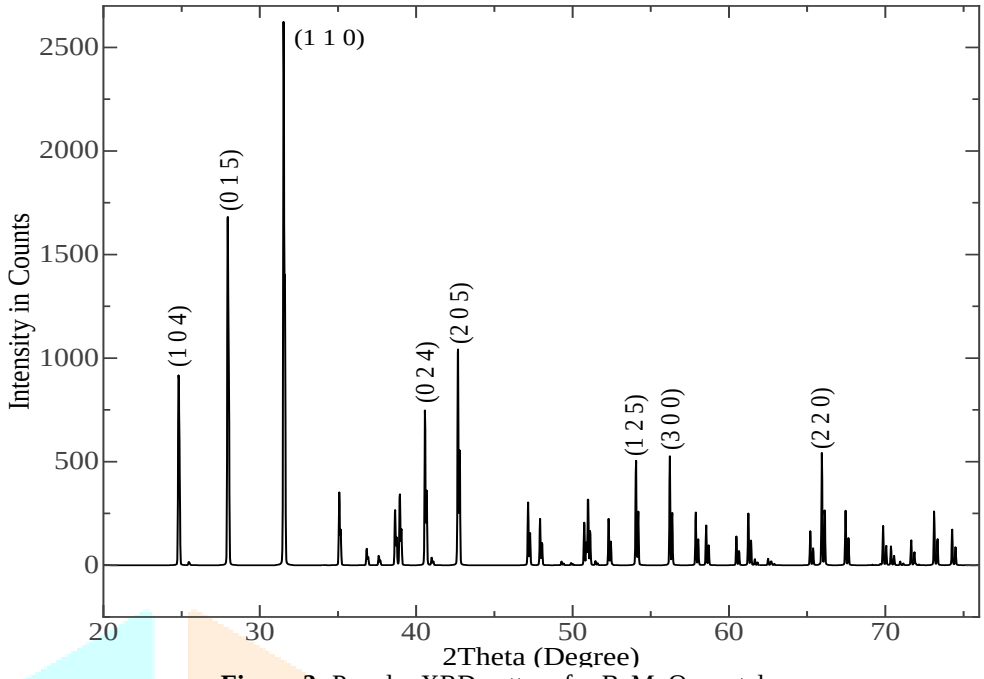

Figure 3: Powder XRD pattern for BaMnO crystal

4.3 THERMAL ANALYSIS (TGA AND DTA):

The thermal analysis studies were carried out using TGA 55 from TA Instruments United States. The initial mass of the material taken in the form of powder was 5.75 mg and the final mass left after the experiment was 3.325 mg at 600 °C and found the total weight loss is 42.713 %. From the graph (Figure 4) it is seen that barium-manganese oxalate is stable up to 100 ºC. The well-defined sharp peaks from 100-250 °C attribute to major weight loss and measured weight loss about 27%. The horizontal portion 250-270 ºC shows the thermal stability of the mixed crystal. Second decomposition of crystal with the elimination of CO occurs in the temperature range 270- 300 ºC and from 300-390 ºC horizontal portion shows the thermal stability of the crystal. Third decomposition occurs from 390-430 ºC and CO_2 released. On further heating above 700 °C (not shown), the crystal is decomposed into oxide [7, 8]. In the differential thermal analysis, temperature changes in the sample were due to the reactions caused by phase changes, decomposition, oxidation, reduction, or other chemical reactions [15, 16].

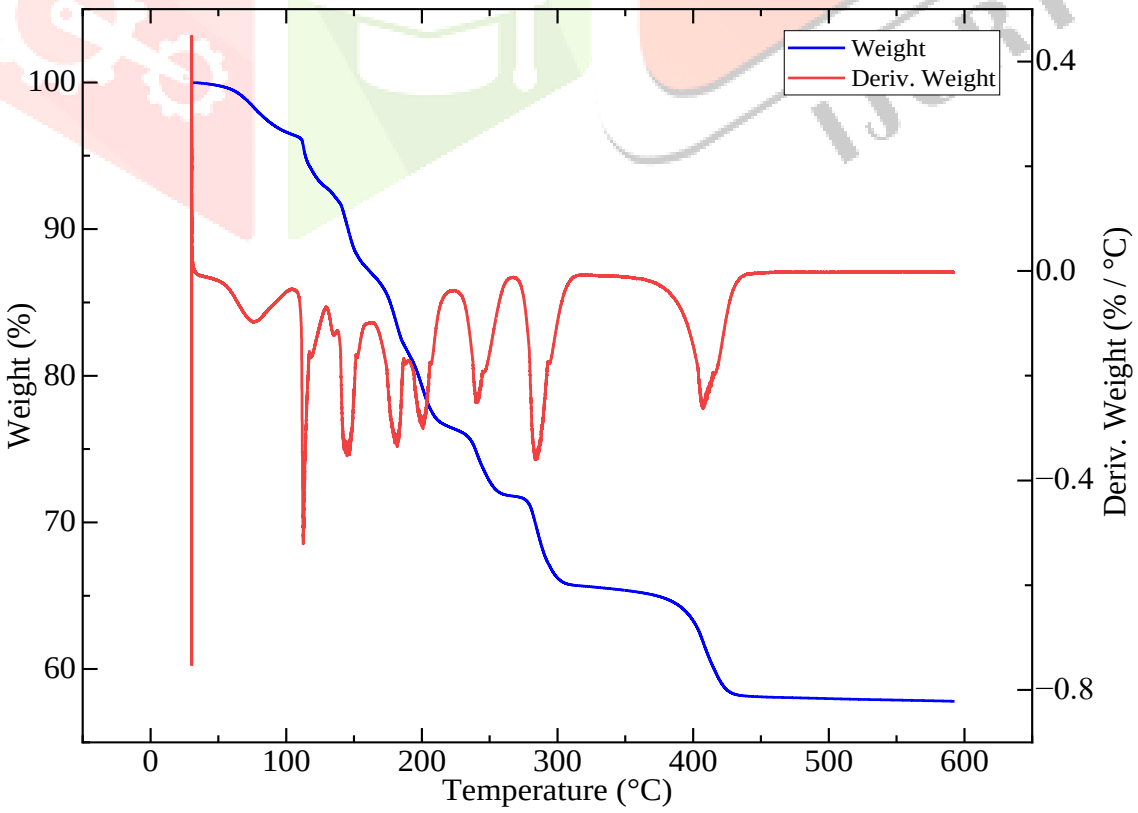

Figure 4: TGA and DTA for BaMnO crystal

5. CONCLUSIONS:

a) These are the first result of barium-manganese oxalates grown in agar-agar gel, and found supportive for crystal growth of mixed crystals of barium-manganese oxalate. This system produced large, transparent, rod and sword shaped crystals of barium-manganese oxalate in aqueous medium, using equimolar concentration.
b) The FTIR portrays presence of metal oxygen bond.
c) Powder XRD shows crystalline nature of barium-manganese oxalate crystals belongs to trigonal crystal system having space group R-3m and lattice parameters obtained a=5.6553 Å, b=5.6553 Å, c=20.8993 Å, α=90.0º, β=90.0º, γ=120.0° and unit cell volume 578.86 $Å^3$.
d) The present work proved that the barium-manganese oxalates are decomposed above 700 °C into oxide.

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REFERENCES:

1. Govindhan, D., Kullaiah, B., Vishwanath P. and Dudley M. (Eds.). 2010. Handbook of Crystal Growth, Springer Heidelberg Dordrecht London New York.
2. Arora, S. K. 1981. Advances in gel growth: A review, Prog. Crystal Growth Charact. 4 (4): 345-378.
3. Agarwal, B. P., Chauhan, K. M. and Bhadbhade. M. M. 1999. Growth and characterization of cadmium oxalates crystals using agar gel, Indian Journal of Pure and Applied Physics, 37: 395-398.
4. Jagtap, U. S. and Patil. A. K. 2022. Gel Grown Oxalate Crystals: A Review, AJCER, 14(1-4): 67-72.
5. Dalal, P. V. and Saraf, K. B. 2006. Growth and study of barium oxalate single crystals in agar gel, Bull. Mater. Sci., 29 (5): 421-425.
6. Dalal, P. V., Saraf, K. B. and Shah. S. 2009. Growth of barium oxalate crystals in agar–agar gel and their characterization, Cryst. Res. Technol., 44: 36-42.
7. Dalal, P. V. 2017. Dielectric behavior of gel grown barium oxalate, International Organization of Scientific Research, 07(08): 53-59.
8. Colthup N. B., Daly L. H. and Wiberley, S. E. 1990. Introduction to Infrared and Raman Spectroscopy, Academic Press, New York, NY, USA.
9. Shedam, M. R., Shedam, Rakesh M. and Mathad, Shridhar N. 2017. Morphological and FTIR Studies of Barium Oxalate Single Crystals, Acta Chemica IASI, 25 (2): 195-207.
10. FullProf Suite (https://www.ill.eu/sites/fullprof/php/downloads.html)
11. Crystallography Open Database (http://www.crystallography.net/cod/index.php)
12. Abdul Salim, M. and Raveendran R. 2008. Characterization, Microhardness and Dielectric Studies of Pure and Doped (Copper, Cadmium) Barium Oxalate Single Crystals Grown in Silica Gel, Asian Journal of Chemistry, 20 (8): 5971-5976.
13. Rohith, P. S., Jagannatha, N. and Pradeepkumar, K.V. 2020. Studies on the Growth and Characterization of Barium Doped Copper Cadmium Oxalate Dihydrate Single Crystals, Journal of Materials and Environmental Science., 11 (5): 788-794.
14. Quasim, I., Firdous, A., Sahni, N., Khosa, S. K., and Kotru. P. N. 2009. Characterization of pure and doped potassium hydrogen tartrate single crystals grown in silica gel, Cryst. Res. Technol. 44 (5): 539-547.
15. Saiyed, B. A. 2012. The Study of Thermal Stability and Decomposition in Cadmium Oxalate Single Crystals, International Journal of Engineering Research and Technology, 1 (8): 1-5.
16. Singh, O. and Singh, K. 2012. Thermal Behaviour and Decomposition Kinetics of a Pr(III) with 4,6-Dihydroxyaurone. International Journal of Science and Nature, 3: 632-634.