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Growth and Study of BaTr single crystals by Gel Technique

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ABSTRACT

In the present investigation, single crystals of Barium tartrate (BaTr) were grown by a simple gel technique using diffusion method. The optimum growth conditions were optimized by varying various parameters such as pH, concentration of the gel solution, setting time of the gel solution and concentration of the reactance. The test tubes were used as crystallization vessels while silica gel as a growth media. Gel was prepared by mixing the solutions acetic acid (CH_3COOH), sodium meta silicate (Na_2SiO_3),barium chloride ($BaCl_2$) and transferred in glass tube of diameter 2.5cm and 15cm in length. The mouth of tube is covered by cotton plug and kept for the setting. After setting the gel, it was left for aging. After two days the supernatant tartaric acid ($C_4H_6O_6$) of 1M concentration was poured over the set gel by using pipette and kept undisturbed by covering the cotton plug on the mouth of tubes. After 48 hours of pouring the supernatant, the small nucleation growth was observed at below the interface of gel. Good quality spherulites crystals were grown in 45 days. The grown BaTr crystals were observed in small size. These crystals were characterized by using X-ray diffraction and FTIR analysis.

Keywords: Gel technique, Barium Tartrate Crystal, XRD, FTIR.

INTRODUCTION

The Moiner and Vesque was the first researcher, who records the growth of large crystals by slow diffusion in gel. A systematic study of crystallization in gels begins with Lissegang's famous discovery of periodic crystallization in gels. This method has gained considerable attention because of its simplicity and effectiveness in growing single crystal of certain compound. This technique is an alternative technique to solution growth with controlled diffusion. This growth process is free from convection. This is purifying process, free from thermal strain [1-7].

Crystal habit of various crystals, grown under different conditions and also by different methods viz., Melt growth,Vapour phase growth, Solution growth and Gel growth were described by H. E. Buckley [8], P. Hartman [9], K. Kem [10], A. A. Chernov [11], W. K. Burton [12] and J. W. Mullin [13]. A number of factors such as degree of saturation, type of solvent [14], pH of the gel media [15, 16], presence of impurities [17] and the change in growth temperature also presumably affect significantly the morphology of the crystal [18]. The crystals, which cannot satisfactorily grow from melt and vapour, are grown successfully by using this method [19 -22].

H.K.Henisch explained the use of gel to grow the crystals [23].This technique has become more popular because of simplicity of the process [24, 25], crystals having low solubility [26] and its unique advantage in terms of crystal product [27, 28]. Many investigators have grown the single crystal of tartrate compounds by gel method [29, 30]. The rare earth tartrates [31,32], the rare earth oxalates [33-35], the transition metal oxalates [36], alkaline earth metal [37], barium copper oxalates [38] and barium tartrates were grown by using this method [39]. Now a day, this method has applied to the study the crystal formation in human system such as cholesterol stones [40, 41], cholesterol monohydrates crystal in gel medium. In urinary stones, calcium hydrogen phosphate dehydrates (CHPD) crystals were found. These CHPD crystals were carried out by this gel technique [42]. Recently, the crystals of biological macromolecules were also grown by this technique.

In the present research work, single crystals of BaTr were grown by a simple gel technique using diffusion method. The optimum growth conditions for crystals were determined. Optimum conditions were established by varying various parameters such as pH, concentration gel solution, setting time of the gel solution and concentration of the reactance. These crystals were characterized by using X-ray diffraction and FTIR analysis.

MATERIALS AND METHODS

The test tubes were used as crystallization vessels while silica gel as a growth media. The gel was prepared by using CH_3COOH and Na_2SiO_3 having different pH values varying from 4.0 to 4.3. The chemicals used for growth of single crystal were CH_3COOH, Na_2SiO_3 and $BaCl_2$. All chemical were of AR grade. Different molar mass were tried to determine the optimum growth condition. Gel was prepared by mixing the solutions acetic acid (CH_3COOH), sodium meta silicate (Na_2SiO_3),barium chloride ($BaCl_2$) and transferred in glass tube of diameter 2.5cm and 15cm in length. The mouth of tube is covered by cotton plug and kept for the setting. After setting the gel, it was left for aging. After two days the supernatant tartaric acid ($C_4H_6O_6$) of 1M concentration was poured over the set gel by using pipette and kept undisturbed by covering the cotton plug on the mouth of tubes.

For infrared analysis of the crystal, samples are prepared in the form of pallet by taking about 100 mg of the sample, mixed with 0.5 gm of analytical grade dry potassium bromide. The mixture is finely powdered and taken in a die. The die is first evacuated to a pressure of 10^{-3} torr, and subjected to extremely high pressure (about 1200 kg cm^{-3}) about five minutes. This process results into the formation of a fine pallet, which removed from the die and used for scanning the spectrum. Experiments were carried out by changing different concentrations of the reactants. The chemical reaction inside the gel can be expressed as:

$$2CH_3COOH + Na_2SiO_3 \rightarrow 2CH_3COONa\downarrow + SiO + H_2O$$
$$2CH_3COONa + BaCl_2 \rightarrow (CH_3COO)_2 Ba \downarrow + 2NaCl$$
$$(CH_3COO)_2 Ba + C_4H_6O_6 \rightarrow C_4H_4BaO_6\downarrow + 2\ CH_3COOH$$

RESULTS AND DISCUSSION

Fig. 1 Crystal of BaTr inside the test tube

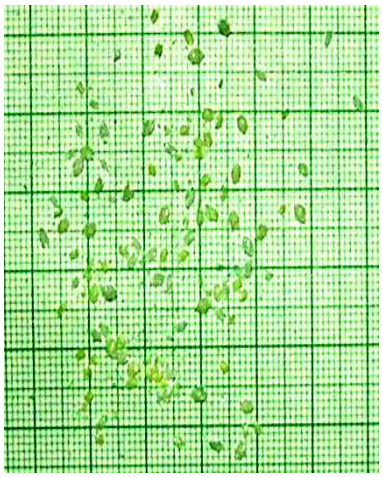

Fig. 2 Few crystals of BaTr

The figure 1 shows transparent crystals of BaTr attached themselves and forming a thick layer at the interface while figure 2 shows a few crystals of BaTr having different habit with their scaling on a graph paper. The grown crystals were of the 3.5mm×2.5mm× 2.5mm size. The various optimum conditions for growing crystals were established and are given in Table 1. We have changed the parameters such as pH of the gel and volume of reactants and observe the growth of BaTr. The Table 2 shows the details of experiment for the growth of BaTr in Silica gel. Tartaric acid ($C_4H_6O_6$) used as upper reactant. Gel age is the time interval between of gel and poring of upper reactant.

Table 1: Optimum conditions for growth of BaTr crystals

Sr. No.	Conditions	BaTr
01	Density of Na_2SiO_3 solutions	1.05 g/cm^3
02	Concentration of CH_3COOH	1.0 M
03	pH of mixture	4.0
04	Temperature	Room Temp.
05	Concentration of $BaCl_2$	1.0 M
06	Concentration of $C_4H_6O_6$ (supernatant)	1.0 M
07	Gel setting time	48 hours
08	Period of crystals growth	6 weeks

Table 2: Details of Experiment for the growth of BaTr crystal

Constant parameter	Variable parameter	Results
$BaCl_2$(1M), CH_3COOH(1M), $C_4H_6O_6$(1M), Gel age 2 days	pH values 4.0 to 4.3	For 4.0 pH the semitransparent platy shape and spherulitic crystals were observed in the interface and interstatical of the gel column. Size of the crystal 3.5mm×2.5mm× 2.5mm

X- Ray Diffraction Analysis

The crystal structure of the sample compound was studied by powder X-ray diffraction method. The X-ray diffraction was recorded using Miniflex-Rigaku model Japan with CuKα radiation of wavelength λ=1.54056Å. The recorded diffraction pattern of the BaTr crystals is shown in the figure 3.

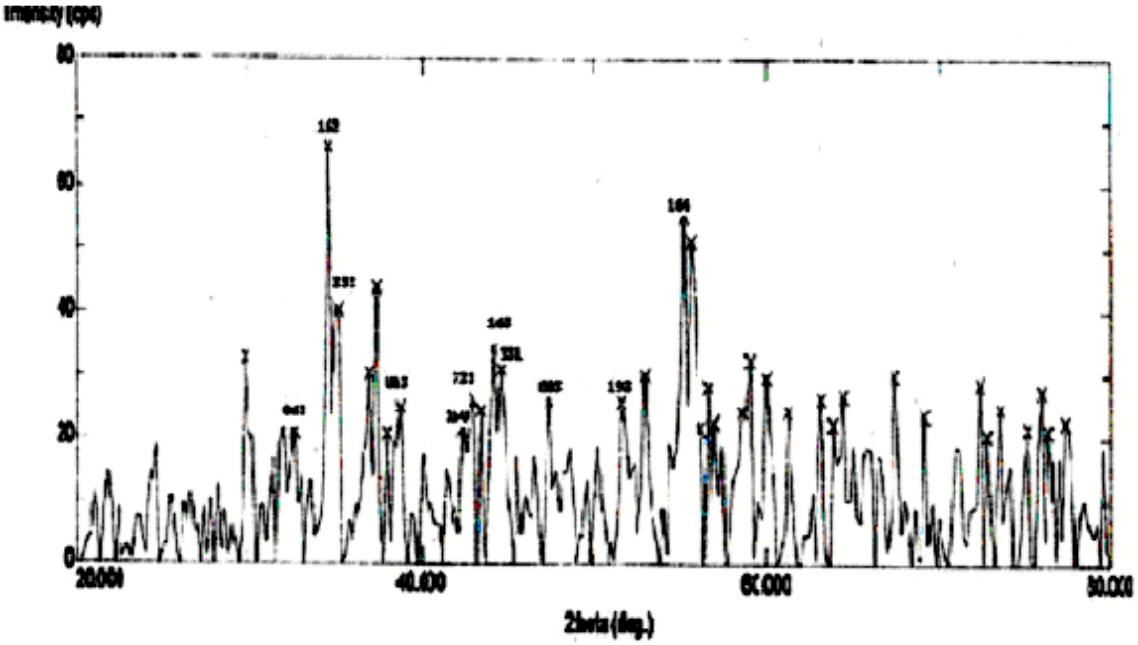

Fig. 3 Powder X-ray diffraction pattern of BaTr Crystal

Determination of Grain size from XRD spectra

From the XRD pattern, it is observed that, each peak has got a finite width. The grain size is determined by measuring the width of the line with highest intensity peak. The grain size can be calculated by using the formula:

$$\text{Grain size } D = 0.9\,\lambda / \beta\cos\theta$$

Where, β is full width of half maxima in radian and D is grain size of the crystal.

$$D = 0.9 \times 1.54056\text{Å} / 0.235\times \cos(17.3)^{\circ}$$
$$= 1.38654/ 0.0039141$$

= 354.42Å = 35.42 nm

The calculated average grain size is 35.42 nm. The analysis of different diffraction peaks indicates the formation of orthorhombic system. The diffraction peaks at 2θ value were measured very carefully and converted into d value using the Bragg's equation putting n=1. By measuring the peak heights above the background in nm and scaling the value up so that the tallest peak has a value of 55 and 66. The preferential orientation is observed from the XRD data is (168) and (162) indicating maximum growth of the crystal in that direction. Orientations of the crystallites along different h, k and l value were present. The intensity of different peaks could give the relative orientation of a particular h, k and l of plane. In the XRD spectra, the main peaks appeared at various diffraction angles 2θ. The values of 2θ, d values, intensity ratio and their corresponding h, k and l plane were shown in the Table 3. From this table, the observed d-values and h, k and l plane were compared with standard data of 2002 JCPDS v. 2.3, 26-0192.

Table 3 Powder diffraction data of BaTr crystal*(λ =1.54056Å)*

Observed data values			Standard data			h k l values
2θ	**d-value**	**Intensity**	**2θ**	**d-value**	**Intensity**	
32.600	2.7444	21	32.765	2.7310	04	0 6 2
34.600	2.5902	66	34.868	2.5710	25	1 6 2
35.200	2.5474	40	35.393	2.5340	12	2 3 2
38.800	2.3189	25	38.887	2.3140	06	0 4 3
42.400	2.1300	21	42.339	2.1330	02	3 6 0
43.00	2.0832	26	43.210	2.0919	02	3 1 2
43.400	2.0832	24	43.384	2.0840	12	2 9 2
44.200	2.0473	34	44.323	2.0420	02	1 6 3
44.600	2.0299	31	44.692	2.0260	02	2 3 3
47.400	1.9163	26	47.331	1.9190	08	0 8 3
51.600	1.7698	26	51.562	1.7710	01	1 9 3
55.200	1.6626	55	55.330	1.6590	02	1 6 8

FTIR Analysis of BaTr crystal

The IR spectrum recorded for BaTr crystal with observed band is shown in the figure 4. The spectrum is scanned in the region 450 to 4000 cm^{-1} by using "Perkin Elmer model 783". The –OH stretching frequency of the sample in IR appeared at 2924 cm^{-1} confirms the presence of water of crystallization in the crystal [43].The moderate absorption around 3104cm^{-1} to 2916cm^{-1} is probably due to stretching vibration of alkali group. 1850cm^{-1} to 2800cm^{-1} may be attributed to hydrogen bonding.

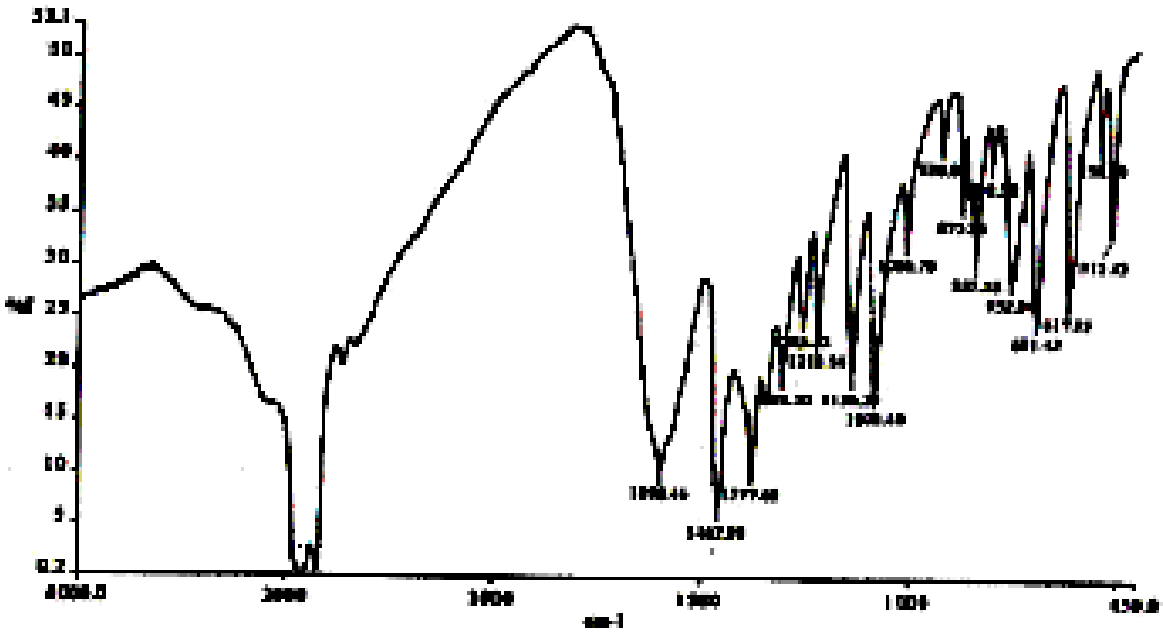

Fig. 4 FTIR Spectrum for BaTr crystal

The broad band at 1598cm^{-1} indicates C=O– functional group whereas sharp band at 1377 cm^{-1} indicates –C–H stretching frequency. The absorption in the spectrum at 1136 cm^{-1} is probably due to –OH bonding and –C–OH stretching vibration respectively. It suggests the coordinate –C–OH group. The FTIR assignments of BaTr crystal are listed in the Table 4. Thus, FTIR spectral results confirm the structure of BaTr. It shows very good agreement with –C–OH the structure of the copper tartrate reported by Kirchner [44, 45].

Table 4: The FTIR assignments of BaTr crystal

FTIR peaks cm^{-1}	Intensity	Assignments
2924	Strong, sharp	–OH Stretching
3104-2800	Weak	Stretching of alkali group
1850-2800	Weak	Hydrogen bonding
1598	Strong, Broad	C=O– Stretching
1459	Strong, sharp	–C–H Asymmetric bending
1377	Strong, sharp	–C–H bending
1136	Strong, sharp	–C–OH Stretching
1979	Strong, sharp	–C–O Stretching
920	Strong, sharp	O–H Stretching
752	Strong, Broad	–C–H Stretching out of plane

CONCLUSION

We have successfully grown BaTr crystal. Single crystals of BaTr were grown by controlled diffusion of Ba^{2+} using the silica Gel. The BaTr is required to maintain the pH of the gel. The parameters such as temperature affect the growth of BaTr Crystal. Gel growth technique is

suitable for growing crystals of the BaTr. The grown BaTr crystals were in small size. The structure of BaTr is the semitransparent platy shape and spherulitic. Unit cell parameter values match very well with the reported XRD standard Data values. The FTIR spectrum confirms the formation of BaTr crystals. The BaTr crystals are shining and quite transparent and they are of good quality.

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