XRD, FTIR and SEM Studies of Gel Grown Barium Tartrate Crystals

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Abstract

In the present research work barium tartrate ($BaC_4H_6O_6$) single crystals have grown successfully by sol gel technique at room temperature. 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. The grown crystals are characterized by XRD, FTIR and SEM. The crystalline nature of grown crystal was confirmed using powder X-ray diffraction technique. The functional groups present in the crystals were identified using FTIR analysis. The scanning electron microscope reveals the morphology of the crystal having tetragonal structures.

Keywords: Gel technique, Barium Tartrate, XRD, FTIR, SEM

1. Introduction

Many investigators have grown the single crystals of tartrate compounds by using single diffusion sol gel method. They studied the effect of various parameters such as type of solvent, pH of the gel media, degree of saturation, the change in the growth temperature and the presence of impurities which affect significantly the morphology of the grown crystal [1-8]. A variety of pure and doped crystals have grown by several investigators for the purpose of research and modern industrial applications [9-13]. The single crystals are the backbone of the modern technological revaluation. The compounds of tartrate found numerous practical applications in the field of science and technology because of their interesting physical properties such as dielectric, ferroelectric, piezoelectric and non-linear optical properties [14-17].

The sol gel method for growing a variety of pure and doped crystals is popular because of its simplicity, inexpensiveness and we can grow the crystals at room temperature without any sophisticated technology. But the challenge of growing pure and doped crystals and opportunities in understanding the growth features and morphology of grown crystals remains here. In this research work, single crystals of barium tartrate were grown by simple single diffusion sol gel method. The optimum growth conditions were established by varying various parameters such as pH, concentration of the gel solution, setting time of the gel solution and concentration of the reactance. The grown crystals are characterized by XRD, FTIR and SEM.

2. Material and Methods

All chemicals used were of AR grade. The chemicals used for growth of single crystal were acetic acid (CH_3COOH), sodium meta silicate (Na_2SiO_3), tartaric acid ($C_4H_6O_6$) and barium chloride ($BaCl_2$). Different molar mass were tried to determine the optimum growth conditions. The gel was prepared by mixing the solutions (CH_3COOH), (Na_2SiO_3), and ($BaCl_2$) having different pH values varying from 4.0 to 4.3. The prepared gel was 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 ($C_4H_6O_6$) 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. Experiments were carried out by changing different concentrations of the reactants. The test tubes were used as crystallization vessels while silica gel as a growth media. The ($C_4H_6O_6$) used as upper reactant. Gel age is the time interval between setting of gel and poring of upper reactant. The crystals of barium tartrate have grown in silica gel in pure form by gel growth method. The X-ray diffraction was recorded using Bruker-D8 Advance, Germany (2θ from 5° to 80°) with CuKα radiation of wavelength λ=1.54060Å. The FTIR spectrum was recorded using Shimadzu FTIR-8400, Japan (400cm^{-1} to 4000cm^{-1}). The FESEM images were recorded using Hitachi S-4800, Japan with X-Flash detector-5030, Bruker, Germany.

The following chemical reactions were involved in the growth of crystals sodium Meta silicate react with acetic acid and forms $2CH_3COONa$.

$$2CH_3COOH + Na_2SiO_3 \rightarrow 2CH_3COONa\downarrow + SiO + H_2O$$

Then taking products $2CH_3COONa$ and adding $BaCl_2$, We get second product $(CH_3COO)_2Ba$.

$$2CH_3COONa + BaCl_2 \rightarrow (CH_3COO)_2\,Ba\downarrow + 2NaCl$$

After 2 days product set the gel, then the supernatant poured over the set gel.

$$(CH_3COO)_2\,Ba + C_4H_6O_6 \rightarrow C_4H_4BaO_6\downarrow + 2CH_3COOH$$

3. Results and Discussion

Figure 1 shows barium tartrate crystals.

The Fig. 1 shows barium tartrate ($BaC_4H_6O_6$) crystals attached themselves and forming a thick layer at the interface while Fig. 2 shows a few grown barium tartrate crystals having different habit with their scaling on a graph paper. The grown crystals were of the 7.5mm×7mm×4.1mm size. The various optimum conditions for growing crystals were established and are given in Table 1.

Figure 2 shows a few grown barium tartrate crystals.

Table 1 Optimum condition for growth of barium tartrate crystals.

Sr. No.	Conditions	Barium tartrate
1	Density of sodium meta silicate solutions (Na_2SiO_3)	1.05 g/cm^3
2	Concentration of acetic acid (CH_3COOH)	1M
3	pH of mixture	4.2
4	Temperature	Room temp.
5	Concentration of ($BaCl_2$)	1M
6	Concentration of ($C_4H_6O_6$) supernatant	1M
7	Gel setting time	2 days
8	Period of crystals growth	6 weeks

3.1 Study of XRD pattern of the grown barium tartrate crystal

The crystal structure of the sample compound was studied by powder X-ray diffraction method. The X-ray diffraction was recorded using Bruker-D8 Advance, Germany (2θ from 5° to 80°) with CuKα radiation of wavelength λ=1.54060Å. The Fig. 3 shows the X-ray powder diffraction pattern of barium tartrate. The crystal is found to be crystallized in tetragonal structure with a = 7.704Å, b = 7.704Å, c = 9.835Å and α = β = γ = 90˚ [18, 19].

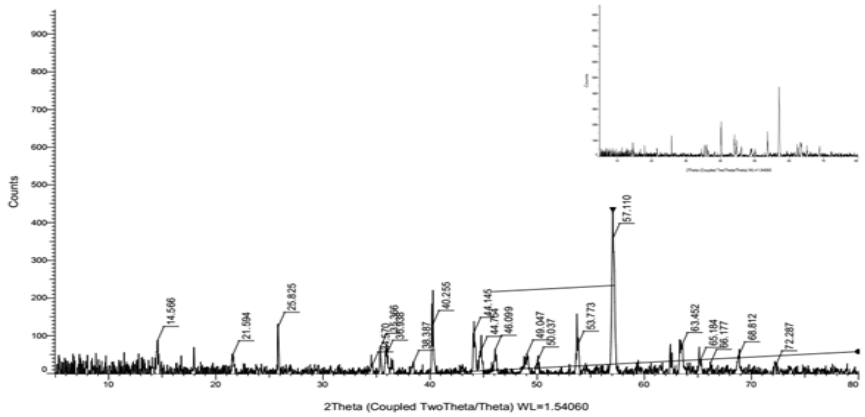

Figure 3 shows the X-ray powder diffraction pattern of barium tartrate.

3.2 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 highest intensity peak line. 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 at Half Maxima in radian and D is grain size of the crystal.

$$D = 0.9 \times 1.54060\text{Å}./\ 0.2362\times \cos(28.555)^\circ$$
$$= 1.38654/\ 0.2362\times 0.87835866$$
$$= 1.38654/\ 0.20746831$$
$$= 6.68314115\text{Å}$$
$$= 66.83\ \text{nm}$$

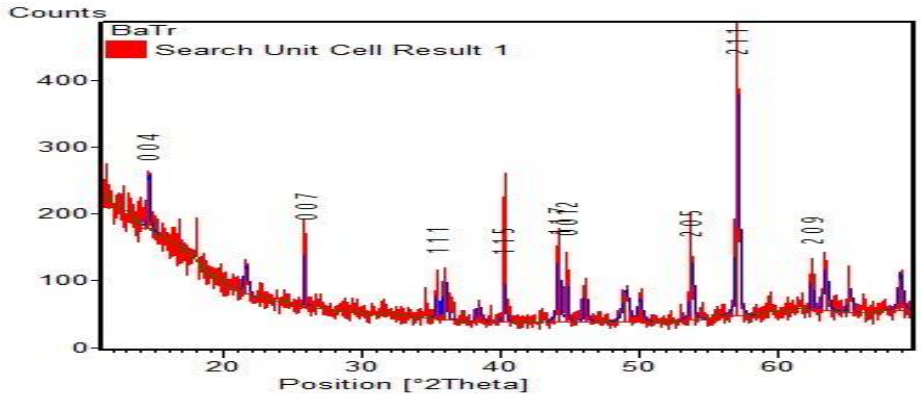

Figure 4 Shows graphics of the X-ray powder diffraction pattern of barium tartrate by X'Pert HighScore PANalytical Software.

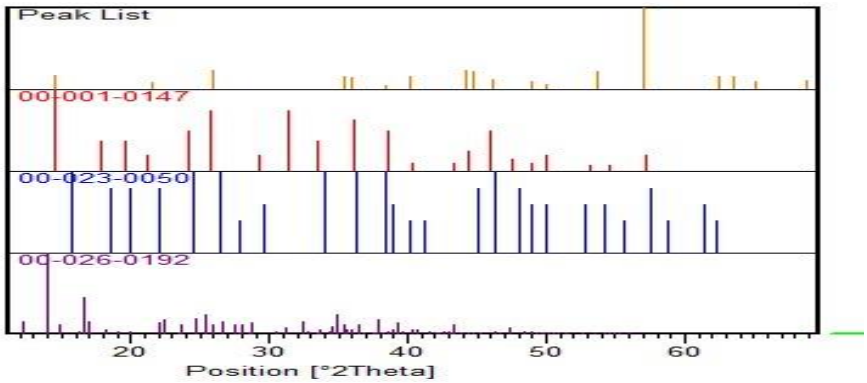

Figure 5 shows plot of Identified Phases of the X-ray powder diffraction pattern of barium tartrate by X'Pert HighScore PANalytical Software.

Table 2 XRD data of barium tartrate crystal (λ =1.54060Å).

Observed Data Values			Standard Data Values						Matched by X'Pert HighScore PANalytical Software
2θ	d -value	Net Intensity	2θ	d -value	Rel. Intensity	h	k	l	
14.566	6.07617	86.7	14.5814	6.07499	16.91	0	0	4	00-001-0147
25.825	3.44707	124	25.8405	3.44792	23.24	0	0	7	00-001-0147; 00-026-0192
35.366	2.53599	68.4	35.3669	2.53800	16.08	1	1	1	00-026-0192
35.938	2.49693	50.2	35.9538	2.49790	14.42	1	0	7	00-001-0147; 00-026-0192
38.387	2.34304	23.4	38.3867	2.34500	5.41	1	1	4	00-001-0147; 00-023-0050; 00-026-0192
40.255	2.23853	129	40.2282	2.24181	16.40	1	1	5	00-001-0147; 00-023-0050; 00-026-0192
44.145	2.04986	111	44.1357	2.05198	23.39	1	1	7	00-001-0147; 00-026-0192
44.754	2.02228	60.6	44.7871	2.02364	22.57	0	0	12	00-026-0192
46.099	1.96742	63.3	46.1059	1.96878	12.86	1	1	8	00-001-0147; 00-023-0050; 00-026-0192
49.047	1.85584	51.0	49.0140	1.85856	10.04	0	0	13	00-001-0147; 00-023-0050; 00-026-0192
50.037	1.82144	32.5	50.0451	1.82265	6.94	2	0	0	00-001-0147; 00-023-0050; 00-026-0192
57.110	1.61149	360	57.0827	1.61354	100.00	2	1	1	00-001-0147

The intensity of different peaks could give the relative orientation of a particular h, k and l plane. In the XRD spectra, the main peaks appeared at various diffraction angles 2θ. Table 2 shows the values of 2θ, d values, net and relative intensity and their corresponding h, k and l plane and matching peaks of barium tartrate crystals. The crystalline phases and d-values obtained from the XRD have been compared with the JCPDS data by X'Pert HighScore PANalytical Software. The XRD pattern of figure 4 matches with the JCPDS files **001-0147, 026-0192, 023-0050**, indicating that the sample consisted of barium tartrate crystalline. The Lattice parameters of ($BaC_4H_4O_6$) crystals were shown in the Table 3.

Table 3 Lattice parameters of barium crystals.

Lattice parameters	Barium tartrate
System	Tetragonal
Bravais Lattice Type	Primitive(P)
a	7.704 Å
b	7.704 Å
c	9.835 Å
$\alpha = \beta = \gamma$	90^0

3.3 Study of FTIR spectrum of the grown barium tartrate crystal

The Fig. 6 shows the FTIR spectrum of the barium tartrate and Table 4 presents the observed absorption frequencies and their assignments in relation to their characteristic vibrational modes. The FTIR spectrum was recorded using Shimadzu FTIR-8400, Japan ($400cm^{-1}$ to $4000cm^{-1}$).

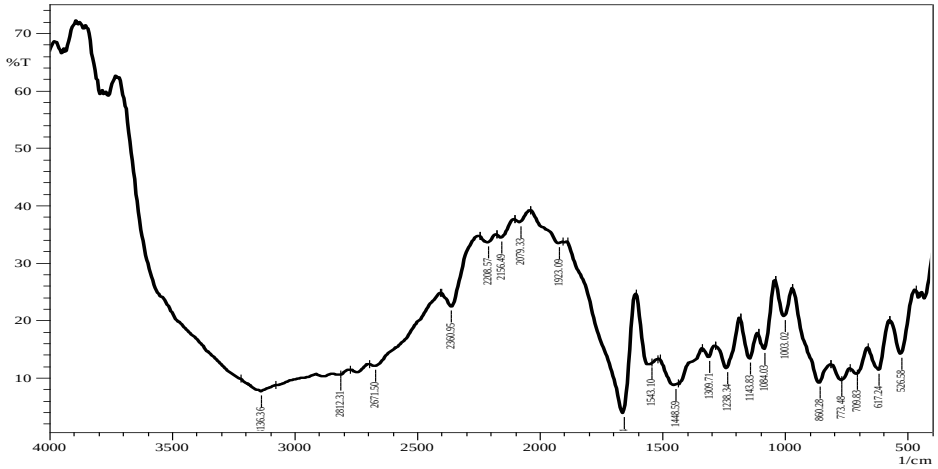

Figure 6 shows the FTIR spectrum of the barium tartrate.

The absorption peaks positioned in between 3136.36 - 2812.31 cm^{-1} corresponds to O-H stretching which confirms the hydrous nature of the compound. The band at 2671.50 - 2079.33 cm^{-1} corresponds to hydrogen bonding. The peak at 1923.09 cm^{-1} corresponds to -C-O stretching. The peak at 1543.10cm^{-1} is the band corresponding to C=OH stretching. The band at 1448.59 cm^{-1} is the band corresponding to C-H asymmetric bending. The band at 1309.71-1238.34cm^{-1} is the band corresponding C-O stretching and OH in plane bending in the tartrate of the compound. The band at 1084.03cm^{-1} is the bands corresponding to -C-H stretching. The band observed at 773.48cm^{-1} is the characteristic bands of -C-H stretching out of plane in tartrate. The bands at 617.24-526.58cm^{-1} correspond to metal oxygen bonding [19-20].

Table 4 The assignment of FTIR bands of barium tartrate.

Sr. No.	Frequency of bands (cm^{-1})	Assignments of absorption peaks
01	3136.36 - 2812.31	O-H stretching
02	2671.50 – 2079.33	Hydrogen bonding
03	1923.09	-C-O Stretching
04	1543.10	C=O stretching
05	1448.59	C-H asymmetric bending
06	1309.71-1238.34	C-O stretching and OH in plane bending
07	1084.03	-C-H stretching
08	773.48	-C-H stretching out of plane
09	617.24-526.58	Metal oxygen bonding

3.4 Study of SEM of the grown barium tartrate crystal

The Fig. 7 shows the SEM image of barium tartrate. The FESEM image was recorded using Hitachi S-4800, Japan with X-Flash detector-5030, Bruker, Germany. The scanning electron microscope reveals the morphology of the crystal having flat and rectangular shape, triangular shape, looks like cubes of different shapes and sizes of tetragonal structures.

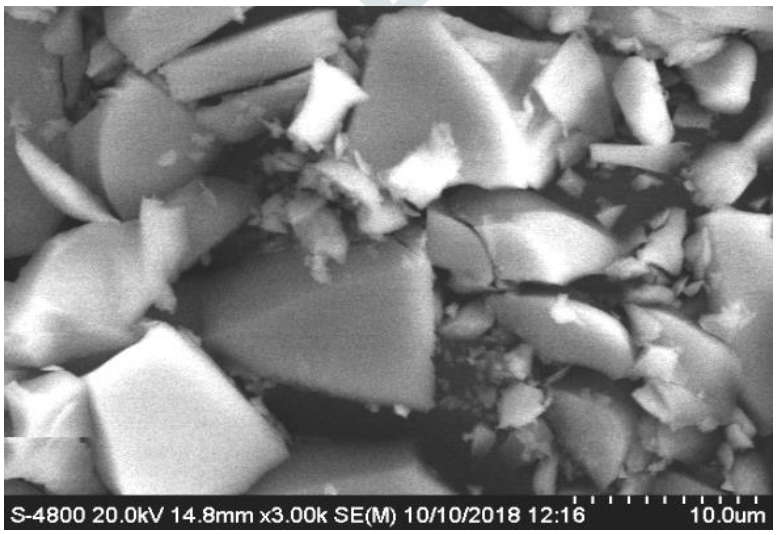

Figure 7 shows the SEM image of barium tartrate.

4. Conclusion

The crystals of barium tartrate have successfully grown by sol gel method. This technique is suitable for growing the barium tartrate crystals. The XRD study shows that the barium tartrate has crystallized in tetragonal structure. These crystals are shiny, quite transparent and are of good qualities. The absorption peaks positioned in between 3136.36 - 2812.31cm^{-1} corresponds to O-H stretching which confirms the hydrous nature of the compound. The FTIR study shows the presence of O-H bond, C-H bond and metal–oxygen bond. The FTIR spectrum confirms the formation of barium tartrate crystals. The scanning electron microscope reveals the morphology of the crystal having tetragonal structures.

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