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Structural and thermal characterization Strontium dopoed Barium Tartrate crystal grown by gel technique

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ABSTRACT

The single crystals of Strontium doped Barium tartrate crystals were grown by Single diffusion technique, in silica gel at room temperature. Effect of Strontium doping on the Barium tartarate has been studied. The XRD pattern shows that Strontium barium tartarate crystals are polycrystalline, having orthorhombic structure. SEM pictures reveals that crystals are grown by layer deposition. The thermal stability was studied by the TGA and DSC.

Keywords: Crystal growth techniques Single diffusion, XRD, SEM, TGA, and DSC

INTRODUCTION

Now a day's crystal growth is the rapid growing field in research because of huge demand of crystal for several applications and recently researchers focused on the tartrat. Commercially the tartrate compound can be used in various applications like as antimony in veterinary drugs [1] ferroelectric applications of sodium-potassium tartrate [2], potassium- chromium tartrate in medicine [3] and so on. Many people studied various tartrate compounds likes calcium-strontium mixed levo tartrate [4] zinc tartrate [5] cadmium tartrate [6] with respect to their properties such as dielectric, magnetic, ferroelectric, piezoelectric, optical and other pertinent characteristics [7-12].

Many researchers grow the series of pure and mixed crystals to find out the new material for various purposes [13-16]. There are various techniques for growing crystals like melt growth, vapour phase, solution growth and etc. The gel technique has attracted more attention towards it because of its simplicity and cost effectiveness. The crystals can be grown at room temperature.

Barium Tartrate (BaTr) is a quite interesting compound and hence some attempts have been made to grow its Sr doped barium tartarate crystals. Here cobalt doped barium tartaric crystals are grown by gel technique in silica gel medium and the grown crystals analyzed under the various characterizations.

MATERIALS AND METHODS

The chemicals used in this work are sodium meta silicate $Na_2SiO_3.5H_2O$, AR grade, Acetic acid CH_3COOH, AR grade, Barium tartarate ($BaCl_2$), AR grade, Strontium Chloride ($SrCl_2$), AR grade and Tartaric acid, GR grade. Silica gel was prepared by adding the sodium meta silicate solution of specific gravity 1.05 gm/cc drop by drop with constant stirring by using magnetic stirrer into the 5cc (1N) acetic acid till the pH value 4.2 was set for the mixture. To the above sodium meta silicate solution of pH 4.2, the inner reagent which was the mixture of 15cc and 10cc aqueous solution of 0.1M $BaCl_2$ and 0.05M, $SrCl_2$ was added with constant stirring.

This mixture was then transferred to the test tube of length 15 cm and 2.5 cm diameter. To keep the solution free from dust and impurities. This care was taken to cover the test tube. The gel was usually set within 5 days. It was left for two more days for ageing and then the outer reagent of 0.1M $C_5H_6O_6$ was added on to the top of the gel. The outer reagent was added slowly along the sides of test tube using a pipette and not directly on to the gel medium. Due to the diffusion of the outer reagent into the gel medium and its reaction with the inner reagents, crystals started growing.

Nucleation was observed within 24 hours after addition of the outer reagent Spherical, prismatic, shining, crystal aggregates, crystals were observed as shown in figure 1. All experiments leading to the growth of crystals were carried out at room temperature. The reaction between Barium Chloride, strontium Chloride and Tartaric acid in gel medium resulted in the growth of Sr doped Barium tartarte crystals.

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

$$2CH_3COONa + BaCl_2 + SrCl2 \rightarrow (CH_3COO)_4\,BaSr\downarrow + 4NaCl$$

$$(CH_3COO)_4\,BaSr + C_4H_6O_6 \rightarrow C_4H_4BaSrO_6\downarrow + 4CH_3COOH$$

Table 1. Optimum conditions for growth of strontium-doped Barium tartarate crystals

Parameters	Optimum conditions
Density of sodium meta silicate solution	1.05 gm/cc
Volume of sodium meta silicate solution	17.5 cc
Volume of 1N acetic acid	5 cc
pH of the gel	4.2
Concentration of $C_5H_6O_6$	0.1M
Volume of $C_5H_6O_6$	5 cc
Concentration of $BaCl_2$	0.1M
Volume of $BaCl_2$	15 cc
Concentration of $SrCl_2$	0.05M
Volume of $SrCl_2$	10 cc
Gel setting time	5 days
Gel ageing time	2 days
Period of growth	6 weeks
Temperature	Room Temp.

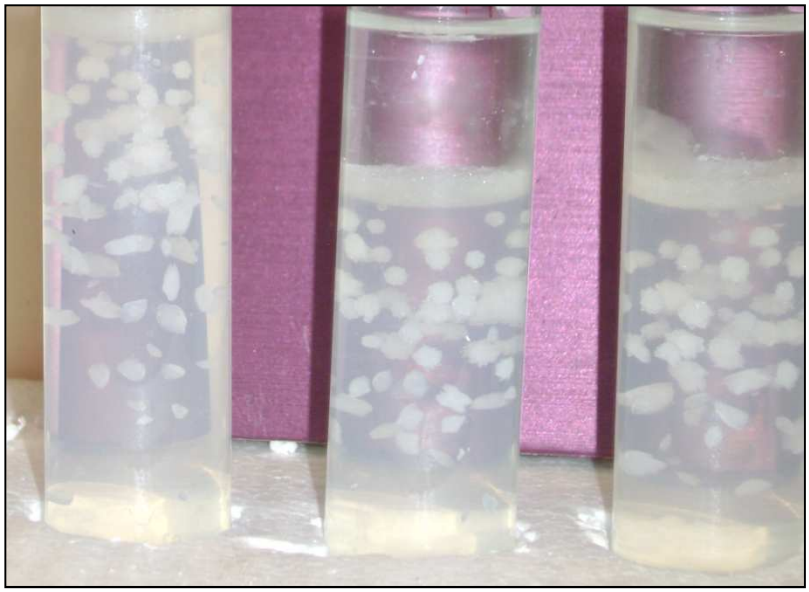

Figure 1: Sr doped of Barium tartarate crystals 0.05M

Figure 2 : Few 0.05M strontium-doped crystals of Barium tartarate crystals

RESULTS AND DISCUSSION

3.1 X-ray powder diffraction analysis(XRD)

The XRD result revealed the crystalline property of crystal. The XRD diffraction patterns of 0.05M Sr doped Barium tartarate crystals were obtained using (Bruker - Model Foxit Software) X-ray diffractometer at University of Pune. All diffraction patterns. Obtained using CuKa radiation λ = 1.54060 at 40Kv and 40MA. Measurements were made from $2\theta = 20^0$ to $80^0$with steps of 0.02^0.

The hkl and d values of Sr:$BaC_4H_4O_6$ crystals were Table 2. Hkl and d values were found to be in good agreement with the JCPDS data card no. 26.0192 and 89-4045. The crystal structure of Sr doped Barium tartarate is determined to be orthorhombic. It is evident from the XRD data that there are no extra peaks due to Strontium doped and did not change the crystalline structure of Barium tartarate and indicating that the grown crystals are single phase. The Sr ion was understood to have substituted the Ba site without changing the orthorhombic structure of the parent crystal.

The results show a slight shift in the position of diffraction peaks to lower value reflecting a slight elongation along a, b and c axis and hence slight increase in cell volume with increase in concentration of Dopants .The sharp XRD peaks with maximum intensity , indicating the formation of well defined crystallites .The variations in intensity of peaks and lattice parameters attribute to the incorporation of the dopant in the crystal. The grain size of the particles of powder samples were calculated (49.28 nm) using Scherrer equation $d = 0.9\lambda / \beta\cos\theta$, where β represents the full width at half maximum.

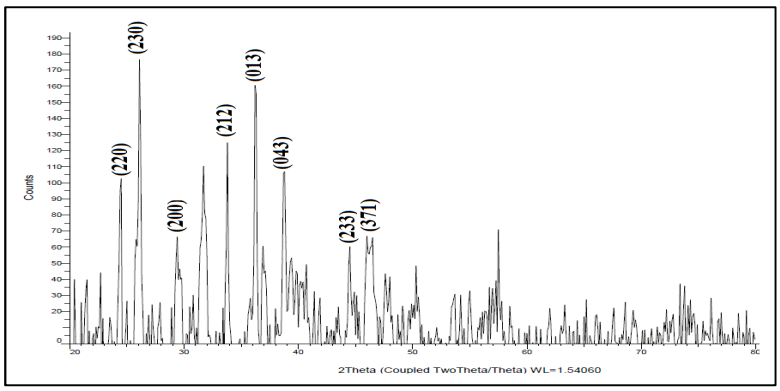

Figure 3. XRD pattern of the crystals of $SrBaC_4H_4O_6$ 0.05M

Table 2. XRD data of 0.05 M Sr doped Barium tartarate crystals λ =1.54060

Observed Values from XRD				Standared data values		
Sr No	2θ	d-Values	Intensity	2θ	d-Values	h k l
1	24.600	3.6159	274	24.606	3.6149	2 2 0
2	26.000	3.4243	329	26.009	3.4230	2 3 0
3	29.300	3.0457	233	29.374	3.0382	2 0 0
4	33.700	2.6574	203	33.718	2.6560	2 1 2
5	35.900	2.4994	139	35.936	2.4969	0 1 3
6	38.800	2.3190	210	38.887	2.3140	0 4 3
7	44.600	2.0299	127	44.692	2.0260	2 3 3
8	46.300	1.9594	154	46.308	1.9590	3 7 1

3.2 Scanning electron microscopy (SEM):

In the present work powdered sample of Sr:$BaC_4H_4O_6$ crystals were examined by using LEICA S440 SEM instrument at the North Maharashtra university Chemical technology Laboratory, Jalgaon. Figure 4. Illustrate the SEM images of single crystals of 0.05M strontium-doped Barium tartarate crystals respectively. All SEM photo mages shown triangular, pentagonal, rod, and plate like crystals morphology and crystals are grown by layer deposition. broad layers are seen in figured. The individual plates of samples are flat and the plates with the broad edges were observed. On some plates further plate like growth was observed. It was found that morphological changes take place due to doping.

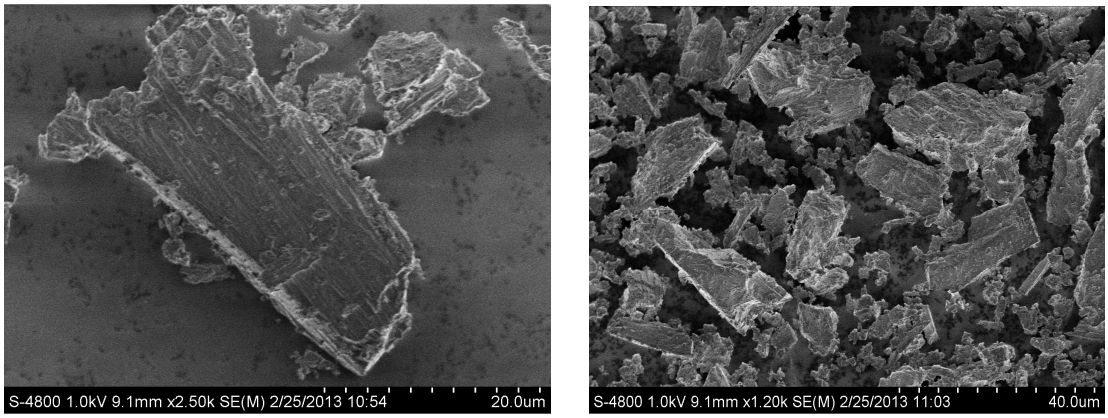

Figure 4. SEM picture of 0.05M Sr-doped Barium tartarate crystals

3.3 Thermogrvimetric analysis (TGA):

TGA curves shows in figure 5. The percentages of the weight loss in the different stages of decomposition of strontium barium tartrate are presented in table 3. There is a good agreement between the observed and calculated weight losses.

Strontium barium is water coordinated compound .Therefore there is a possibility that this crystal may lose some of its water molecules while heating. TGA of strontium barium tartrate showed clearly four stages of decomposition as expected.

1) dehydration 2) Strontium barium tartrate to Strontium barium oxalate 3) Strontium barium carbonate to Strontium barium oxides similar observations are known from the literature on Rochelle salt and rare earth tartrates.

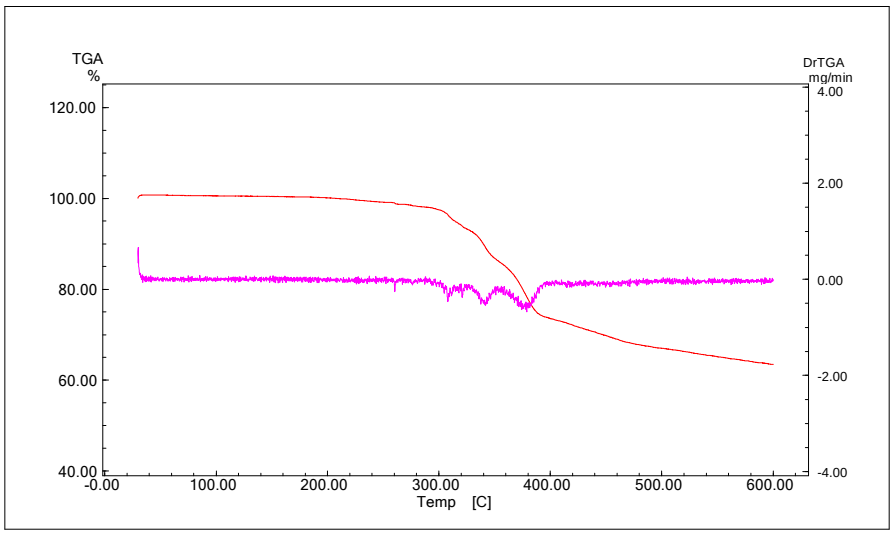

Fig 5. $SrBaC_4H_4O_6$ 0.05 M Crystals

The TGA curve did not show the appreciable weight change in the temp range 27^0C indicating that the strontium barium tartrate crystals are thermally stable in this range and no transformation took place.

First step observed that the decomposition begins at 260^0C. It was observed that in the temperature range 27^0 C to 260^0 in which weight loss of water molecules1.75agrees very well with the calculated weight loss of 2.36% it is clear that strontium barium tartrate crystals are hydrated and the weight loss calculation clearly indicates that strontium barium tartrate crystals have $0.5H_2$o water loss calculation clearly indicates that strontium barium tartrate crystals have $0.5H_2O$water molecules as water of crystallization.

In Second step indicates the formation of anhydrous strontium barium tartrate decomposes into strontium barium oxalate. of decomposition total weight loss of 15.72% was observed in the temperature range 260^0C-360^0C which corresponds to the loss of 2CO&$2H_2$. And the calculated weight loss 17.70% .this weight loss aggress very well decomposes into strontium barium carbonate. In the temperature range 360^0C to 400^0C is attributed to the stable Strontium barium oxalate.

In the third step of decomposition total weight loss of 11.53% was observed in the temperature range 360^0C-400^0C which corresponds to the loss of CO_2. The calculated weight loss11.51 % .this weight loss aggress very well decomposes into strontium barium carbonate. in the temperature range 360^0C to 400 is the attributed to the stable strontium barium carbonate.

Finally in the forth stage the temp range of400^0c to 599^0c, total weight loss of 7.28%was obtained. This loss is attributed to the loss of CO. This is in well agreement with calculated weight loss of 7.33%. thus the strontium barium carbonate finally turns into oxides of strontium barium at 599^0C.Beyond 600^0Cupto the end of analysis there is stable Sr:BaO

Tabale 3. TGA data of 0.05 strontium Barium tartarate crystals ($SrBaC_4H_4O_6$ $0.5H_2O$)

Stage	Temperature range	Observed % weight loss	Calculated % weight loss	Loss of molecule in stage
I	27.78-260^0C	1.75	2.36	-0.5H2O
II	260-360^0C	15.72	15.70	-2CO 2H2
III	360-400^0C	11.53	11.51	-CO2
IV	400-599^0C	7.28	7.33	-CO

3.4 Differential scanning calorimetry (DSC):

The differentials scanning calorimetric analysis of the grown crystals was recorded between 20^0C to 400^0C in the nitrogen atmosphere using Metals TA 4000 Instrument at nmu jalgaon . The initial weight of sample was 0.100mg and heating rate was maintained at 10^0C/min. The DSC curve for Sr doped Barium tartarate gel grown crystals is shown in figure 6.Since the instrument cannot go beyond 400^0C,complete endothermic be recorded.
The four stages of DSC curve under study are as follows.

Stage-I.The initiation temperature is 202.25^{0}c and initiation of phase change to starts completed at peak end-down temperature of 223.45^{0}c.The temperature at which the sample and the reference come to thermal equilibrium by thermal diffusion. The peak appeared in the DSC curve at 240.46^{0}c indicates the phase tar formation due to loss of 0.05H_2water molecules and formation of stable anhydrous $BaSrC_4H_4O_6$crystals. The is in good agreement with the TGA curve.

I. Heat area under the curve is -65.05mj
Stage-II. The initiation temperature is 284.35^{0}c and initiation of phase change to starts completed at peak end-down temperature of 288.47^{0}c.The temperature at which the sample and the reference come to thermal equilibrium by thermal diffusion. The peak appeared in the DSC curve at 303.56^{0}c indicates the phase tar formation due to loss of 2CO and$2H_2$ formation of stable $BaSrC_2O_4$crystals. The is in good agreement with the TGA
II. Heat area under the curve is -26.75mj
Stage-III.The initiation temperature is 306.94^{0}c and initiation of phase change to starts completed at peak end-down temperature of 310.52^{0}c.The temperature at which the sample and the reference come to thermal equilibrium by thermal diffusion. The peak appeared in the DSC curve at 319.56^{0}c indicates the phase tar formation due to loss of CO_2 formation of stable $BaSrCO_2$crystals. The is in good agreement with the TGA
III.Heat area under the curve is -25Mj
Stage-IV. The initiation temperature is 331.64^{0}c and initiation of phase change to starts completed at peak end-down temperature of 344.76^{0}c.The temperature at which the sample and the reference come to thermal equilibrium by thermal diffusion. The peak appeared in the DSC curve at 363.25^{0}c indicates the phase tar formation due to loss of CO formation of stable Sr:BaO crystals. The is in good agreement with the TGA .
IVHeat area under the curve is -91.76m

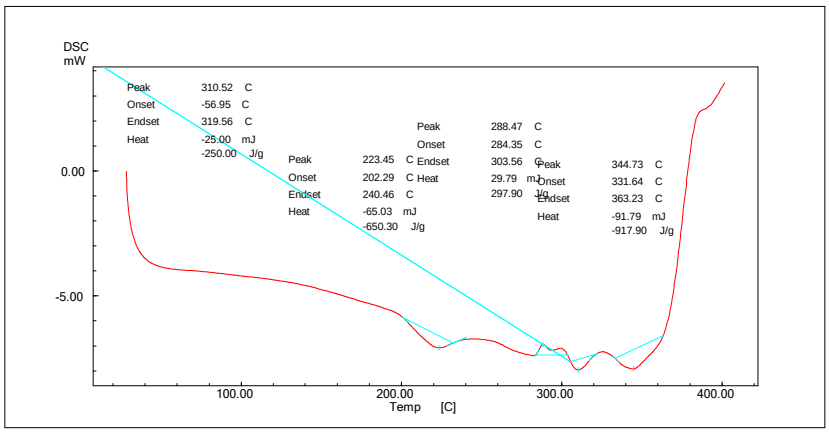

Figure 7. DSC of Sr doped Barium tartarate Crystals

Table 3. DSC data of Sr doped Barium tartarate Crystals

Peaks	Temprature	On set	Endset	Heat
Endothermic	223.45	215.25	230.46	-65.05mj
Endothermic	288.47	284.35	303.56	-29.75mj
Endothermic	310.52^{0}C	306.94^{0}C	319.56^{0}C	-25.00mj
Endothermic	373.61^{0}C	363.43^{0}C	378.95^{0}C	-70.82 mj

CONCLUSION

Silica hydro gel is suitable for growing the crystals of strontium-doped Barium tartarate. Singal diffusion method is convenient for the growth of the strontium-doped Barium tartarate crystal aggregate, spiky sperulitic, good quality and sized crystals were obtained. Size of the doped crystals increases with the concentration of Sr dopant. Lattice constant a, b and c the unit volume are sensitively affected by the dopant concentrations. The powder X-ray diffraction study confirmed that grown crystals are very much crystalline in nature having orthorhombic structure. Surface morphology was affected significantly by the doping. TGA, and DSC, analysis suggest that the thermal stability of Barium tartarate crystal Decreases to strontium doping

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