Comparative Study of Thermal Stability of Strontium Doped Barium Tartrate Crystals by Silica Gel Technique

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Abstract

In the present research work, the single crystals of strontium doped barium tartrate ($SrBaC_4H_4O_6$) crystals were grown by single diffusion technique. The optimum growth conditions for ($SrBaC_4H_4O_6$) crystals were optimized by varying various parameters such as pH of the gel solution, gel concentration, gel setting time, concentration of the reactance. The platy shaped crystals were obtained in silica gel at room temperature. The effect of Strontium (Sr) doping on the barium tartrate ($BaC_4H_4O_6$) has been studied. The XRD pattern shows that ($SrBaC_4H_4O_6$) crystals are polycrystalline, having orthorhombic structure. The SEM pictures reveal that these crystals are grown by layer deposition. Thermo Gravimetric Analysis (TGA) curves show the percentages of the weight loss in the different stages of decomposition of barium tartrate. Differential Scanning Calorimetry (DSC) curves show the phase transformation due to loss of water molecules and formation of stable anhydrous ($SrBaC_4H_4O_6$) crystals.

Keywords: Sol gel technique, Strontium, Barium, XRD, SEM, TGA, DSC.

1. Introduction:

Commercially, the tartrate compound can be used in various applications like antimony in urinary drugs [1], ferroelectric applications of sodium-potassium tartrate [2], potassium-chromium tartrate in medicine etc. [3]. Many people studied various tartrate compounds like calcium-strontium mixed levo-tartrate [4], zinc tartrate [5] and cadmium tartrate [6] with respect to their properties such as dielectric, magnetic, ferroelectric, piezoelectric, and optical and other pertinent characteristics. Crystal habits of various crystals, grown under different conditions and also by different methods were described by Buckley [7], Hartman [8], Kern [9], Chernor [10], Burton [11] and Mullin [12].

A number of factors such as degree of saturation, type of solvent [13], pH of the gel media [14, 15], presence of impurities [16] and the change in growth temperature also presumably affect significantly the morphology of the crystal. The crystals, which can't satisfactorily grow from melt and vapour, are grown successfully by using this method

Hydro silica gel is very good medium for growing better quality doped and undoped crystal of barium tartrate. In present investigation, doped and undoped barium tartrate crystals were grown by silica gel method using single diffusion technique. Strontium is used as dopant. In this comparative study we study the effect of strontium doping in the barium tartrate crystals. The grown crystals are characterized by XRD, SEM, TGA, and DSC techniques.

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 ($C_4H_6O_6$), strontium chloride ($SrCl_2$) 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), ($BaCl_2$) and ($SrCl_2$) 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. The concentration (0.05M) of ($SrCl_2$) in an aqueous solution was used to grow (Sr) doped barium tartrate crystals. To grow well defined crystals of strontium-doped barium tartrate, several experiment were carried out by varying growth parameters like gel pH, gel age, gel density, and molarities of lower and upper reactions, in order to establish the optimum condition for the growth. The optimum growth conditions for the growth of high quality ($SrBaC_4H_4O_6$) crystals established by varying various parameters are given in Table 1.

Table 1 Optimum condition for growth of ($SrBaC_4H_4O_6$) crystals.

Sr. No.	Optimum growth Conditions	($SrBaC_4H_4O_6$)
01	Density of sodium meta silicate solutions (Na_2SiO_3)	1.05 g/cm^3
02	Concentration of acetic acid (CH_3COOH)	1M
03	pH of mixture	4.3
04	Temperature	Room Temp.
05	Concentration of ($BaCl_2$)	1M
06	Dopand Concentration of $SrCl_2$)	0.05M
07	Concentration of supernatant ($C_4H_6O_6$)	1M
08	Gel setting time	2days
09	Period of crystals growth	6 weeks

3. Results and Discussion

3.1 X-ray powder diffraction analysis (XRD) study

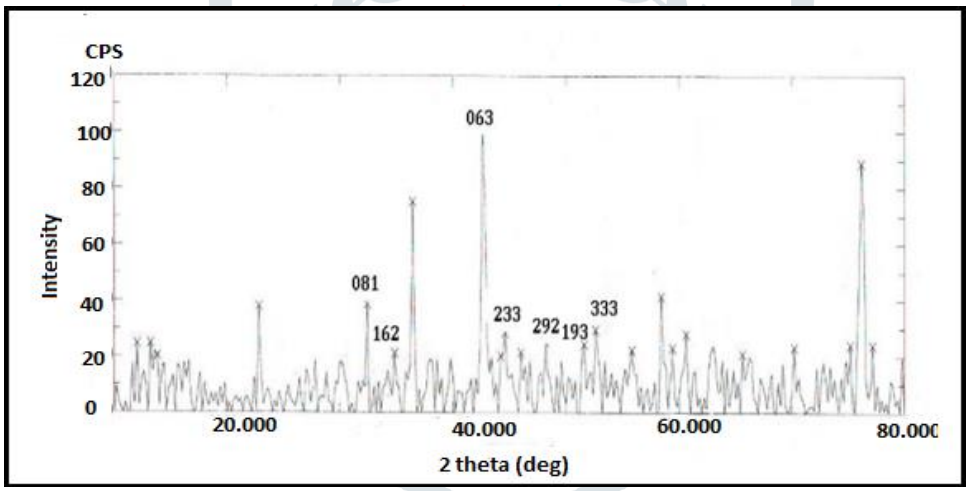

Figure 1 the XRD pattern of barium tartrate Crystal.

The Fig.1 shows the XRD pattern of barium tartrate whereas Fig.2 shows the XRD pattern of ($SrBaC_4H_4O_6$) crystals. The XRD study reveals that barium tartrate crystal belongs to orthorhombic system and the incorporation of the dopant has not changed the structure of the parent crystal. The slight shift of XRD peaks, variations in intensity and lattice parameters of doped barium tartarate crystals indicated that dopands are really doped into the ($BaC_4H_4O_6$) structure. Table 2 shows the XRD data of barium tartrate and Table 3 shows the XRD data of (Sr) doped barium tartrate crystals. The calculated h k l values were found to be in good agreement with the JCPED card no. 26-0192 and 89-4045.

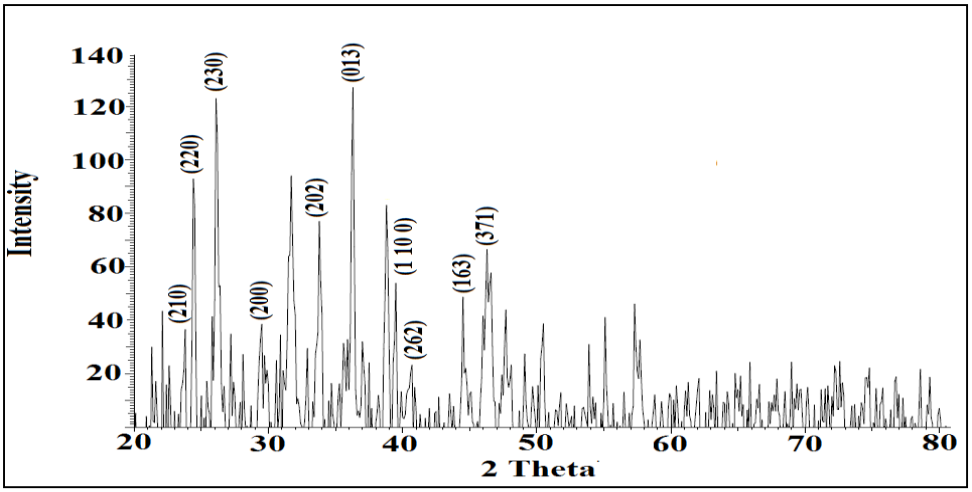

Figure 2 the XRD pattern of ($SrBaC_4H_4O_6$) crystals (0.05M.)

Table 2 The XRD data of barium tartrate crystal (λ =1.54056Å).

Observed data values			Standard data values			
2θ	d-value	Intensity	2θ	d-value	Intensity	h k l
32.400	2.7609	39	32.375	2.7630	16	0 8 1
34.800	2.5758	21	34.864	2.5709	25	1 6 2
42.600	2.1204	103	42.590	2.1210	4	0 6 3
44.600	2.0299	28	44.692	2.0260	2	2 3 3
48.200	1.8864	25	48.402	1.8790	4	2 9 2
51.600	1.7698	24	51.563	1.7710	1	1 9 3
52.600	1.7384	30	52.584	1.7391	2	3 3 3

Table 3 The XRD data of (Sr) doped barium tartrate crystals (λ =1.54060Å).

Observed data values			Standards data values		
2θ	d-Values	Intensity	2θ	d-Values	h k l
23.700	3.7510	305	23.726	3.7470	2 1 0
24.600	3.6159	287	24.606	3.6149	2 2 0
26.000	3.4243	269	26.009	3.4230	2 3 0
29.300	3.0457	182	29.374	3.0382	2 0 0
33.400	2.6805	123	33.718	2.6560	2 1 2
35.900	2.4994	143	35.936	2.4969	0 1 3
39.600	2.2739	113	39.690	2.2690	1 10 0
40.700	2.2150	86	40.700	2.2150	2 6 2
44.300	2.0430	75	44.324	2.0420	1 6 3
46.300	1.9594	150	46.308	1.9590	3 7 1

The slight shift in the position of diffraction peaks to lower value reflecting a slight elongation along a, b and c axes. Lattice parameter values and the grain size of doped and undoped barium tartrate crystals are given in the Table 4. The grain size data for grown crystals was derived by using Scherrer formula. The grain size of the undoped barium tartrate crystals is around 35.44 nm while average grain size is around 49.28 nm. It was observed that the grain size of the undoped barium tartrate crystal increases with (Sr) doping and subsequent doping shows the increasing tendency in grain size.

Table 4 the comparative studies of lattice parameters and grain size of doped and undoped ($BaC_4H_4O_6$) crystals.

Comparative study	Lattice Parameters			Grain size (nm)
	A	B	C	
Undoped ($BaC_4H_4O_6$) crystals (1M)	7.590	23.780	7.536	35.44
Doped ($BaC_4H_4O_6$) crystals with Sr (0.05M)	8.539	24.665	8.326	49.28

3.2 Scanning Electron Microscopy (SEM) study

The SEM pictures of Fig. 3(a) and Fig.3 (b) shows that the doped and undoped barium tartrate crystals are looks like plate, pentagonal, triangular, rod like crystals morphology and these crystal are grown by layer deposition. The broad and flat layers are observed [17]. From Fig.3 (b), it is found that the morphology of the doped crystal is affected significantly by the doping.

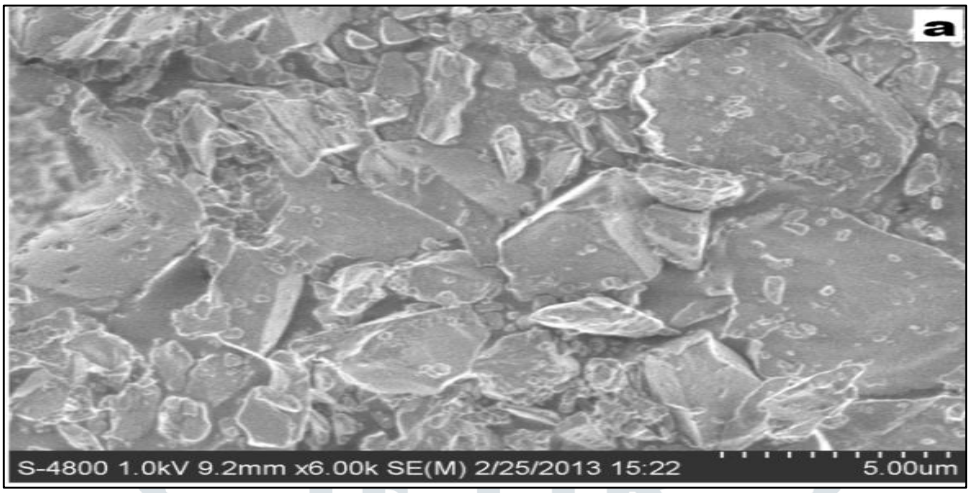

Figure 3(a) The SEM picture of barium tartrate crystals.

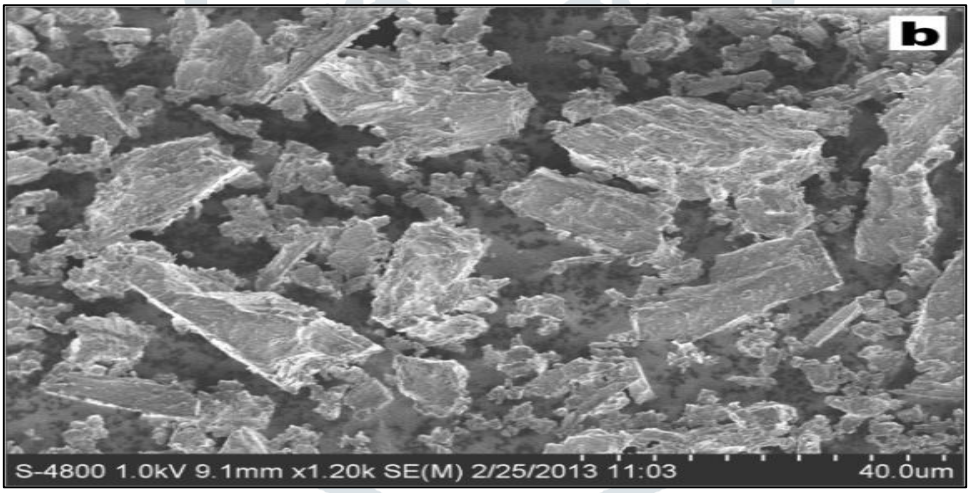

Figure 3(b) The SEM picture of (Sr) doped barium tartrate crystals.

3.3 Thermal analysis study

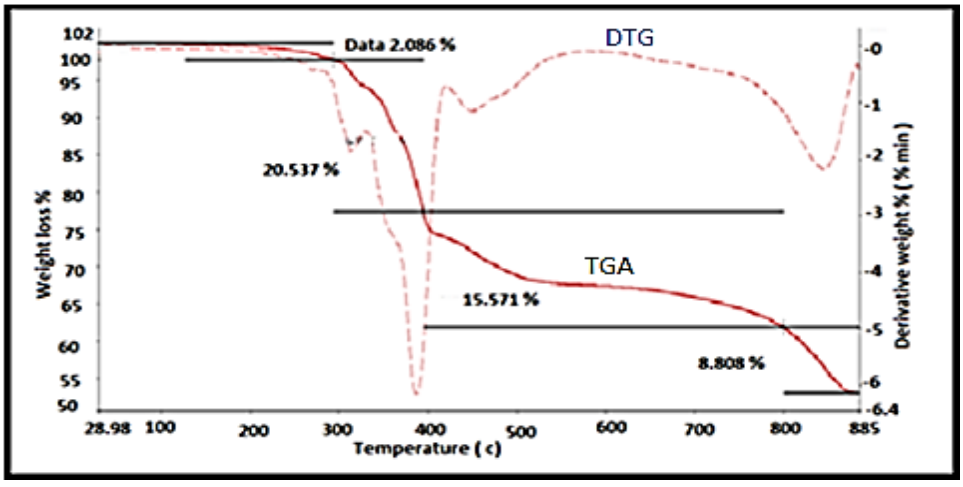

Figure 4 TGA & DTG curve of barium tartrate crystals.

The Fig. 4 shows TGA & DTG curves of barium tartrate and the Fig. 5 shows TGA & DTG curves (Sr) doped ($BaC_4H_4O_6$) crystals. Thermal analysis of doped and undoped barium

tartrate crystals shows remarkable thermal stability which is the key requirement for materials. The crystal decomposes in two stages. Barium tartrate and strontium barium tartrate crystals are thermally stable up to 292^0C and 245^0C temperature. Above this temperature, they decompose with the evolution of barium tartrate.

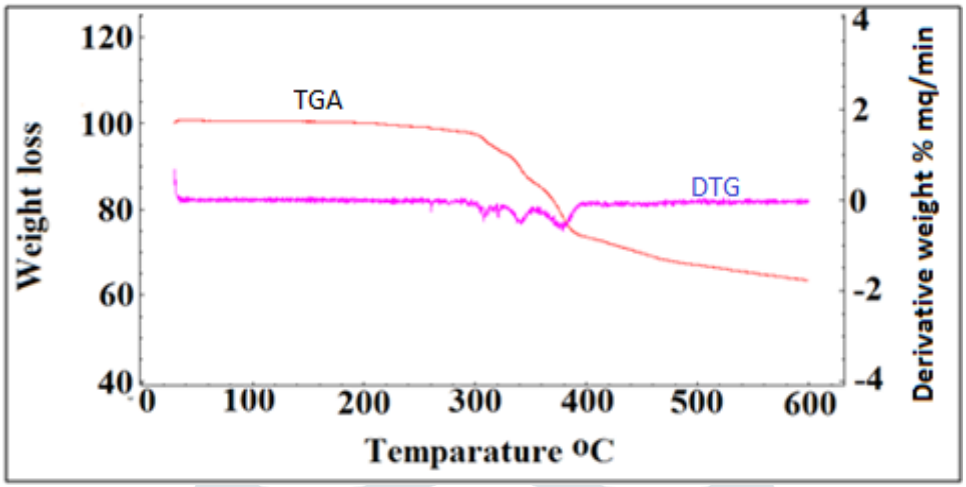

Figure 5 TGA & DTG curve (Sr) doped ($BaC_4H_4O_6$) crystals (0.05 M).

Table 5 TGA data of doped and undoped barium tartrate crystals.

Crystals	Step	Temperature range (^{0}C)	Observed % weight loss	Calculated % weight loss	Probable loss of molecules
$BaC_4H_4O_6$ (1M)	I	29- 292	2.09	03.05	$-0.5H_2O$
	II	292-393	20.53	20.38	$-2CO2H_2$
	III	393- 799	15.57	16.30	$-CO_2$
	IV	799- 883	8.80	09.51	-CO
Sr:$BaC_4H_4O_6$ (0.05M)	I	27.78-245	1.75	2.36	$-0.5H_2O$
	II	245-360	15.72	15.70	$-2CO\ 2H_2$
	III	360-400,	11.53	11.51	$-CO_2$
	IV	400-599,	7.28	7.33	-CO

The percentages of the weight loss in the different stages of decomposition of doped and undoped barium tartrate crystals are presented in Table 5. There is a good agreement between the observed and calculated weight losses. Strontium barium tartrate 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 dehydration, strontium barium tartrate to strontium barium oxalate, strontium barium carbonate to Strontium barium oxides [18, 19].

3.4 Differential Scanning Calorimetry (DSC) Study

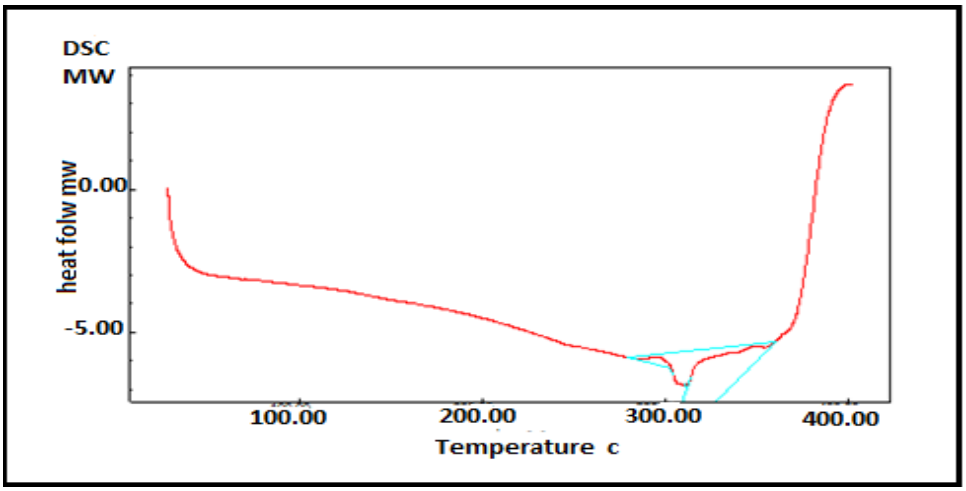

Figure 6 (a) Barium tartrate Crystals.

The differential scanning calorimetry (DSC) analysis of the grown crystals was recorded between 20^0C to 400^0C in the nitrogen atmosphere using Metals TA 4000 Instrument. The initial weight of sample was 0.100mg and heating rate was maintained at 10^0C/min. The Fig.6 (a) shows the DSC curves of barium tartrate crystals. The initiation temperature is 302.77^0C phase change complete at peak end-down temperature of 310.90^0C. The peak appeared in the DSC curve at 318.06^0C indicates the phase transformation due to loss of water molecules and formation of stable anhydrous ($BaC_4H_4O_6$) crystals. This is in good agreement with the TGA curve. The heat area under the curve is -166.33mj.

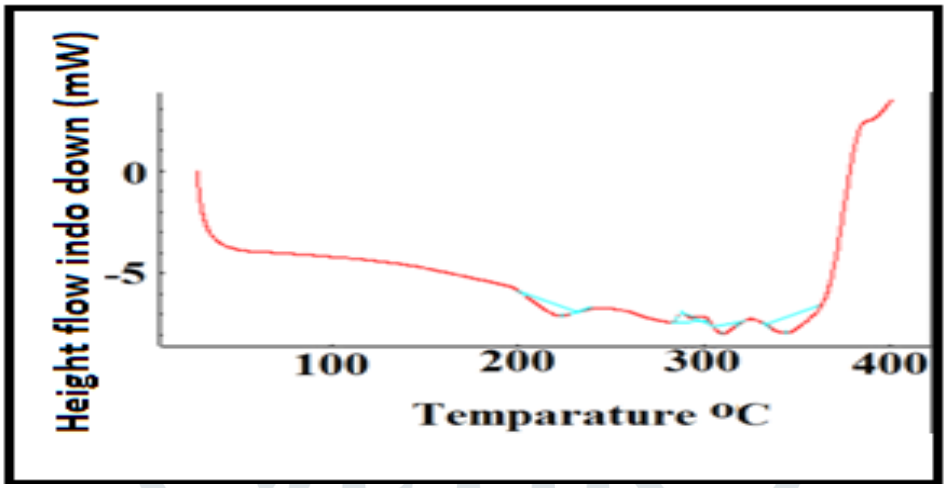

Figure 6 (b) Strontium doped barium tartrate Crystals.

Fig. 6(b) shows DSC curves of (Sr) doped barium tartrate crystals. The initiation temperature is 202.25^0C and initiation of phase change to starts completed at peak end-down temperature of 223.45^0C.The temperature at which the sample and the reference come to thermal equilibrium by thermal diffusion. The peak appeared in the DSC curve at 240.46^0C indicates the phase transformation due to loss of $0.05H_2$ water molecules and formation of stable anhydrous ($SrBaC_4H_4O_6$) crystals. This is in good agreement with the TGA curve. The heat area under the curve is -65.05mj. The initiation temperature is 284.35^0C and initiation of phase change to starts completed at peak end-down temperature of 288.47^0C. The peak appeared in the DSC curve at 303.56^0C indicates the phase transformation due to loss of 2CO and $2H_2$ and formation of stable ($SrBaC_4H_4O_6$) crystals. This is in good agreement with the TGA. The heat area under the curve is -26.75mj.

The initiation temperature is 306.94^0C and initiation of phase change to starts completed at peak end-down temperature of 310.52^0C. The peak appeared in the DSC curve at 319.56^0C indicates the phase transformation due to loss of CO_2 formation of stable ($BaSrCO_2$) crystals. This is in good agreement with the TGA. The heat area under the curve is -25.00mj. The initiation temperature is 331.64^0C and initiation of phase change to starts completed at peak end-down temperature of 344.76^0C. The peak appeared in the DSC curve at 363.25^0C indicates the phase transformation due to loss of CO formation of stable (SrBaO) crystals. This is in the good agreement with the TGA [20]. The heat area under the curve is -70.82mj.

4. Conclusions

The silica hydro gel is suitable for growing the crystals of strontium-doped barium tartrate by Signal diffusion method. The colorless, translucent, spherulitic, good quality crystals are obtained. The size of the doped crystals is increases with the increase in the concentration of (Sr) dopant. Lattice constant a, b and c, and 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 and incorporation of the dopant has not altered the structure of the parent barium tartrate crystal. As a result of (Sr) doping, the XRD peak values shifted toward lower angle, indicating that an increase in the values of lattice constants. The grain size of the undoped barium tartrate crystals are increases on (Sr) doping and subsequent doping shows increasing tendency in

grain size. The SEM study reveals that the surface morphology was affected significantly by the doping. The TGA and DSC, analysis suggests that the thermal stability of Barium tartrate crystal increases due to strontium doping. The residual strontium barium oxide (SrBaO) identified from TG analysis confirms the presence of strontium barium (SrBa) in the grown crystals.

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