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Crystal Growth and Characterization of Cobalt Doped Barium Tartrate Crystals by Silica Gel Method

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ABSTRACT
Single crystals of Cobalt doped Barium tartrate crystals were grown by single diffusion technique at room temperature. Effect of Cobalt doping in the Barium tartarate crystals has been studied and reported. The XRD pattern shows that Cobalt barium tartarate crystals are polycrystalline in nature and having orthorhombic structure. SEM pictures infer that crystals were grown by layer deposition. The elemental analysis has been carried out by EDAX. The chemical analysis has been performed by FTIR to denote the functional group of grown crystal. The thermal stability has been studied by the TGA, DTG and DSC.
Keywords - Single diffusion, XRD, SEM, FTIR, Thermal analysis.

I. INTRODUCTION

Now a day's crystal growth is the rapid growing field in research because of huge demand of crystals for several applications. Crystals which are insoluble or sparingly soluble were synthesized by gel technique. There are various types of crystals which can be grown by this simple and inexpensive technique. We have turned our attention towards the tartarate crystals as these crystals are having good application and can be synthesized by gel technique. Commercially, the tartrate compound can be used in various applications like 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 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, optical and other pertinent characteristics [7-12].

Many researchers have grown the series of pure and mixed crystals to find out the new material for various purposes [13-17]. 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 or at constant temperature.

Barium tartarate (BaTr) is a quite interesting compound as they are having good applications. Hence in the present course of investigation it has been decided to synthesize and characterize Co-doped Barium tartarate crystals by silica gel method. As grown crystals are characterized by different techniques and reported.

II. EXPERIMENTAL WORK

The cobalt doped barium tartarate crystals were grown by single diffusion method by silica gel at room temperature. The Sodium Meta Silicate solution prepared by dissolving 22 gm Sodium Meta Silicate in to the 250ml distilled water with constant stirring and kept in dark and cool place. 15 ml acetic acid dissolved in 250 ml distilled water and stored as the stock solution. Then, 6 ml solution taken in to the beaker, over this solution, solution of Sodium Meta Silicate added drop by drop with constant stirring till 4.2 pH of the solution obtained. After that 15 ml solution of $BaCl_2$ with 0.1M and 10 ml solution of $CoCl_2$ with 0.05M added in to the gel solution slowly.

This mixture was then transferred in to the test tube of 15 × 2.5 cm dimension. The open end of the tube was closed with cotton, to prevent evaporation and contamination of the exposed surface. These tubes were kept into the test tube stand, at room temperature.

After setting the gel in 7-10 days, the 10 ml tartaric acid with 1M allow to fall steadily along the wall of the tube above the set gel, to prevent the gelled surface from cracking. Crystals were visible within about a week and well shaped crystals grow approximately within one month. Figure 1 shows the cobalt doped barium tartarate crystals. The reaction between Barium Chloride, Cobalt Chloride and Tartaric acid in gel medium resulted in the growth of Co-doped Barium Chloride crystals.

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

$$2CH_3COONa+BaCl_2+CoCl2 \rightarrow (CH_3COO)_4BaCo\downarrow+4NaCl$$

$$(CH_3COO)_4BaCo+C_4H_6O_6 \rightarrow C_4H_4BaCoO_6\downarrow+4CH_3COOH$$

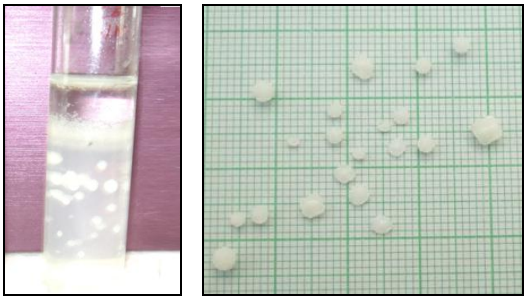

Figure1. 0.05M Co doped of Barium tartarate crystals

As grown crystals were characterize for structural, morphological, elemental and thermal properties. The structural characterization of sample was carried out by X – Ray diffractometer (Bruker - CuKα radiation) within the 2θ range of 20° - 80°. Surface morphological study was carried out by using Scanning Electron Microscope (Zeiss EVO 50), operating with an accelerating voltage 10 KV. The elemental analysis of the sample was carried out by Energy dispersive X-ray Analyzer (EDAX) attached with SEM. The FT-IR spectrum of the powdered crystalline sample in KBr medium was recorded within 450 to 4000 cm-1 by using "Perkin Elmer model 783". The thermal decomposition behavior of grown crystals was studied by thermo gravimetric analysis (TGA) and differential scanning calorimeter analysis (DSC) within the range of 27 to 600 °C at 10 °C/min heating rate in the nitrogen atmosphere.

III. RESULT AND DISCUSSION

1. XRD ANALYSIS

The XRD pattern of 0.05M cobalt doped barium tartarate crystal grown by single diffusion technique is shown in figure 2.

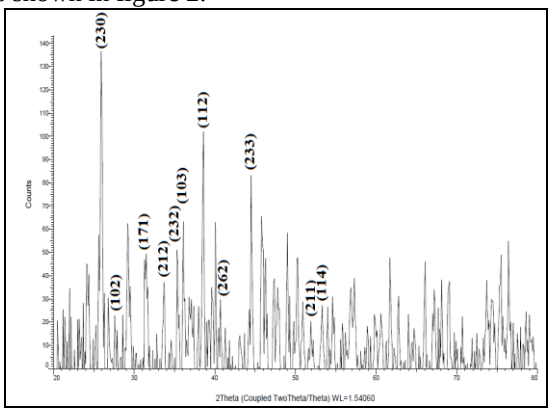

Figure2. XRD pattern of the crystals of $CoBaC_4H_4O_6$ 0.05M

The XRD pattern reveals that sample is polycrystalline in nature having orthorhombic phase. The 2θ peaks observed at 26.00°, 27.60°, 31.10°, 33.70°, 35.20°, 36.10°, 38.60°, 40.70°, 44.50°, 51.90° and 53.30° which corresponds to the (230), (102), (171), (212), (232), (103), (112), (262), (233), (211) and (114) plane of reflection respectively. These results are well in agreement with JCPDS data card no (01-1278 and 26-0192). The grain size was found to be 47.83 nm by using Debye–Sherrer's formula:

$$D = \frac{0.94\,\lambda}{\beta \cos\theta}$$

Where, λ is the X-ray wavelength, θ is the Bragg angle and β is full width at half maxima. The lattice parameters a, b, c and volume was found to 7.59, 23.78, 7.53 Å and 1360.17 respectively.

2. SEM ANALYSIS

The morphology of cobalt doped barium tartarate was studied by Scanning electron microscopy (SEM). Figure 3a and 3b illustrates the SEM images of same sample.

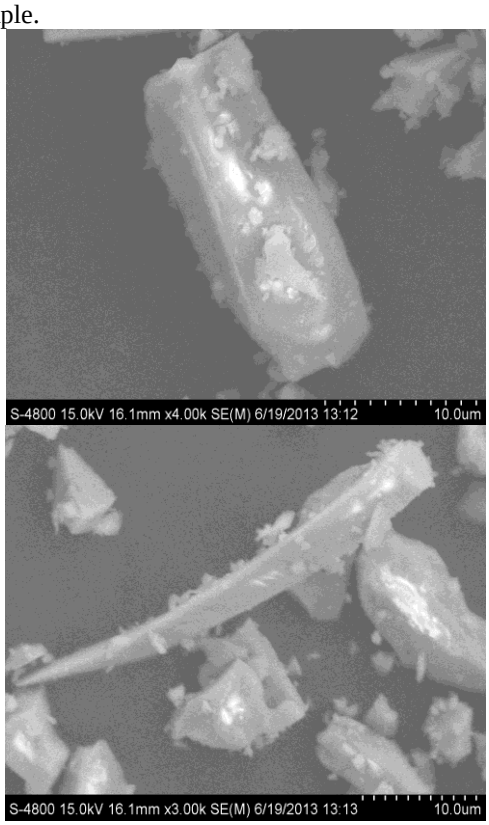

Figure 3a-b. SEM picture of 0.05M Co doped Barium tartarate crystals

The SEM photographs shows crystals are grown by layer deposition having triangular, pentagonal, rod and plate like crystals morphology. The individual plates of samples are flat and the plates with the broad edges were observed. It was found that, the structure of the as grown crystals does not affect the morphology of the crystals by doping. The shining of the crystals found to be increased in some amount.

3. EDAX ANALYSIS

The elemental analysis of as grown crystal has been done by EDAX in binding energy region within 0 to 15 KeV. Figure 4 shows the EDAX pattern of Cobalt doped Barium tartarate crystals. The spectrum shows the detection of expected elements. The atomic percentage of present element C, O, Co and Ba was found to be 42.20, 42.77, 1.95, 13.07 percent respectively.

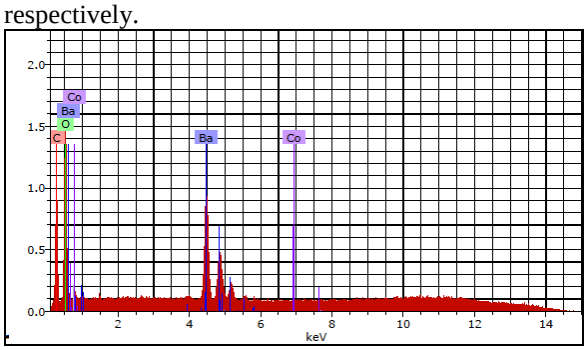

Figure4. EDAX spectrum of 0.05M Co doped Barium tartarate

4. FT-IR ANALYSIS

The functional group of cobalt doped barium tartarate crystal involved in vibration frequency has been identified using FTIR spectroscopy. The FTIR spectrum of gel grown single crystal is shown in figure 5. The spectrum shows the peaks within the range of 450 to 4000 cm^{-1}.

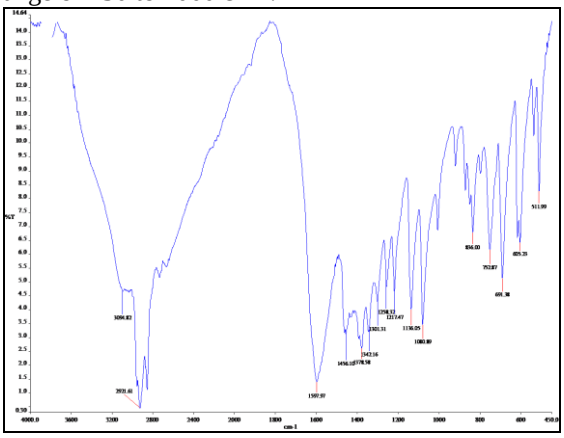

Figure5. FTIR Spectrum of Co:$BaC_4H_4O_6$ 0.05M

The FTIR spectrum recorded for Co: $BaC_4H_4O_6$ crystal with observed band. The bands around 3094 to 2853 cm^{-1} are attributed to asymmetric and symmetric –OH stretching of water. The –OH stretching frequency of $CoBaC_4H_4O_6$ appeared at 2921 cm^{-1}. The moderate absorption around 2921 to 2821cm^{-1} is probably due to stretching vibration of alkali group. The absorption at 2821 to 2921 cm^{-1} may be attributed to hydrogen bonding. The presence of the –C–O– group is indicated by the occurrence the sharp and intense band at 1597 and 1456 cm^{-1} indicate asymmetric –C–H bending. The peaks at 1378 cm^{-1} is due to –O – CH stretching mode. These bands may be assigned respectively to –C–O– asymmetric and symmetric stretching. The bonding mode of water of crystallization overlaps with the new asymmetric –C–O– frequency band. i.e. the region of for the broadness of the absorption around 1597 cm^{-1}.The absorption at 1136 cm-1 are probably due to –O–H bending while –C–OH stretching vibration represents the co-ordinate of –C–OH group. With the help of the assignment made above, 1080 cm^{-1} represents C – O stretching indicate that C – O bond stretching in alcohol –C – OH group. The absorption siuated below 836 cm^{-1} are due to barium-cobalt-oxygen stretching vibrations table1 shows the assignments of FT-IR spectrum.

Table1: FTIR data of Cobalt doped Barium tartarate crystals

Sr.	Absorption	Assignment
1	3094-2921	-OH stretching and water of crystallization.
2	1597	C=O stretching vibrations
3	1458	-C-H indicated asymmetric bending.
4	1378-1218	C-O stretching Vibration.
5	1136-1080	C-H stretching vibration.
6	836-511	Metal Oxygen(Co-Ba-O) stretching vibrations

5. TGA ANALYSIS

The thermal stability of the grown crystals and the number of water molecules associated with grown crystals determined by conducting thermo gravimetric analysis (TGA).

Figure 6 shows the TGA pattern of grown crystal. The TGA data in the different stages of decomposition are presented in table 2.

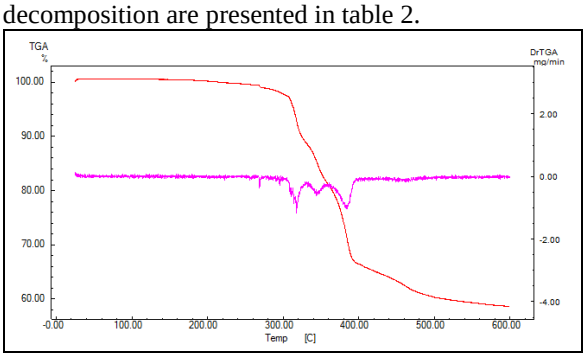

Figure6. Spectrum of $CoBaC_4H_4O_6$ 0.05 M Crystals

In stage I, it was observed that in the temperature range of 27 – 311 °C in which weight loss of 2.56 %, agrees very well with the calculated weight loss of 2.54 %. It is clear that Cobalt barium tartrate crystals are hydrated and the weight loss calculation clearly indicates that Cobalt barium tartrate crystals have 0.5H2O water loss

In stage II, In the temp range of 311- 361 °C, the total weight loss of 17.65 % is seen, which is due to the loss of 2CO and 2H2 this well arrangement with calculated weight loss of 16.98 %. Then anhydrous Cobalt Barium tartarate decomposes into Cobalt Barium oxalate. Cobalt barium oxalate stable within the temperature range 311-361 °C.

In stage III, the total weight loss of 12.86% was observed in the temperature range 361-397 °C which corresponds to the loss of CO_2. This weight loss aggress very well with the calculated weight loss 12.45% and decomposes into Cobalt barium carbon dioxide.

In stage IV, total weight loss of 8.05% was observer within 397- 600 °C. This loss is attributed to the loss of CO. This is in well agreement with calculated weight loss of 7.92 %. Thus the Cobalt barium carbon dioxide finally turns into Cobalt barium oxides at 600 °C.

Table2: TGA data of 0.05 cobalt Barium tartarate crystals ($CoBaC_4H_4O_6$)

No	Temperature °C	Observed weight %	Calculated weight %	Loss of molecule in stage
I	27-311^{0}C	2.56	2.54	-0.5H_2O
II	311-361^{0}C	17.65	16.98	-2CO2H_2
III	361-397^{0}C	12.86	12.45	-CO_2
IV	397-599^{0}C	8.05	7.92	-CO

6. DTG Analysis

The loss of molecules can be determined by using DTG analysis. The figure 6 shows the spectrum of DTG.

i. In the first stage of decomposition, Major endothermic peak at 270 °C is attributed to loss of 0.5H_2O. The peak observed in the DTG Curve corresponds to the weight loss 2.56% in the TGA curve.
ii. The endothermic peak at 318 °C in the second stage of decomposition is attributed to loss of 2CO and H_4. The peak observed in the DTG curve corresponds to the weight loss 17.65% in the TGA curve.
iii. The endothermic peak at 365 °C in the third stage of decomposition is attributed to loss of CO_2.The peak observed in the DTG curve corresponds to the weight loss 12.86% in the TG curve.
iv. In the fourth stage the endothermic peak 401°C decomposition is attributed to loss of CO. The peak observed in the DTG curve corresponds to the weight loss 8.05% in the TG curve.

Beyond the 600 °C, the reaction proceeds and finally stable residue CO:$BaC_4H_4O_6$ remains up to the end of analysis.

7. DSC Analysis

The DSC analysis of the grown crystals was recorded between 20-400 °C in the nitrogen atmosphere. The figure 7 shows the DSC curve for Co doped Barium tartarate crystals. The DSC analysis has been done in two stages. From the DSC curve the endothermic peaks are found in both stages. The DSC data is represented in table 3.

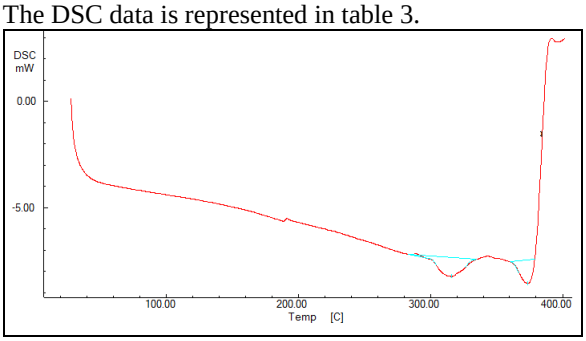

Figure7. DSC curve of Co doped barium tartarate Crystals

Table3: DSC data of Co doped Barium tartarate Crystals

No	Peaks	Temperature °C	Onset °C	Endset °C	Heat mJ
I	Endo-thermic	316.21	301.64	330.50	-119.11
II	Endo-thermic	373.61	363.43	378.95	-70.82

IV. Collusion

The cobalt doped Barium tartarate crystals were grown by single diffusion method. The XRD illustrates that the grown crystals are polycrystalline in nature and orthorhombic phase. SEM pictures shows crystals are grown by layer deposition. The incorporation of Co in the crystals of Barium tartarate has been confirmed by EDAX. The chemical analysis has been done by FTIR to denote the functional group of grown crystal. The thermal stability was studied by the TGA, DTG and DSC.

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