

Optical and Thermal Studies on Barium Doped Cadmium Tartrate Oxalate Single Crystals by Sol Gel Technique

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Abstract: Cadmium Tartrate Oxalate single crystals doped with barium were grown by controlled diffusion in silica gel at ambient temperature. The maximum uptake of barium in Cadmium Tartrate oxalate single was determined. Effect of barium dopant on the growth and morphology of Cadmium Tartrate oxalate single crystal was studied. In the gel preparation process sodium Meta silicate (Na_2SiO_3) is mixed with the mixed solution of oxalic acid ($\text{C}_2\text{H}_2\text{O}_4$) and tartaric acid ($\text{C}_4\text{H}_6\text{O}_6$) in the desired mole fraction. The harvested crystals were characterized by X- ray powder Diffractogram, Fourier Transform Infrared Spectroscopy, quantitative elemental analysis of EDAX and Scanning Electron Microscope. Powder XRD results indicates the polycrystalline nature of this materials. FTIR for these crystals show all the bands expected from the metal tartrate oxalate with water of crystallization. Further the presence of cadmium, carbon and oxygen is confirmed by EDAX.

Keywords: Gel growth, barium doped Cadmium tartrate oxalate, XRD, FTIR, EDAX, TGA and SEM.

1. Introduction

Single crystals are the backbone of the modern technology of logical revolution [1-3]. The impact of single crystal, is clearly visible in industries like semiconductors, optics etc. Growth and characterization of Cadmium Tartrate Oxalate single crystals, both pure and doped have attracted many researchers single crystals of barium mixed Cadmium Tartrate Oxalate crystal have been grown and reported. Now a day great attention has been devoted on the growth and characterization of doped Cadmium Tartrate Oxalate crystal with the aim of identifying new materials for practical purposes [4, 5]. The effect of doping on various purpose of crystal is of great interest from solid state science as well as technological point of view. The crystals of Cadmium Tartrate oxalate grown in silica gel medium in doped with Barium, Strontium, Lithium and Calcium have already been reported [6,7]. The growth of Barium doped Cadmium Tartrate oxalate crystals yet had not been reported. In the present work we have attempted to grow pure and Barium doped Cadmium Tartrate oxalate crystal by Gel Technique.

2. Materials and Methods

All chemicals used such as oxalic acid, tartaric acid, sodium metasilicate, barium chloride and cadmium chloride were of AR grade to avoid impurity accumulations. Barium doped Cadmium Tartrate Oxalate crystals were grown from free solution of oxalic acid, tartaric acid, barium chloride and cadmium chloride. Silica gel were prepared by adding oxalic acid (1M) and tartaric acid (1M) mixture to sodium meta silicate (water glass) solution of specific gravity 1.04 drop by drop till the p^{H} of the gel adjusted to 3.5, 4.0 and 4.5. Continuous stirring is needed to avoid excessive local ion concentration, which may cause premature local gelling and make final solution inhomogeneous. The solution with the desired value of pH is transferred to several glass tubes. The gel

found to set in 30min to 24 hours, depending upon its P^H and the environmental temperature. Once gelled, feed solution of aqueous barium chloride and cadmium chloride of concentration 1.5M was carefully placed with the help of a pipette over the set gel in order to avoid the surface damage and breakage of the gel. The Cd ions diffuses slowly through narrow pores of the gel to react with the oxalate and tartrate ions, giving rise to the formation of single crystals.

After harvesting the fully grown barium doped Cadmium Tartrate Oxalate crystals, structural characterization was performed using X-ray powder diffraction technique. XRD patterns were obtained using a Philips analytical X-ray diffractometer with $cuK\alpha$ ($\lambda=1.5406\text{\AA}$) radiation. The FTIR spectra were recorded for the crystals in the wave number range of 400-40000 cm^{-1} using bruker vector 22 spectrometer using KBr pellet technique.

3. Results and Discussion

3.1. Growth kinetics

The crystal size as a function of time was noted every day and it was observed that the crystal size gradually increases with time and finally the growth rate ceased after a period of 240 hrs as shown in Fig.1. This is mainly due to the decrease of solute concentration of feed Solution and non-availability of the ions in the gel after a period of 10 days. The nucleation rate of barium doped cadmium oxalate tartrate crystals grown for three different p^H values were recorded and their variations. It is evident that the number of crystals increases as the growth period increases are shown in Fig 2. This is only due to the impregnation of the outer reagent which forms more number of crystals as time advances. Further, on decreasing the P^H values from 4.5 to 3.5, the nucleation rate is considerably reduced. Also it was observed that the lowest p^H value limit is 3.5, below which the crystal formation is absolutely not possible.

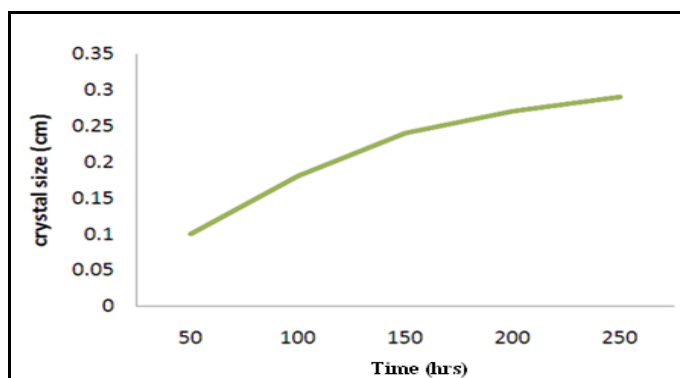


Fig.1. Crystal size variation with time.

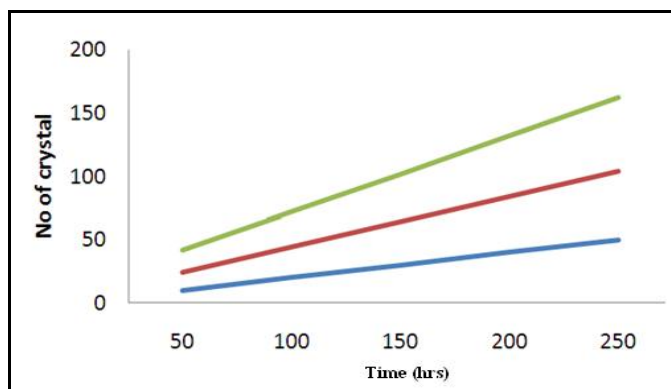


Fig.2. Time vs. No of crystals.

The size and parameters of single barium doped cadmium Tartrate oxalate crystal grown in silica gel. The crystal size as a function of time was noted every day. It was observed that the crystal size gradually increases with time.



Fig.3. Shows photo graph of prepared barium doped cadmium tartrate oxalate crystal.

Table-1: Optimized growth parameters of crystals.

S. No.	Various process parameters	Values
1.	Density of Na ₂ SiO ₃	1.04 g/cm ³
2.	Concentration of Oxalic acid	1M
3.	Concentration of Tartaric acid	1M
4.	Concentration of Cadmium chloride	1.5M
5.	Concentration of Barium chloride	1.5M
6.	Gel setting period	10h
7.	Gel aging	3 weeks
8.	Period of growth	30days
9.	Temperature	Room temperature

3.2. X-Ray Diffraction Analysis

The crystal structure of a sample compound was studied by powder X-ray diffraction method. The X-ray diffraction was recorded using Miniflex-Rigaku model Japan with CuK α radiation of wavelength $\lambda=1.54056\text{\AA}$. The recorded diffraction pattern of the barium doped cadmium oxalate tartrate crystals is shown in the Fig.4.

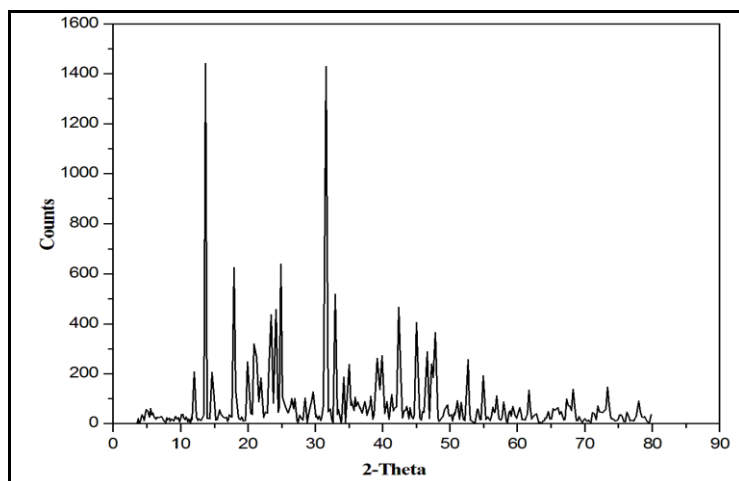


Fig. 4. Powder diffraction pattern of barium doped cadmium oxalate tartrate crystal.

3.2.1. 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:

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

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

$$D = \frac{0.9 \times 1.54056}{0.182 \times \cos(31.576)}$$

$$= 8.9451 \text{ \AA}$$

The calculated average grain size is 0.89451 nm. The analysis of different diffraction peaks indicates the formation of system. The diffraction peaks at 2θ value were measured very carefully and converted into d value using the Bragg's equation putting $n=1$. The size of the crystal is very small compared to the Cadmium Tartrate Oxalate Single Crystals. This variation in size explains the influence of addition of Barium on the size of the crystal.

3.3. FTIR spectral analysis

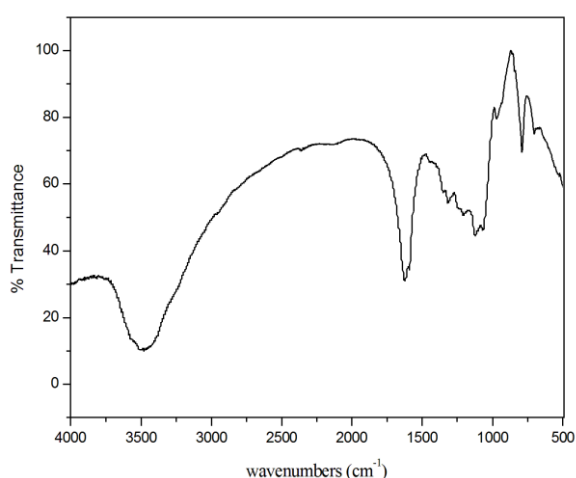


Fig.5. FT-IR Spectrum of Barium doped Cadmium tartrate oxalate crystals.

IR spectroscopy is very helpful for the identification of a compound [8,9]. The FT-IR spectroscopic studies of humboldtine and of cadmium Tartrate oxalate have been reported [10,11]. FT-IR spectrum of gel grown cadmium oxalate crystals was recorded in the region $400\text{--}4000 \text{ cm}^{-1}$ on "Perkin Elmer Spectrum, GX-Spectrometer." The spectrum is shown in Figure 5. Strong and very broad band appeared at 3480.59 cm^{-1} which is attributed to O-H stretching vibration. Very intense but broad band appeared at 1620.05 cm^{-1} which may be due to O-H bending vibration [12]. The sample that has oxalate (C_2O_4)₂ ion is supported by the broad peak merged in the strong broad band in the region 1620.05 cm^{-1} , which is attributed to the asymmetric stretch of CO_2 [13]. And the well-pronounced sharp peak at 1316.46 cm^{-1} and a weak but sharp peak at 1348.01 cm^{-1} correspond to the CO_2 symmetric stretching. The strong and very sharp band which was observed at 791.68 cm^{-1} is due to the combined effect of in-plane deformation of CO_2 and the presence of a metal-oxygen bond. A moderate sharp band appeared at 471.23 cm^{-1} which might be due to CO_2 wagging.

3.4. Surface analysis (SEM)

A SEM photograph reveals that the flower type structure on the top of the edge. The petals of boundary were clear. Fig. 8 shows the SEM photographs with two different photographs of pure CdTr crystals. The high depth of field of the SEM images makes it especially suitable for the study of the fractured surfaces and complex microstructure such as those found in composite material. These crystals are grown by layers deposition. Thick and thin layers are seen in figures. The plates with the sharp edges were observed and some plate further growth was observed.

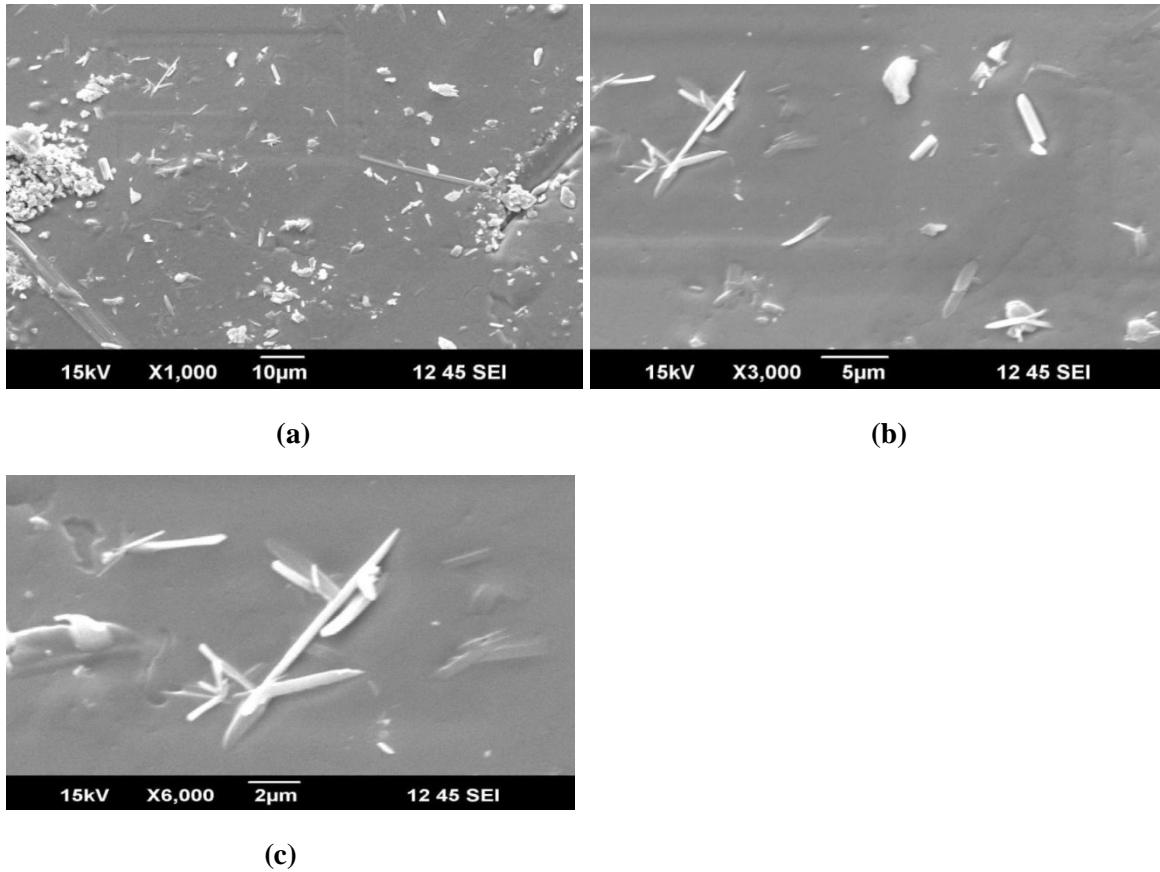


Fig.6. SEM images for barium doped cadmium oxalate tartrate crystal with different magnification.

3.4.1. EDAX

In order to confirm the presence of cadmium and barium, quantitative elemental analysis were performed on the application of EDAX. The EDAX spectrum of barium doped cadmium oxalate tartrate crystal as shown in Fig.7. It reveals prominent Peaks due to cd L α , CK α and OK α . This confirms the formation of cadmium tartrate oxalate crystals. The weight [%] and atomic weight [%] calculated from the peaks height further confirms the expected proportion of carbon, oxygen and cadmium crystals.

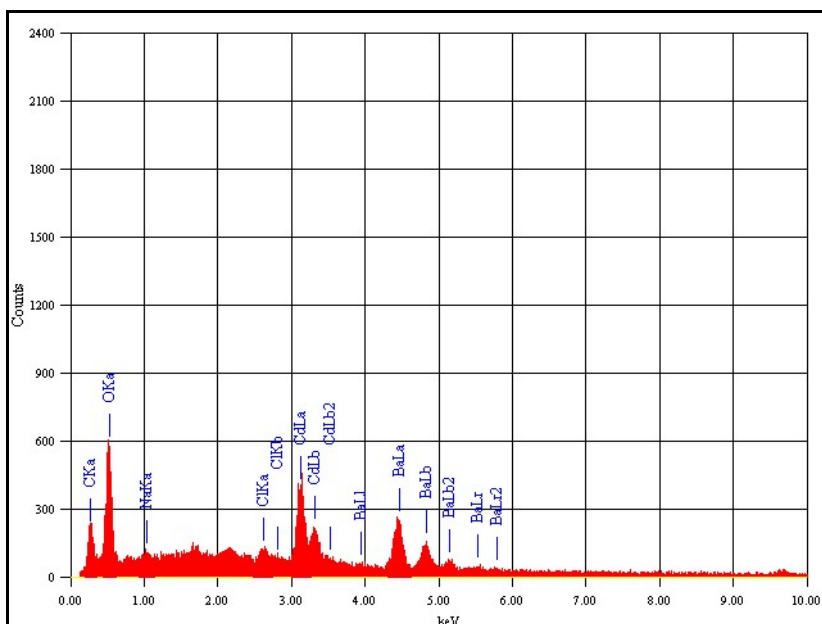


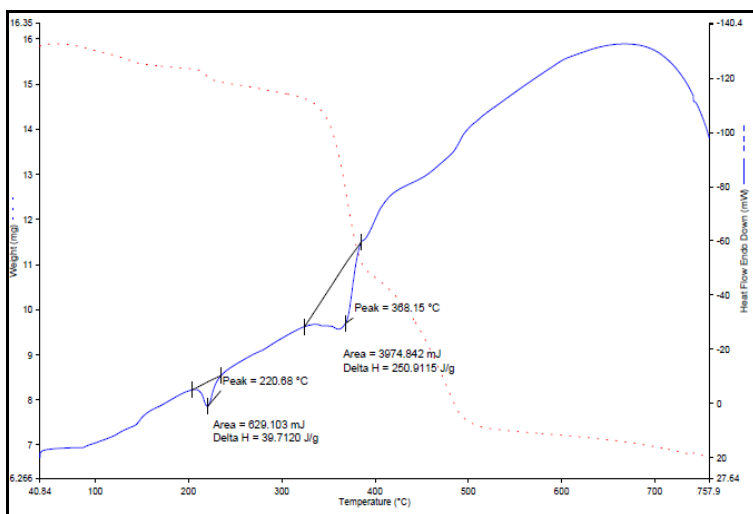
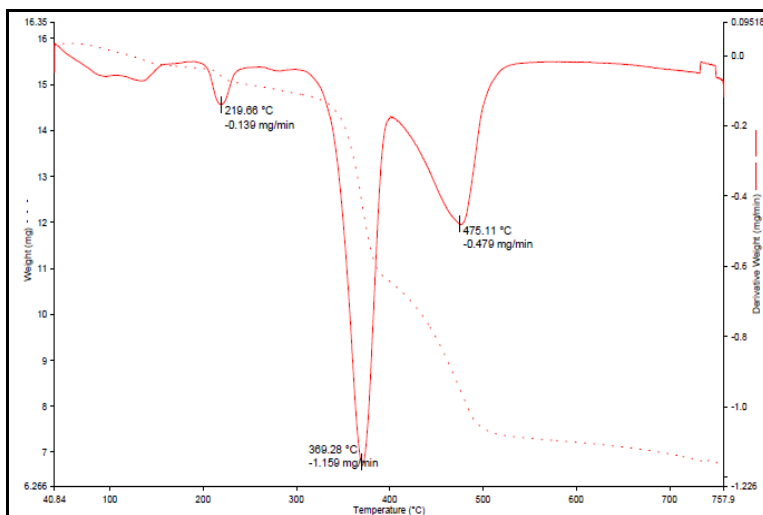
Fig. 7. EDAX analysis for barium doped cadmium oxalate tartrate crystal.

Table-2: Elemental analysis for barium doped cadmium oxalate tartrate crystal.

	(keV)	Mass%	Atom%	K
C K	0.277	10.09	34.72	2.5867
O K	0.525	14.66	37.87	1
Na K	1.041	0.41	0.74	0.7693
Cl K	2.621	1.76	2.05	1.1033
Cd L	3.133	39.26	14.44	3.7857
Ba L	4.465	33.82	10.18	5.3064
Total		100	100	

3.5. Thermal Analysis

In the first stage of decomposition, in fact, the dehydration, which begins at 50°C and continues up to, or terminates at, 195°C. The net weight loss (0.3%) as observed between 50°C and 195°C corresponds to loss of the water molecules, suggesting that the grown crystals were initially trihydrated. The coordinated molecules of water lost during this stage leads to the formation of anhydrous barium doped cadmium oxalate tartrate. The second stage of decomposition sets in at around 220°C and is completed at around 300°C; this stage of reaction corresponds numerically to 1% of the total weight loss. Then, in the third stage of decomposition, which seemingly occurs in the temperature interval of 350–390°C, the complex is decomposed to form barium doped cadmium oxalate tartrate as the second intermediate product.

**Fig. 7(a). TG and DTG for barium doped cadmium oxalate tartrate crystal.****Fig. 7(b). TG and DTA for barium doped cadmium oxalate tartrate crystal.**

This is of course confirmed by the fact that 3.3% of the total mass is found to have been lost. DTA shows an endothermic at 220.08°C corresponding to DTG peak at 368.15°C with a shoulder in DTG at about 180°C. Simultaneous loss of 6H₂O and 2C can be confirmed from the peak is observed in DTG curve at 219.66°C and 475.11°C since only one peak is observed in DTG curve corresponding to two peaks in DTA curve.

4. Conclusion

Sol-Gel method is found suitable for growing barium doped Cadmium Tartrate Oxalate crystal. The growth of single crystal of barium doped Cadmium Tartrate Oxalate crystal was accomplished using single test tube diffusion method. Different habits of barium doped Cadmium Tartrate Oxalate crystal can be obtained by changing parameters like gel density, gel ageing, pH of gel, concentration of reactants etc. EDAX studies reveals that grown crystal are barium doped Cadmium Tartrate Oxalate indeed. Water of Crystallization present in grown crystal and presence of barium and Cadmium is confirmed in the crystal. The SEM images shows morphology of crystal studies suggested 2-D layer deposition growth.

5. References

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