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Structural and thermal studies of barium doped cadmium tartrate crystals grown by gel method

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ABSTRACT

The effect of Barium doped Cadmium Chloride (BCT) solution, on the size and transparency of cadmium tartrate crystal are presented in this paper by controlled diffusion of cadmium chloride into gel with tartaric acid at room temperature. Crystal size can be determined by XRD analysis. The transparency of Cadmium Tartrate can be enhancing by the Barium doping. Thermal behavior of BCT crystals were studied by using Thermo Gravimetry (TGA/DTG/DSC) which reveals, water molecules are locked up in the lattice with different strength in the grown crystals.

Keywords: XRD, kinetic parameter, Thermodynamic parameter, DSC etc.

INTRODUCTION

Single crystals are the backbone of the modern technology of logical revolution [1-2]. The impact of single crystal, is clearly visible in industries like semiconductors, optics etc. This type of crystal inventions of LASER, and the field of the nonlinear optics and the practical implementations was possible with the applications of nonlinear optical crystal [3]. Now a day's great attention has been devoted to the growth and characterization of doped tartrate crystal with the aim of identifying new materials for practical purposes [4, 5]. The effects of dopant on various purpose of crystal are of great interest from solid state science as well as technological point of view. The crystal of cadmium tartrate grown in silica gel medium in doped with Barium, strontium, Lithium, Calcium have already been reported[6]. The growth of Barium doped Cadmium Tartrate crystal yet had not been reported. In the present work we have attempted to grow pure and Barium doped cadmium Tartrate crystal by Gel Technique. This Growth experiment yielded crystal in the Gel using solution Gel Technique [7].

MATERIALS AND METHODS

Most of the tartrate compounds are insoluble in water and decompose before melting. Hence, such type of compounds cannot be grown by either slow evaporation or melt technique. But can be grown by solution gel method. A single diffusion method (Henish 1973) was employed to grow pure and Barium doped Cadmium tartrate crystal in the gel method [8]. The AR grade (Loba) chemicals were used for the present work. The crystallization apparatus employed was Borosilicate glass tubes (25mm diameter and 200mm length). Gel was prepared by mixing sodium meta silicate solution of appropriate specific gravity and one molar solution of tartaric acid so that the desired pH of the mixture could be obtained. The specific gravity and pH were varied between 1.02 gm/cc to 1.05 gm/cc and 4 to 5 respectively. After mixing the solution was allowed to set for about 48 hours. Over the set Gel, one molar cadmium chloride solution was gently poured with the help of a pipette, so as to allow the solution to fall steadily along the walls of the tube without disturbing the gel surface The supernatant ions (Ba^{++} and Cd^{++}) slowly diffuse into the gel medium where it reacts with inner reactant. The open end of the test tube was closed with cotton to avoid dust from the entering into the glass tube. The solution was faint milky and transparent, initially, but with

lapse of time its color slightly change. The test tubes were kept undisturbed at room temperature. To grow doped crystal, an aqueous solution of Barium chloride of varying concentration 0.2- 1.0 M was mixed with the top solution. After one month the crystal was taken out from the test tube and cleaned for the further characterization [9]. The best quality crystals were grown for 4.2 pH as shown in fig-1.

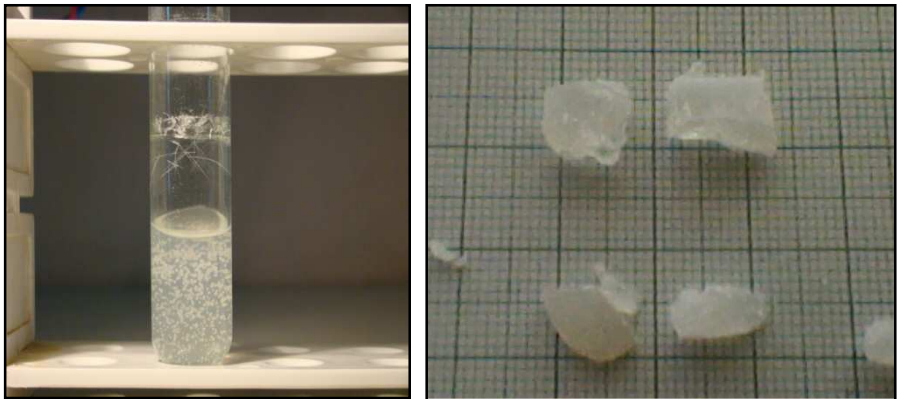

Figure 1a-b: Barium doped cadmium tartrate crystal

RESULTS AND DISCUSSION

3.1 XRD Analysis:

X-ray diffraction technique is used to investigate the inner arrangement of atoms or molecule in the crystalline material. The grown BCT crystalswere subjected to powder diffraction pattern of the grown crystal was carried out using BRUKER AXSD8-Advance model Germany. X-ray diffraction with CuKα1 radiation of wave length (λ=1.54056 Å) operating at a voltage of 40KV and a current 20 mA. The scanning rate was maintained at 2º/min over a 2θ range of 20- $80^{0.}$ The XRD powder pattern of barium doped cadmium tartrate crystal is shown in fig-2. The sharp peaks with maximum intensity characterize the XRD pattern, indicating the formation of well defined crystallites.

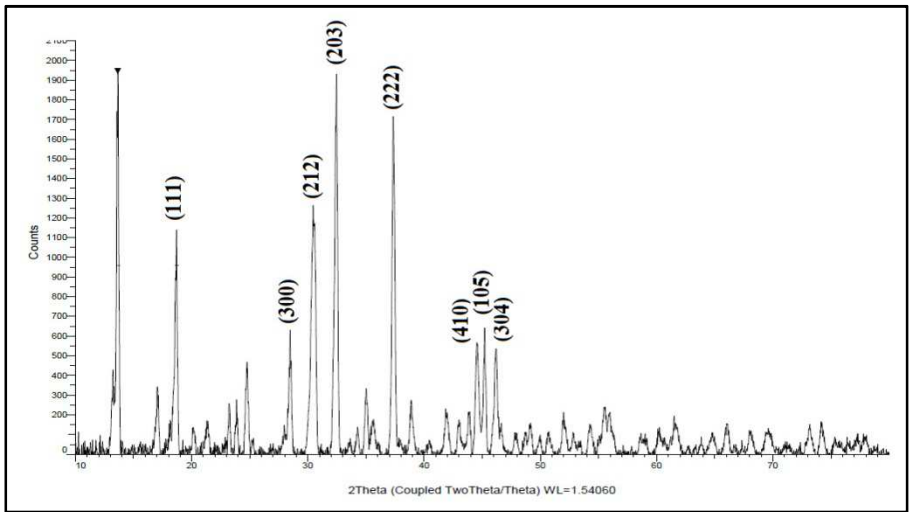

Figure 2 Powder X-Ray diffraction of BCT Crystal

Table 1 Powder diffraction data of BCT crystal

From present work				From JCPDS file			
2θ	Observed d-value	Intensity	h k l values	2θ	Standard d-value	Intensity	h k l values
18.648	4.75441	1081	111	18.659	4.75438	68	101
28.483	3.13116	363	300	28.772	3.13106	26	200
30.439	2.93426	1120	212	30.441	2.93430	756	211
32.415	2.75976	1419	203	32.589	2.75970	911	112
37.325	2.40723	928	222	37.837	2.40728	311	103
44.551	2.03215	708	410	44.608	2.03220	17	402
45.155	2.90632	718	105	45.831	2.90645	4	431
46.153	1.96524	104	304	46.073	1.96521	3	204

The spectrum match with the data reported in JCPDS file No26-0282[11]. From this diffraction pattern intensity and (h, k, l) values were computed. The XRD data of the grown crystals are indexed in table-1. The unit cell parameter satisfy the condition for hexagonal system that is a= b≠ c and α=β=90^0 γ = 120°. The diffracting index observed d values are in good agreement with calculated values. It is very interesting to note that BCT crystals are polycrystalline nature and hexagonal structure. The unit cell parameter is a=10.74,b=10.74, c =10.2,V=74.46. Percentage of crystallinity is very good and it is 88.6% and crystal size is 5.2nm.and FWHM is 0.214.

Analysis composition determines by chemical analysis 49.9% Ba and 50.1% Cd and space group Pm-3m (221).

3.2 Thermal analysis of barium cadmium tartrate crystal (TGA)

The thermal decomposition behavior of grown crystals was studied by Thermo Gravimetric Analysis (TGA) and Differential Scanning Calorimeter analysis (DSC). The TGA was carried out from room temperature to 800 ºC, at heating rate of 10 ºC/min in the atmosphere of air by using BRUKER system.

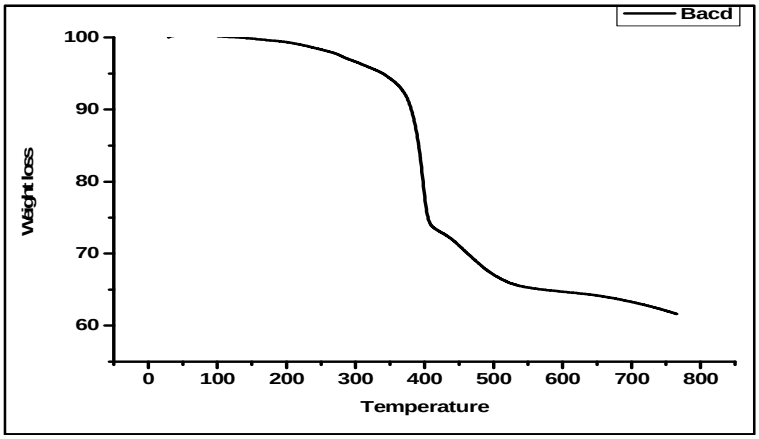

Figure 2 TGA curve of barium cadmium tartrate crystal

Table 2 TGA data of BCT crystal

stage	Temperature range	Observed %weight loss	Calculated %weight loss	Loss of molecule in stage
1	100 to 310℃	4%	4.42 %	H_2O
2	310 to 380℃	21.63%	21.60 %	$2CO_2$
3	380 to 410℃	7.86%	7.68%	$CO2H_2$
4	410 to 685℃	5.83%	6.88%	CO

The TGA curve for BCT crystal is shown in figure 2. The percentages of the weight loss in the different stages of decomposition of BCT crystal are presented in table 2. There is a good agreement between the observed and calculated weight losses. BCT crystal is water coordinated compound. Therefore there is a possibility that this crystal may lose some of its water molecules while heating. TGA of BCT crystal showed clearly four stages of decomposition as expected:

1) Dehydration
2) Barium Cadmium tartrate to Barium Cadmium oxalate
3) Barium Cadmium oxalate to Barium Cadmium carbonate
4) Barium Cadmium carbonate to Barium Cadmium oxide BaCdO.

Stage-I $BaCdC_4H_4O_6\ H_2O \rightarrow H_2O\uparrow\ BaCdC_4H_4O_6\downarrow$
Stage-II $BaCdC_4H_4O_6 \rightarrow 2CO_2\uparrow BaCdC_2O_4\downarrow$
Stage-III $BaCdC_3O_4 \rightarrow CO2H_2\uparrow BaCdCO_2\downarrow$
Stage-IV $BaCdCO_2 \rightarrow Co\uparrow Ba{:}CdO\downarrow$

The use of thermo gram data to evaluate kinetic parameter of solid state reaction involving weight has been investigated by many workers [15]. The shape of the curve is determined by the kinetic parameters of BCT such as order of reaction, frequency factor, and energy of activation. Fig shows thermo gram of BCT crystal. The thermal behavior of BCT crystal is as summarized in table no2. The value of theoretical weighted percentage and observed weight percentage at different stages was motioned in the table 2. From the thermo gram, it was found that the BCT crystal were first dehydrated and decomposed.

The first stage of the decomposition occurred at 100 ºC-310°C one water molecule are dehydrate and loss H_2O.Second stage of the decomposition occurred at 310-380°C it was converted in to barium cadmium oxalate and loss of $2CO_2$ molecule. The third stage of the decomposition occurred at 380-410°C. It was converted in to barium cadmium carbonate and loss $2H_2CO_2$ molecule. The fourth stage of the decomposition occurred at 410-685°C. It was converted in to barium cadmium oxide and loss of CO molecule.

Kinetic and thermodynamic parameter can be evaluated from the thermo gram. In present investigation the Coats and Redfern relation [16-20] was use to evaluate the kinetic parameter from the thermo gram as shown in fig-2. The TG curve did not show the appreciable weight change in the temp range 175^0C indicating that the BCT crystal are thermally stable in this range and no transformation took place. It was observed that the decomposition beginning at 175^0Cand crystal is unstable beyond 175^0C. The use of thermo gram data to evaluate kinetic parameter of solid state reaction involving weight has been investigated by many workers [15].The shape of the curve is determined by the kinetic parameters of BCT such as order of reaction, frequency factor, and energy of activation.fig shows thermo gram of BCT crystal. The value of theoretical weighted percentage and observed weight percentage at different stages was motioned in the table. From the thermo gram, it was found that the BCT crystal were first dehydrated and decomposed. The Coats-Redfern relation is as fallows:

$$log10\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = log10\left[\left(\frac{AR}{\alpha E}\right)\left(1-\frac{2RT}{E}\right)\right] - \left\{\frac{E}{2.3\ RT}\right\} \quad \ldots (1)$$

For n≠1

Where α = fraction of original substance decomposed at time t, n = order of reaction, A = frequency factor, E = activation energy of the reaction, R = gas constant, a = heating rate in °C/min.

To determine the value of activation energy and order of reaction, Coats-Redfern plot,

$Y = -log10\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right]$Verses X = 1/T. is drawn for different values of n and the best linear plot gives the correct value of activation energy. Equation (1) cannot be use for n=1, Therefore it is modified as follows

$$-log10\left[-log10\frac{(1-\alpha)^n}{T^2}\right] = log10\left[\left(\frac{AR}{\alpha E}\right)\left(1-\frac{2RT}{E}\right)\right] - \left\{\frac{E}{2.3\ RT}\right\} \quad \ldots (2)$$

For n=2

In present investigation the best linear fit was obtained for n=2. The values of activation energy and frequency factor are found.

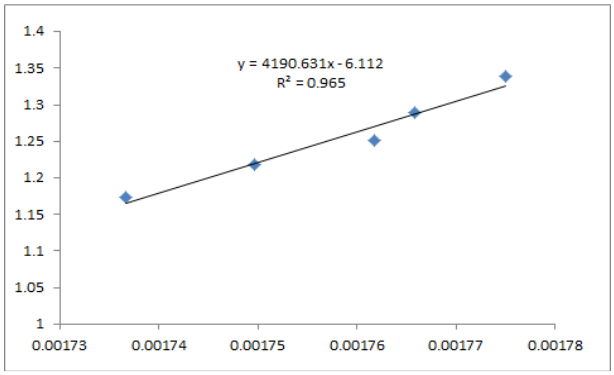

Figure 3 Coats and Redfarn Plot of BCT crystal

Table 3 Kinetic parameter of dehydration and decomposition of BCT crystal

Kinetic parameter	Symbol	Value
Activation energy	E	95.47
Frequency factor	A	1.27E+07
Order of reaction	n	2

Table 4 Thermodynamic parameter of dehydration and decomposition of BCT

Thermodynamic parameter	Symbol	Value
Standard Entropy of activation	$\Delta\ddagger S^o$	5103.92 $KJMol^{-1}$
Standard Enthalpy of activation	$\Delta\ddagger H^o$	9546.5 $KJMol^{-1}$
Standard Gibbs energy of activation	$\Delta\ddagger G^o$	4546.6 $KJMol^{-1}$
Standard Internal energy of activation	$\Delta\ddagger U^o$	5215.23 $KJMol^{-1}$

CONCLUSION

1) Gel method is found suitable for growing barium cadmium tartrate crystal.
2) The growth of barium cadmium tartrate crystal was accomplished using single test tube diffusion method. Optimum condition for growth ware worked out.
3) Different habits of barium cadmium tartrate crystal can be obtained by changing parameters like gel density, gel ageing, pH of gel, concentration of reactants etc.
4) The XRD pattern revels that the grown crystals exhibits crystalline nature and confirms the unit cell parameter value with those available in the literature.
5) The thermo gram of BCT crystal indicated that the compound was stable up to 175°C and then decomposes in to barium cadmium carbonate. The values of kinetic parameter were evaluated.

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