ISSN : 2393-8188 (print)
2393-8196 (online)
www.milliyasrcollege.org.journal.php

# THERMAL STUDIES ON COPPER DOPED BARIUM TARTRATE SINGLE CRYSTALS BY SILICA GEL TECHNIQUE

**Suresh K.Bachhav*, Hemant.G. Bangale[2], K.B. Patil[3]**

[1,3]J.D.M.V.P.Co-op Samaj's , Arts Commerce and Science College, Varangaon Dist. Jalgaon (M.S), India
[2]J.D.M.V.P.Co-op Samaj's , Arts Commerce and Science College, Yawal Dist. Jalgaon (M.S), India

*Correspondingauthoremail:sureshbachhav47@gmail.com

**Abstract:** In the present research work, the single crystals of copper doped Barium tartrate were grown by single diffusion technique. The optimum growth conditions of copper doped Barium tartrate 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 copper doping on the Barium tartarate has been studied. The XRD pattern shows that Copper doped barium tartarate crystals are polycrystalline, having orthorhombic structure. Thermo gravimetric analysis (TGA) and Differential thermal analysis (DTA) curveshows the percentages of the weight loss in the different stages of decomposition of barium tartrate. Differential scanning calorimetry (DSC) curveshows the phase transformation due to loss of water molecules and formation of stable anhydrous $CuBaC_4H_4O_6$ crystals.

***Keywords***:Crystal growth techniques Single diffusion, XRD, TGA, DTA and DSC.

## 1. INTRODUCTION

In the present work, doped and undoped barium tartrate crystals were grown by silica gel method using single diffusion technique. Copper is used as dopant. However, there is not a single research paper available in the literature survey on the growth and characterizations of these barium tartrate crystals.

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 urinary drugs, ferroelectric applications of sodium-potassium tartrate [1], potassium-chromium tartrate in medicine [2] and so on. Many people studied various tartrate compounds like calcium-strontium mixed levo tartrate [3], zinc tartrate [4] and cadmium tartrate [5] 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 [6], Hartman [7], Kern [8], Chernor [9], Burton [10] and Mullin [11]. A number of factors such as degree of saturation, type of solvent [12], pH of the gel media [13, 14], presence of impurities [15,16] and the change in growth temperature also presumably affect significantly the morphology of the crystal [17]. The crystals, which can't satisfactorily grow from melt and vapor, are grown successfully by using this method [18- 20]. Barium tartarate 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 Copper doped Barium tartarate crystals by silica gel method. The grown crystals are characterized by XRD, TGA, DTA and DSC techniques.

## 2. MATERIAL AND METHODS

**Table 1: Optimum condition for growth of strontium-**

**doped barium tartrate crystals.**

| Sr. no | Optimum growth Conditions | Single diffusion |
|---|---|---|
| 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 | Dopend Concentration of $CuCl_2$) | 0.05M |
| 07 | Concentration of supernatant ($C_4H_6O_6$ ) | 1M |
| 08 | Gel setting time | 2days |
| 09 | period of crystals growth | 6 weeks |

10All 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 ($C_4H_6O_6$), Copper Chloride ($CuCl_2$) and barium chloride ($BaCl_2$). Different molar mass was tried to determine the optimum growth conditions. The gel was prepared by mixing the solutions ($CH_3COOH$), ($Na_2SiO_3$), ($BaCl_2$) and ($CuCl_2$) 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.

Hydro silica gel is very good medium for growing better quality doped and undoped crystal of barium tartrate. The 0.05M concentrations of $CuCl_2$ in an aqueous solution were used to grow Cu doped barium tartrate crystals. To grow well defined crystals of Copper-doped barium tartrate, several experiment were performed 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 high quality crystals established by varying various parameters are given in Table 1.

## 3. RESULTS AND DISCUSSION

### 3.1 X-ray powder diffraction analysis (XRD)

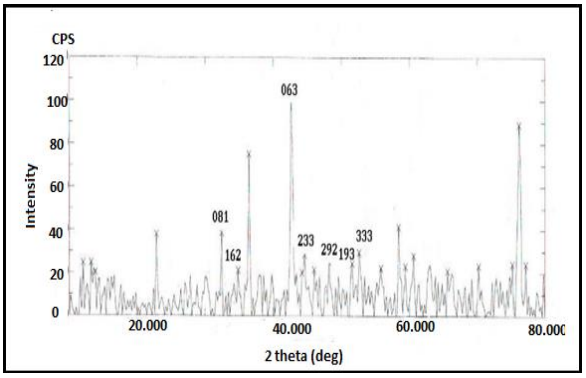



**Figure 1 the XRD pattern of barium tartrate Crystal.**

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 dopend 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 04-0836.

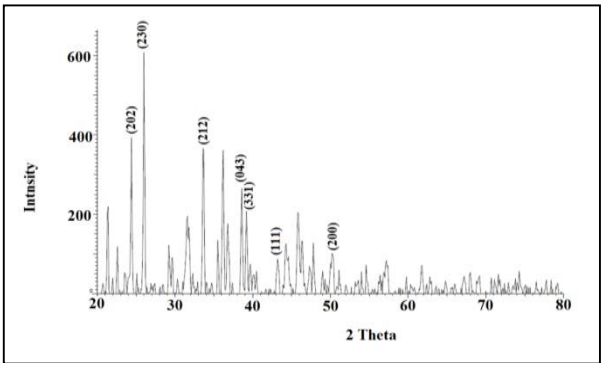



**Figure 2 the XRD pattern of $CuBaC_4H_4O_6$ crystals (0.05M.)**

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

| Observed data values | | | Standard data values | | | |
|---|---|---|---|---|---|---|
| 2θ | d-value | Int en. | 2θ | d-value | Inte n. | 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 |

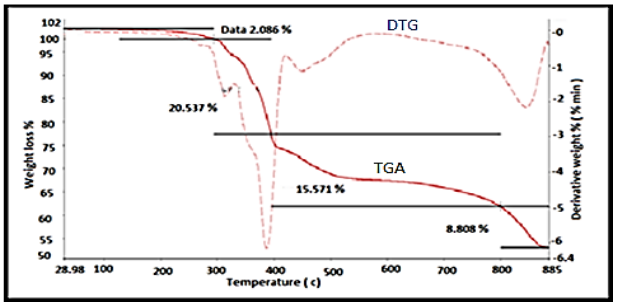
**Table 3. The XRD data of Cu doped barium tartrate crystals (λ =1.54060Å).**

| observed values from XRD | | | | standard data values | | |
|---|---|---|---|---|---|---|
| Sr. No | 2θ values | d values | Inten. | 2θ values | d values | h k l |
| 1 | 24.600 | 3.6159 | 323 | 24.606 | 3.6149 | 2 2 0 |
| 2 | 26.000 | 3.4243 | 873 | 26.009 | 2.4230 | 2 3 0 |
| 3 | 33.700 | 2.6574 | 525 | 33.718 | 2.6560 | 2 1 2 |
| 4 | 37.500 | 2.3964 | 151 | 37.489 | 2.3970 | 3 0 1 |
| 5 | 38.900 | 2.3133 | 159 | 38.889 | 2.3140 | 0 4 3 |
| 6 | 39.200 | 2.2963 | 137 | 39.204 | 2.2960 | 3 3 1 |
| 7 | 43.400 | 2.0883 | 179 | 43.290 | 2.0883 | 1 1 1 |
| 8 | 50.400 | 1.8091 | 120 | 50.431 | 1.8081 | 2 0 0 |

The slight shift in the position of diffraction peaks to lower value reflecting a slight elongation along a, b and c axes. Lattice parameters 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 Cu doping and subsequent doping shows the increasing tendency in grain size.

**Table 4. Calculated Comparative study 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 Cu (0.05M) | 8.868 | 24.729 | 8.421 | 43.95 |




**3.2 Thermal analysis**

**Figure 4. TGA & DTG curve of barium Tartrate crystals.**

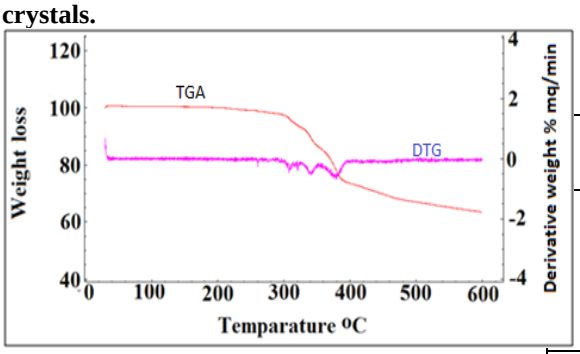



**Figure 5. TGA & DTG curve Cu doped $BaC_4H_4O_6$Crystals (0.05 M).**

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. Copper 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 Copper barium tartrate showed clearly four stages of decomposition as dehydration, Copper barium tartrate.

**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 | -0.5$H_2O$ |
| | II | 292-393 | 20.53 | 20.38 | -2Co2$H_2$ |
| | III | 393- 799 | 15.57 | 16.30 | -$Co_2$ |
| | IV | 799- 883 | 8.80 | 09.51 | -Co |
| $CuBaC_4H_4O_6$ (0.05M) | I | 27-200$^0$C | 2.45 | 2.51 | -0.5$H_2O$ |
| | II | 200-365$^0$C | 17.34 | 16.76 | -2Co & $H_4$ |
| | III | 365-383$^0$C | 12.72 | 12.29 | -$Co_2$ |
| | IV | 383-599$^0$C | 8.11 | 7.82 | -Co |

**3.3 Derivative Thermo Gravimetric Analysis (DTG):** In figure 5.9 shows the decomposition peaks and studies as follows.

I. In the first stage of decomposition, major endothermic peak at 190$^0$C is attributed to loss of 0.5$H_2$. The peak observed in the DTG curve corresponds to the weight loss 2.45% in the TG curve.

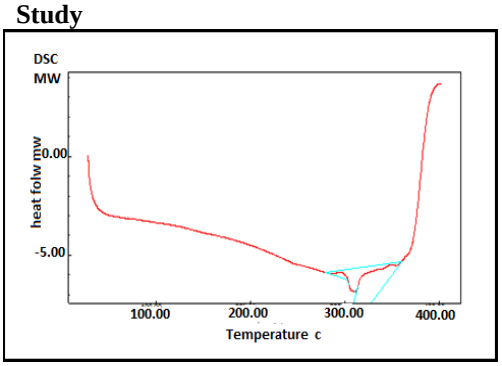
II. There are two endothermic peaks at 345$^0$C and 360$^0$C in the second stage of decomposition is attributed to loss of 2CO and $H_4$. The peak observed in the DTG curve corresponds to the weight loss17.34% in the TG curve.

III. The endothermic peak at 385$^0$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 12.72% in the TG curve.

IV. In the fourth stage there is no endothermic peak; decomposition is attributed to loss of CO. The peak observed in the DTG curve corresponds to the weight loss 8.11% in the TG curve.

Beyond the temperature 599$^0$C, the reaction proceeds and finally stable residue Cu: $BaC_4H_4O_6$ remains up to the end of analysis.

### 3.4 Differential scanning Calorimetry (DSC) Study




The differentials scanning calorimetry (DSC) analysis of the grown crystals was recorded between 20$^0$C to 400$^0$C in the nitrogen atmosphere using Metals TA 4000 Instrument. The initial weight of sample was 0.100mg and heating rate was maintained at 10$^0$C/min. The Fig.6 (a) shows the DSC curves of Barium tartrate crystals. The initiation temperature is 302.77$^0$C phase change complete at peak end-down temperature of 310.90$^0$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 318.06$^0$C indicates the phase transformation due to loss of water molecules and formation of stable anhydrous BaC4H4O6 crystals. This is in good agreement with the TGA curve.

**Table 6. The DSC data of barium tartrate Crystals.**

| Peaks | Temperature | On set | End set | Heat |
|---|---|---|---|---|
| Endothermic | 310.90$^0$C | 302.77$^0$C | 318.06$^0$C | -166.33mj |

Fig 6(b) The two stages of DSC curve under study are as follows.

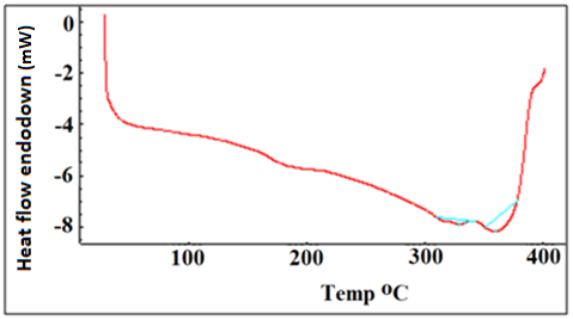
Stage-I

The initiation temperature is 310.29$^0$C and initiation of phase change to starts completed at peak end-down temperature of 328.94$^0$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 336.46$^0$C indicates the phase transformation due to loss of water molecules and formation of stable anhydrous Cu: $BaC_4H_4O_6$ crystals. This is in good agreement with the TGA curve.

II. Heat area under the curve is -22.44mj

Stage-II

The initiation temperature is 350.85$^0$C and initiation of phase change to starts completed at peak end-down temperature of 359.55$^0$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 377.72$^0$C indicates the phase tar formation due to loss of 2CO and$H_4$ formation of stable Cu: $BaC_2O_4$ cupper crystals.




II. Heat area under the curve is -71.94mj

**Figure 6 (b) *Cu doped barium tartrate Crystals***

**Table 7. DSC data of Cu 0.05M doped barium tartrate Crystals**

**Table 7. DSC data of Cu 0.05M doped barium tartrate Crystals**

| Peaks | Temperature | On set | Endset | Heat |
|---|---|---|---|---|
| Endothermic | 328.94$^0$C | 310.29$^0$C | 336.46$^0$C | -22.44mj |
| Endothermic | 359.55$^0$C | 350.85$^0$C | 377.72$^0$C | -71.94 mj |

## 4. CONCLUSIONS

Thesilica hydro gel is suitable for growing the crystals of copper-doped barium tartrate bySignal diffusion method. The colourless, translucent, spherulitic, good quality crystals are obtained.The size of the doped crystals is increases with the increase in the concentration of Cu dopant.Lattice constant a, b and c, the unit volume is 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 Cu doping, the XRD peak values shifted toward lower angle, indicating that an increase in the value of lattice constants.TheTGA, DTG and DSC, analysis suggests that the thermal stability of Barium tartrate crystal increases due to copper doping.The residual Copper

barium oxide (CuBaO) identified from TG analysis confirms the presence of strontium barium (CuBa) in the grown crystals.

**References**


1] Armington A F and O'Cornnar J J 1968 J. Cryst. Growth 3 367
2] Henisch H K 1970 Crystal Growth in gels (Pennsylvania State Univ. Press
3] K. Sangwal, A.R. Patel, J. Crystal Growth,23,4,1974,282-288.
4] Dalal P.V saraf K.B, Bull mater of Sci 29(**2006**)421.
5] Arora S.K Patel V. Kothari an Amin B, a crystal growth and design. **2004**
6] Raghavan P S &Ramasamy P, Crystal Growth Process and Methods, KRU publication, **2000**.
7] M.V. Jhon, M.A. Ittayachen, Cryst. Res. Technol., 2001, 36, 2, 141.
8] p. Gao, Mu Gu, Xiao Lin-Liu, Cryst. Res. Technol., 2008, 43, 5, 496.
9] S. Bhat, P.N. Kotru, Materials Chemistry and Physics, 1994, 39, 118.
10] B.B. Parekh, R.M. Vyas, Sonal R. Vasant, M.J. Joshi, Bull. Mater Sci., 2008, 31, 2, 143.
11] A. B. Patil and K. B. Saraf, Phy. D Thesis- "Growth and Characterization of Doped and undoped Lead Iodide single Crystals", (**2003**).
12] http://en.Wikipedia.org/ wiki/ Second-harmonic generation.Franken P. Hill, A. Peters C. Weinreich, G. Physical Review Letters, (**1961**), 7, 118
13] Alpert N. L., Keiser w. E. and Wiberley S. E. Theory and Practical's of Infrared spectroscopy, Plenum Press, New York, (**1970**).
14] Colthrup N. B., Daly L. H. and Wiberley S. E. Introduction to Infrared and Raman Spectroscopy, Academic Press, New York, (**1990**).
15] Gardiner D.J. Practical Raman spectroscopy, Springer-Verlag, (**1989**)
16] Willard H. W., Dean J. A., Merritt Jr> L. L. and Settle F. A. Instruments Methods of Analysis, CBS Publishers and Distributor, India, (**1986**).
17] Gardn D.D., Thermo analytical Methods of Investigation, Academic Press, New York (**1964**).
18] Keatch C. J., an Introduction to Thermo Gravimetry, Hegdon, London, (**1969**).
19] Mackenzie R. C., Differential thermal Analysis, Vol. l, Academic Press, London, (**1970**).
20] Redfern J. P., Thermal analysis reviews, Vol. 1-6, (**1964**).