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Growth and Study of Calcium Mixed Barium Oxalate Single Crystals in Silica Gel

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***Abstract*— Single crystals of Calcium Barium Oxalate of size 0.15X0.20X0.25mm^3 were crystallized by gel growth technique. The powder X-ray diffraction analysis revealed that the mixed grown crystals belong to monoclinic system. Prismatic and platy shaped of well fascinated crystals were characterized and reported by FTIR, XRD, EDAX and TGA/DTA.**

Key words— Calcium Chloride, Barium Chloride, Oxalic Acid and Sodium Meta Silicate, XRD, FTIR, EDAX, TGA/DTA.

I. INTRODUCTION

Crystals of high perfection have been achieved by the use of gel technique in the ambient temperature. The crystal growth in gel is an inexpensive and simple technique for growing single crystals for certain classes of materials like alkaline earth metal oxalates because of their low solubility in water and decompose before melting [1, 2]. Actually gel grown crystals are bioactive and their influence on animals is considerably increased nowadays. Various metal oxalates such as barium oxalate, cadmium oxalate and cobalt oxalate are used in the field of pyro technology, dying and ceramic industries and also the preparation of nanomaterials due to their thermal decomposition reactions' of end products of metal oxides' stability at high temperatures more than 500°c . Growth of single crystals of calcium oxalate has been reported [3]. In the field of crystal growth, gel technique has become popular and has been used by several investigators due to its simplicity and it can be successfully used at room temperature to suppress nucleation centres.In the present work, due to various roles of metal oxalate crystals have prompted the author to study the growth of mixed crystals of calcium doped barium oxalate crystals grown in silica gel and are identified and characterized by different techniques, viz. XRD, FTIR, TGA/DTA and EDAX.

II. EXPERIMENTAL

The growth of calcium barium oxalate crystals were carried out in hydro silica gel. All chemicals such as oxalic acid, calcium chloride, and barium chloride and sodium Meta silicate were of AR grade. In the present work, silica gel was preferentially used for the growth of crystals by single diffusion techniques. A test tube having 15 cm in length and 1.5 cm in diameter was employed. In single diffusion sodium meta silicate solution of 1.04 specific gravity was acidified by 2M oxalic acid in such a manner that pH 4.5 could be set for the mixture. This was transferred into different test tubes and allowed to set into the gel form. Thereafter the supernatant solutions of 0.5M of barium chloride and 0.5M of calcium chloride were mixed and poured over the set gel. Different parameters such as concentration of reactants, pH of gel, impurities in the solvent, gel setting time, *etc.* have considerable effect on growth rate. In the steady state which favours growth of spherulite crystals. To increase the size of the grown crystal 4.5 m NaCl of 8 ml was added on each test tube. After passing some days, good quality, highly transparent and small rectangular needle shaped single crystals of calcium doped barium oxalate were grown in the gel.

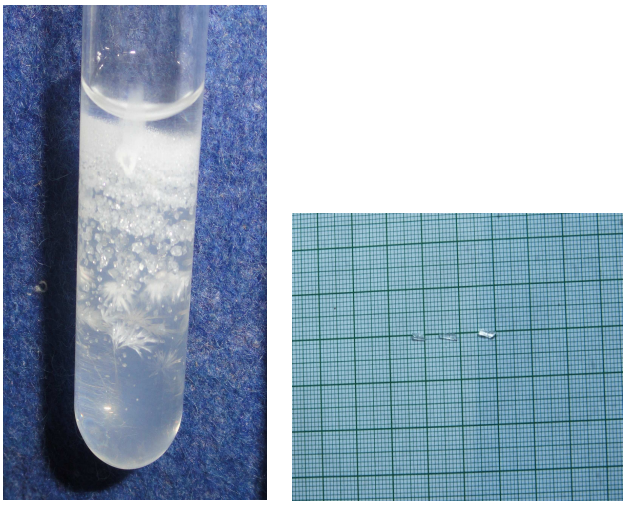

Figure 1 shows growth of Ca Ba OX crystal.

The reaction which leads to the growth of crystal was expressed as

(0.5M)$BaCl_2$+ (0.5M) $CaCl_2$+$H_2C_2O_4$ →$CaBaC_20_4$.(0.5)H_2O+HCl.

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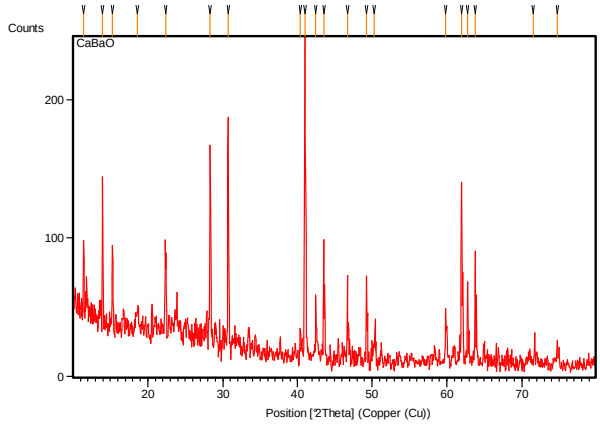
III. RESULTS & DISCUSSION

Table 1: The optimum condition for the growth of CaBaOx crystal

CONDITION	SINGLE DIFFUSION
density of sodium mete silicate	1.05
pH of gel	4
Concentration of $BaCl_2$	1M
Concentration of $Cacl_2$	1M
Gel setting period	6 Days
Gel aging	48 hours
Period of growth	80 Days
Temperature	Room temperature
Quality	Transparent , rectangular
Size	with needle shaped 0.15X0.20X0.25mm^3

The optimum condition for the growth of CaBaOx crystal is given in Table 1. The dissociation of the oxalic acid system is given prismatic and needle shaped growth of well faceted crystals using single diffusion reaction method. The different parameters such as concentration of reactants, pH of gel, impurities in the solvent, gel setting time, gel ageing time etc. has considerable effect on the growth rate. However, as the reactants diffused in deep through the gel as their concentrations were, in decreasing stage, the controlled reaction resulted out the best quality and well developed crystals.

IV. XRD



X-ray powder diffract gram results were recorded using Diffract meter system=XPERT-PROlima III model (CuKa radiation, scanning speed, 10% min). The figure shows X-ray diffract gram of single crystals of calcium barium oxalate. From the diffract grams, d values for different hkl (h = -2.58, k = -3.21, l = 3.36) were calculated. In the present work, calcium doped barium oxalate crystals grown in silica gel of unit cell parameters were identified, and the structure of the crystal belongs to the monoclinic system were calculated using the computer program PCDWIN were shown in Table 2. Further they were compared with the pure barium oxalate crystals which already have been reported [4] and proved that they were in fair agree with them.

Table 2: Unit cell parameter values of the CaBAOx crystal

Crystal sample	A (A°)	B (A°)	C (A°)	Volume of the cell (A°)^3	α (°)	B (°)	□ (°)
Pure barium oxalate	6.6562	8.0464	2.8090	149.38	90	96.832	90
calcium doped cadmium oxalate	10.07	7.938	6.860	464.8	90	122.07	90

V. FTIR

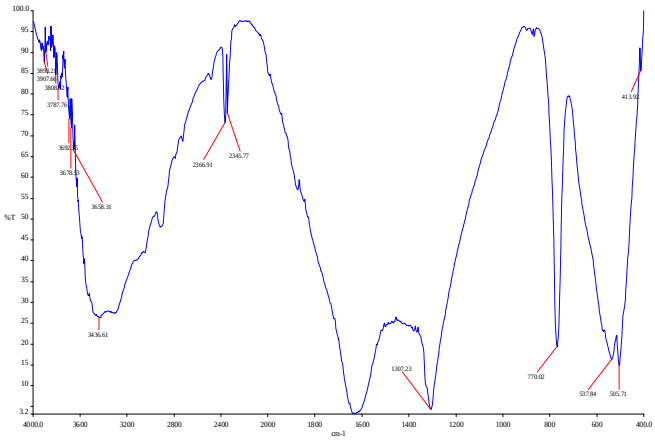


Figure 4: FT-IR spectrum of CaBaOx crystal

FTIR absorption spectrum was recorded using RX1 model, Perkin Elmer (make) FTIR spectrometer. The observation of peaks around at 3658.3 cm^{-1} and 3436.61 cm^{-1} are due to the O-H stretching mode and water of hydration. The band at1630 cm^{-1} is attributed to carboxyl ate group. The strong peak at 1307.23 cm^{-1} is assigned to C=O Symmetric and (o-c=o) modes. The very sharp and deep peak at 770.02 cm^{-1} is due to the appropriate frequency range for deformation vibrations of CO_2.The absorption peaks between 537 cm^{-1} to 413.02 cm^{-1} are identified to metal-oxygen bonds. From this spectrum all the functional group for the appropriate molecular elements of the grown crystals were confirmed and compared with already reported values of the pure barium oxalate crystals [5] to identify their existence of bonds at the required frequency.

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Table 3: The functional groups of CaBaOx crystal

Pure BaOx crystal Frequency (cm^{-1})	Ca doped BaOx crystal Frequency(cm^{-1})	Functional groups
1615	1630.00	O-$H_{bending}$ (presence of oxalate)
1333.58	1307.23	C=O (presence of CO_2)
782.84	770.02	M-O (presence of metal-oxygen bond)

VI. EDX

EDX measurements are made at different points on the surface of the crystals and the average value obtained in the spectrum confirms the presence of the essential substances of calcium, carbon, oxygen and barium at various composition levels in the grown crystal.

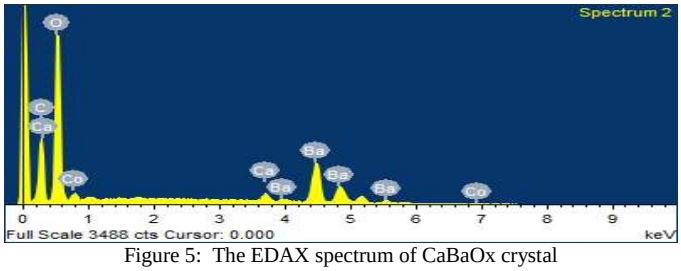

Figure 5: The EDAX spectrum of CaBaOx crystal

Table 4 :The functional groups of CaBaOx crystal

Element	Weight	Atomic%
C K	10.67	30.80
O K	23.86	51.73
Ca K	1.99	1.73
Co L	-0.86	-0.50
Ba L	64.33	16.25

VII. THERMAL ANALYSIS

TGA and DTA of growing crystals were carried out at the National Institute of Technology, Tiruchirappalli by Mettler TA4000 system in the Argon Gas Atmosphere.

- TGA curves show the constant non-isothermal heating rate decomposition behaviour of the calcium doped barium oxalate crystal with the heating rate of 40^0c /min in the Argon gas atmosphere between the temperatures 35^0c - 950^0c. Here the reaction appears to be the three stages of reaction. The TGA curve did not show the appreciable change in the temperature range 30^0c -54^0c indicating that the barium calcium oxalate crystals are thermally stable in this temperature range and no transformation took place. Beyond which they begin to decompose implies that the presence of weak ionic bonds. On the DTA curve, there is one endothermic peak at 128.8^0c due to decomposition of hydrated barium calcium oxalate to anhydrous barium calcium oxalate. The maximum reaction rate temperatures of 128.8^0c and 382.5are denoted by T_M resulting the maximum decomposition states of the compound. The exothermic peak at 382.5^0c and 552.8^0c are due to the decomposition of barium calcium oxalate in to barium calcium carbonate and barium calcium oxide resulting the formation of CO and CO_2. The first stage of decomposition starts from the temperature range 54.2-152^0c resulting in a weight loss of 3.2% and thereafter it remains stable in the temperature range of 3380c -416.8^0c. After this temperature there is further weight loss of 10.7% occurred due to dissociation of barium calcium oxalate into barium calcium carbonate releasing CO. In the final stage of temperature range 416.7-683.2^0 c is leading to a weight loss of 5.6% suggest liberating CO_2. This thermal behavior were compared with the already reported results of the pure barium oxalate crystals(6) and found that it was slightly varied in the reactions as well as the stability of third stage product of metal oxide overtakes higher the temperature range 960^0c than the pure cadmium oxalate crystal reveals their enhanced thermal property.

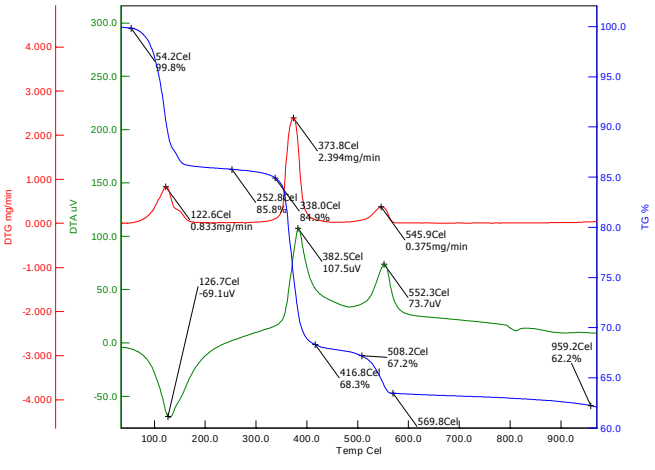

Figure 6: The TGA/DTA spectrum of Ca Ba Ox crystal

Table 5. The decomposition stages vs mass loss% of Ca Ba Ox crystal

Temperature range(^{0}c)	Mean range(^{0}c)	Mass loss%(calculated)	Mass loss %(observed)
54.2-151.8	103.05	3.2	3.2
252.8-488.6	370.7	10.7	10.5
416.8-683.2	559.0	5.6	5.6

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Decomposition steps;

I. Ca Ba C_20_4 $_{0.5H2O}$ —> Ca Ba C_20_4 $+0.5H_2O$.

II. Ca BaC_20_4 —> Ca $BaCO_3$+CO

III. $Ca_{)}$ $BaCO_3$ —> Ca BaO+CO_2

The weight loss of the grown sample is further supported by DTA analysis of the respective temperature.

VIII. CONCLUSION

From the studies we observe that:

(i) The gel growth technique is suitable for growing crystals of calcium, barium oxalate with high purity.

(ii) EDAX confirmed the doping of calcium on barium oxalate crystal. Powder XRD showed the crystalline nature of the Ca Ba Ox crystal and belong to Monoclinic crystal group as same as barium oxalate system depending on the lattice parameters obtained **a=**10.07cm^{-1}, b=7.938cm^{-1}, and c = 6.860cm^{-1}

(iii) FTIR results supported the presence of oxalate, metal-oxygen bonds and other fascinated groups at the appropriate frequencies.

(iv) The thermal studies has been suggested that the barium oxide from barium oxalate was the end product of a stable compound up to 990°c (5) but from the present work proved that the stability of calcium doped barium oxide from calcium barium oxalate exceeded up to1000°c. The endothermic and exothermic peaks were higher temperatures than the pure crystal.

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