

MORPHOLOGICAL AND FTIR STUDIES OF BARIUM OXALATE SINGLE CRYSTALS

M. R. Shedam^a, Rakesh M. Shedam^b, Shridhar N.Mathad^{c*}

^a*Shri Shikshan maharshi D.B. Patil Research center. The New College,
Kolhapur*

^b*Department of Physics, GKG college, Kolhapur 416 012, India*

^c*K.L.E.I.T, Gokul Road, Hubballi, Karnataka, India*

Abstract: The conditions for the gel growth of barium oxalate single crystals in silica gels were studied in this paper. We describe the growth mechanism, effect concentration of feed solution, interchanging of the reactants, the effect of temperature and detailed study of microstructures of barium oxalate single crystals. At higher concentration of feed solution dense fibers were observed. With interchanged feed solution precipitate and spherulites have been obtained. The effect of temperature on growth barium oxalate crystals showed that there was a decrease in nucleation density at higher temperature. The crystals growth were observed under the electron microscope which revealed that the crystal have needle and spherulites structures. We also report the FTIR studies of barium oxalate crystals.

Keywords: silica gel, nucleation density, crystal growth, FTIR studies.

Introduction

Crystal growth is one of the fascinating fields where the atomic nature of matter clearly establishes itself to the observation made in laboratories. Crystals are promising materials due to wide applications in

* Shridhar N.Mathad, *e-mail*: physicssiddu@gmail.com

the field of ceramics, physics, chemistry, metallurgy, mineralogy, medicine, engineering etc. Single crystals are the backbone of the modern technology of logical revolution,¹ which have numerous applications like data storage devices, lasers, advanced displays, luminescence, catalysts and permanent magnets.^{2,3} Oxalate ions (C_2O_4)²⁻ are employed in constructing a large variety of molecular structures and frameworks by incorporating suitable metal ions in the crystal lattice, which can act like monodentate, bidentate, tridentate or tetradentate donor ligand.^{4,5} The oxalate compounds are exhibiting interest due to versatile applications like precipitation agent,⁶ precursor for superconductive oxides,⁷ nanoparticles synthesis,⁸ magnetic and luminescent devices.⁹ Among the metallic ions studied, Sm^{3+} cation doped rare earth oxalates,¹⁰ potassium boro-oxalate (KBO) single crystals,¹¹ cadmium tartrate oxalate,¹² cadmium oxalate crystals.^{13,14}

The cadmium (Cd) and barium (Ba) ions have attracted a plenty of interest owing to it has rather coordination geometry and simple chemistry.^{15,16} The present work mainly aims to investigate the growth parameters and their effect on barium oxalate single crystals. The morphological and FTIR studies of the crystal are also studied in detail. The detailed flow chart of the manuscript has been described in Figure 1.

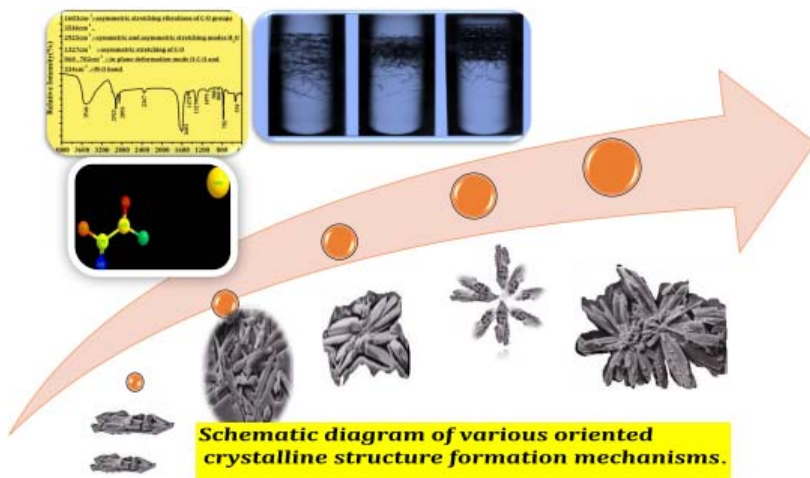
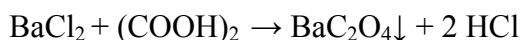


Figure 1. Schematic diagram of various oriented crystalline structure formation mechanism.

Experimental

The crystallization apparatus used in the present work contain: (i) test-tube of 2.5 cm outer diameter and 20 cm length, (ii) 250 ml beaker, (iii) U-tube of 2.5 cm outer diameter and 30 cm length, (iv) beaker – single tube system. Silica gels were prepared by mixing sodium silicate (specific density 1.03 g/cm^3) with required quantity of oxalic acid. The chemical reaction employed through the gel medium was



The gel solution was prepared by mixing pure solution of sodium silicate with required amount of 0.1, 0.5N or 1N oxalic acid. The prepared gel solutions were then transferred into the test tube, U tubes and beaker – single tube system at room temperature and the pH value of gel were also adjusted from 3.5 to 4.5 by adding a few drops of perchloric acid. After the gel was set, feed solution of BaCl_2 (from 0.1 to 1 N) was placed above the gel for crystallization.

Analytical reagent grade (BDH) chemical and doubly distilled water were used throughout the present work. The experiments were performed at ambient temperature. FTIR studies have been carried out in the region 400- 4000 cm^{-1} using KBr pellet technique and morphology from Scanning Electron Microscope (LEICA 4401).

Results and Discussion

Effect of concentration of feed solution

To study the effect of concentration of feed solution, gel of the same pH and density were used.

It is observed that as the pH increases the transparency of gel decreased. The crystals growing at higher pH values were not transparent and well defined. This was due to contamination of crystal with silica gel, because pH increased the box-like network structure of the gel changed to loosely bound platelet structure which lacked cross-linkages: the cellular became less distinct. As the pH increased the number of fibers (crystal) decreased. Figure 2 (a, b, and c) shows fibers growing at three different concentration of the feed solutions. The variation of nucleation density increases with concentration on the feed solution, because of the enhanced availability of barium ions, the nucleation density increases.

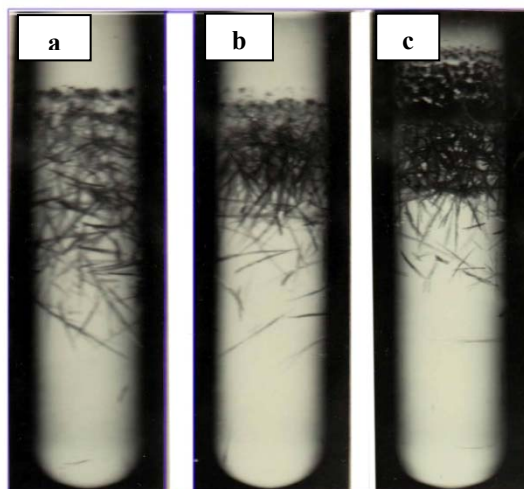


Figure 2. Crystals of barium oxalate growing for different concentrations of feed solution (a) 0.2 N BaCl_2 ; (b) 0.5 N BaCl_2 ; (c) 1 N BaCl_2 .

Inter changing the reactants.

Most of the work on crystal growth in gel has been done by the reaction method. It has a special advantage of growing single crystal which are insoluble in water and which decompose before reaching their melting point. i) the reactant must be soluble in the solvent and product fiber (crystal) must be relatively less soluble; ii) the gel must remain stable in the presence of the reacting solution and must not react with these solution; iii) some solubility of crystal is required. The concentration of feed solution varied (0.2N, 0.5N and 1N). The feed solution with concentration higher than 1 N were used, the density of nucleation centers tremendously increased (fig. 2). It was seen that as barium chloride solution diffused into the gel, fibers thickness increased. For the concentration of feed solution up to 0.3 N, no nucleation above 0.4 N was observed. The nucleation started on the solution gel interface and very thick fibers were observed. After two months the fibers were dissolved and recrystallization into good quality

crystals was observed (fig. 3a). Also, the incorporation of barium chloride inside the gel solution resulted in lower density of nucleation centers and hence good and well defined flower like fibers were observed (fig. 3b).¹⁷



Figure 3. Interchanging the reactant: (a) 0.2 N oxalic acid above gel and 0.5 N BaCl₂ inside gel; (b) 0.2 N BaCl₂ above gel and 0.5 N oxalic acid inside gel.

Effect of temperature

The variation in temperature showed that at constant Ba²⁺ and C₂O₄²⁻ ions concentration, more crystals growing at lower than at higher temperature, as shown in Figure 4.

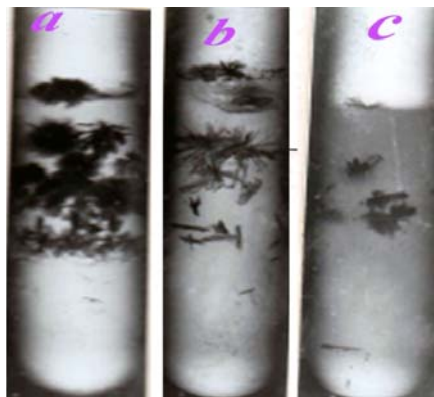


Figure 4. Effect of temperature on the crystals growing :
(a) 22 °C; (b) 30 °C; (c) 37 °C.

The decrease in nucleation density at higher temperature increases the aqueous solubility of barium oxalate. In most of the cases at 37 °C only one spherulite was formed. But their growth ceased after six to seven days. By decreasing the temperature from 37 °C to 22 °C at the rate of 0.1 °C /hour, the growth rate and the size increased as shown in figure 3 which must be due to the gradual increase in super saturation by lowering the temperature.¹⁵

The Gibbs - Thomason relation for super saturation, S, is given as:

$$\log S = \frac{2M\sigma}{RT}$$

where M is the molecular weight of the solute, σ is the surface energy per unit area, R the gas constant, T is the temperature.

It is observed that there is a remarkable change in the habit of crystals when the temperature changes.

Microstructure

Depending on the growth sites in the tubes, different morphologies of the barium oxalate crystals were observed. The grown crystals thoroughly cleaned with acetone, were coated with Au/Pt in a vacuum loading unit and examined under metallurgical and scanning electron microscope (SEM). Figure 5 shows four typically different shapes of barium oxalate single crystals. They were columnar in shaped and could form single needles (figs. 5a and 5b), elongated spherulites were grown; using 0.8 N of barium chloride solution and at lower concentration (i.e 0.1 N) of oxalic acid.

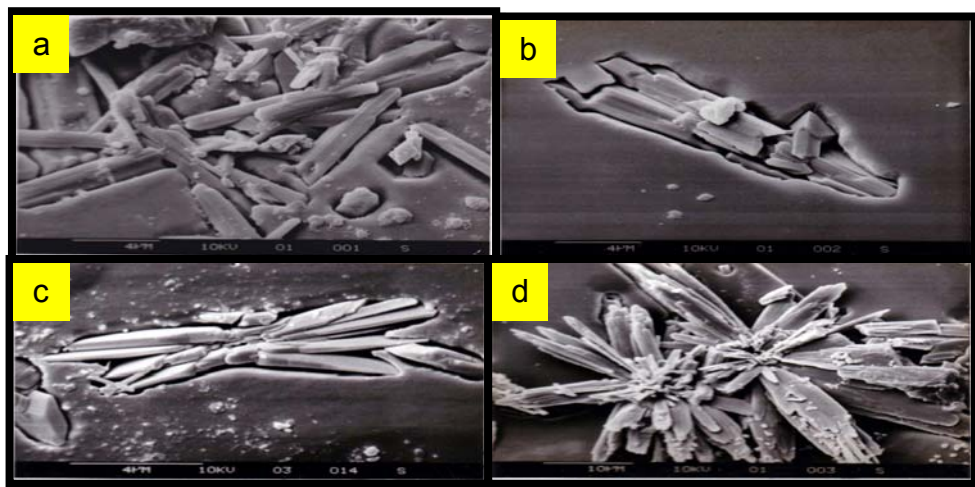


Figure 5. Microstructure of Barium oxalate crystals using SEM: (a) Columnar in shape; (b) Single needle; (c) Elongated spherulites interconnected each other; (d) Two spherulites interconnected each other.

The growth mechanism can be understood¹⁸ in the following way. First needle crystal is formed and as concentration of feed solution increased the lateral sides of the needle were developed. Further it was found that at higher concentration (0.6 N) of the reactants two spherulites inter connected were formed as is shown in Figure 5d. This spherulitic growth may takes place in two stages.¹⁹ During primary crystallization the spherulite grows from an initial fibril or lamella, which leads from the primary nucleus. The thickness of the lamellae is constant determined by the critical size of nucleus and growth occurs by extension of the length and breadth so that it grows into a thin sheet of constant thickness. Nevertheless, as crystallization continues branching occurs until a branched lamellar assembly is produced and these branches bend and twist upon growth to bring-forth a spherical boundary which grows radially. Further radial growth produces larger spherulites until impingement between adjacent stops further growth. Once impingement takes place, further development

occurs via in-filling between the lamellae. Additional secondary crystallization by which the lamellae as primitively laid down thicken with time at the expense of amorphous material between the lamellae. This process has a lower time dependency than that of primary crystallization and is readily distinguished by a change in the analysis of the crystallization kinetics. The rate and extent of secondary crystallization reckons on crystallization temperature.²⁰ They grow radially via fibrillar growth in bundles into the amorphous phase from a nucleus and vary in size and number depending on the crystallization temperature. This determines the critical size of the nucleating center. More prominent spherulites form near the melting point and more numerous smaller spherulites form at lower temperatures.²⁰

FTIR studies

FTIR spectrum of barium oxalate single crystal is shown in Figure 6 and in the 400-4000 cm^{-1} range show well pronounced intense peaks.

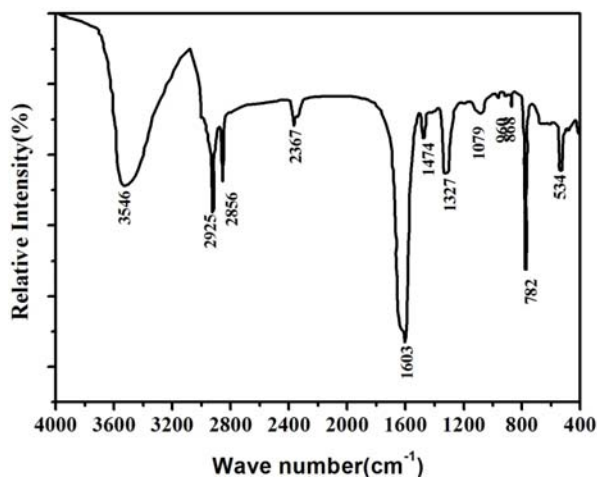


Figure 6. FTIR spectra of barium oxalate crystal.

The broad envelope extending from 2800 to 3600 cm^{-1} is assigned to the symmetric and asymmetric stretching modes of the water molecules. Considerably pronounced peak at 1603 cm^{-1} , is assigned to asymmetric stretching vibrations of C=O groups of the $\text{C}_2\text{O}_4^{2-}$ ions superposed with the O-H bending mode of water. The IR band from 1327 cm^{-1} corresponds to the asymmetric stretching mode of C-O bond. The sharp peak at 534 cm^{-1} confirmed the bonding of metal-oxygen (M-O bond)²¹. FTIR spectroscopic analysis of barium oxalate single crystals confirms the presence of functional groups associated with the oxalate ligands and the metal–oxygen bond and are tabulated in Table 1.^{20,21,10}

Table 1. FTIR bands of barium oxalate single crystal

1603 cm^{-1}	asymmetric stretching vibrations of C-O groups
3546 cm^{-1} , 2925 cm^{-1}	symmetric and asymmetric stretching modes of the H_2O
1327 cm^{-1}	asymmetric stretching of C-O
868 and 782 cm^{-1}	in-plane deformation mode O-C-O
534 cm^{-1}	M-O bond and the weak one around

Conclusions

The present work reports the growth and characterization of barium oxalate single crystals. We have demonstrated the formation of barium oxalate single crystals in silica gels. Barium oxalates exhibits micro-rod-like and spherulitic growth (flower) shape which confirmed by SEM micrographs. It has been found that at higher concentration (above 3 N) of feed solution dense fibers were observed. Further to obtain good quality single crystals of barium oxalate, both reactants –barium chloride and oxalic acid were interchanged. With barium chloride incorporated gels result only

fibers. These facts have been explained by taking in account the interaction of the reactants ions with the sodium and silica ions. The effect of temperature on growth of barium oxalate crystals showed that there is a decrease in nucleation density at higher temperature which is due to the increases of the aqueous solubility of barium oxalate.

FTIR spectra confirm the structural features of barium oxalate crystals. The sharp peak at 534 cm^{-1} confirmed the metal-oxygen bond formation (Ba-O bond). The FTIR spectroscopic analysis of barium oxalate single crystals confirms the presence of functional groups associated with the oxalate ligands and the crystallization water molecules (the crystal is not anhydrous).

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