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Characterization, Microhardness and Dielectric Studies of Pure and Doped (Copper, Cadmium) Barium Oxalate Single Crystals Grown in Silica Gel

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Single crystals of pure barium oxalate, copper doped barium oxalate and cadmium doped barium oxalate crystals are grown by gel method. The double diffusion (U-tube) method is adopted for growing crystals. The crystals are of few mm in size. 5-7 d taken for gel set and 45-60 d taken for complete growth of the crystals. The X-ray diffraction patterns of the samples revealed their crystalline nature. Thermo gravimetric analysis data supported the release of lattice H_2O, CO, and CO_2. The FTIR spectrum of the crystals showed the presence of water molecules and carboxylic acid. The characteristics are slightly different due to the doping with impurities. The microhardness and dielectric studies of grown crystals were also carried out.

Key Words: Doped barium oxalate crystals, Microhardness, Dielectric property.

INTRODUCTION

The varieties of scientifically and technologically important materials have increased tremendously in recent years. The oxalate crystals have more important roles in the urinary crystal fields. The small variations on characteristics and properties due to doping is clear in the analysis results. In present paper, growth, characterization and properties of pure barium oxalate and two doped barium oxalate crystals are tried. Growth by hydrosilica gel[1] is the most suitable method for getting perfect crystals with minimum impurities and imperfections. The pure $BaC_2O_4 \cdot 3.5H_2O$ (barium oxalate hydrate) is monoclinic and $BaC_2O_4 \cdot 0.5H_2O$ is triclinic[2]. But doped crystals are triclinic. The grown crystals were subjected to characteristic studies such as XRD, FTIR and TGA, also subjected to microhardness and dielectric studies.

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EXPERIMENTAL

The silica gel is prepared by mixing sodium metasilicate solution of desired specific gravity with 3 M acetic acid so as to get a pH of 4, then kept 50 mL in U-tube for setting gel[3]. It took 4-6 d for gel to set. 20 mL barium chloride solution (1 M) is gently poured into one limb of U-tube and 20 mL of 1 M oxalic acid on the other limb. By double diffusion, barium ions react with oxalate ions well inside the gel form barium oxalate nuclei, then grow. The procedure is repeated by changing growth parameters. For doped crystals, instead of barium chloride, mixture of barium chloride solution and the desired dopants were taken. In this work pure barium oxalate, copper doped barium oxalate and cadmium doped barium oxalate single crystals were grown. Grown crystals are harvested then washed with distilled water after 50 d, dried and subjected to characterization, microhardness and dielectric studies. The XRD patterns recorded using Siemen X-ray diffractometer (D 5000) having CuKα radiation (λ = 1.54 Å). The thermal analysis data are obtained on 3.5 mg by scanning at 20 ºC/min in nitrogen atmosphere from 28 to 1000 ºC. The device used for it is Perkin Elmer`s Pyris Dimond TG/DTA. Powder samples are used for it. For FTIR spectrum the samples are analyzed with KBr pellet technique. Thermo Nicolet's AVTAR 370 DTGS is used for the analysis.

RESULTS AND DISCUSSION

Single crystals of pure barium oxalate, copper doped barium oxalate and cadmium doped barium oxalate crystals obtained are few mm in size. Pure barium oxalate and cadmium doped barium oxalate crystals are colourless while copper doped barium oxalate crystal is light blue. Depending on the gel pH, gel density concentrations of the reactants and acidity of feed solutions, the nature of crystallization is found to vary widely. It also depends on different growth parameters[4]. Three characteristic curves of all crystals are taken. The crystals are subjected to microhardness and dielectric studies.

The IR peaks of the grown crystals are identified in comparison with earlier reports[5]. The broad peak at 3500-3300 cm^{-1} due to anti-symmetric OH stretching suggest the presence of water of crystallization in the crystals. The peak at 3000 cm^{-1} is due to asymmetric and symmetric stretch of the coordinated water. The peak around 1600 cm^{-1} related to HOH bending also supports the presence of water. The broad peak near it due to asymmetric stretch of CO_2 reveals the presence of oxalate (C_2O_4) ions in the samples. The well defined peak around 1300 cm^{-1} corresponds to CO_2 symmetric stretch also supports the presence of oxalate ions. The sharp peak near 780 cm^{-1} may be attributed to metal-oxygen bond. The peak at 519 cm^{-1} arises due to O-C-O in-plane bending.

The patterns of these three samples were taken at room temperature in order to study the structure of the materials. The grown crystals were found to be single crystalline. The Bragg peaks at different planes revealed the crystalline structure of the compounds. A few changes can be seen in the spectra of samples due to the doping with impurities (Fig. 1).

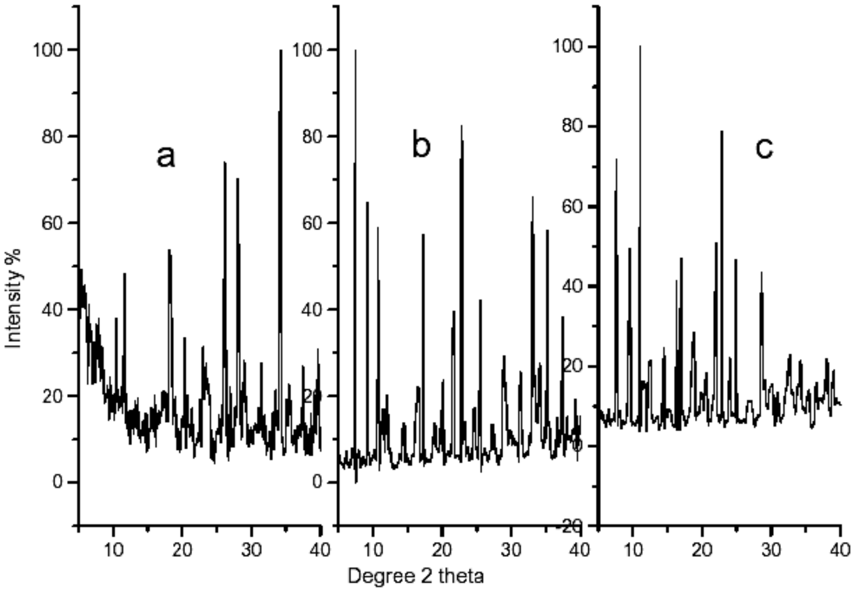

Fig. 1. XRD patterns of barium oxalate crystals (a) pure (b) copper doped (c) cadmium doped

TGA curves of grown crystals show the loss of lattice water, which is characterized by an endothermic peak centered at 120 ºC in DTGA. The release of H_2O, CO and CO_2 at different temperatures are shown in TGA and the corresponding weight losses are calculated. The chemical changes are shown in the given equations:

$MC_2O_4 \cdot H_2O \rightarrow MC_2O_4 + H_2O_4$ (120-228 ºC), water of crystallization evaporates

$MC_2O_4 \rightarrow MCO_3 + CO$ (400-450 ºC), CO exits out.

$MCO_3 \rightarrow MO + CO_2$ (660-830 ºC), CO_2 exits out. MO is stable above 830 ºC. The curves are slightly different for pure and doped crystals.

Microhardness: A Shimadzu HMV-2000 was used for hardness measurements. Indentations were carried out using Vicker's micro indentation hardness test for loads varying from 20 to 100 g , over a time interval of 14 s at 23.4 ºC. For each load, several indentations were made and the average value of the diagonal length was used to calculate the microhardness. The hardness number H_v was calculated using the relation $H_v = \frac{1.8544P}{d^2}$ Kg mm^{-2}, where P is the load and d is the diagonal length. Table-1 shows the microhardness values of the grown crystals for different loads and reveals the hardness variation curve with loads. The grown crystals were resistive to indentation up to a load of 20 g. Above it the hardness number increased with an increase in applied load and attained saturation at 100 g. When load applied was above 100 g, cracks were initiated along and across the diagonals of the indentation mark.

TABLE-1
MICROHARDNESS VALUES OF GROWN CRYSTALS

Sample	Applied load in gf	Hardness value (H_v number)
Pure barium oxalate	20	31.4
	40	33.7
	60	36.6
	80	38.1
	100	39.8
Copper doped barium oxalate	20	35.7
	40	38.5
	60	41.8
	80	43.5
	100	45.1
Cadmium doped barium oxalate	20	36.8
	40	39.4
	60	42.6
	80	44.5
	100	46.4

Dielectric property: Single crystals of pure and doped barium oxalate were subjected to dielectric property studies. The measurements were done by using an hp 4192 ALF impedance analyzer (5 Hz-13 MHz). The measured values of capacitance at different frequencies were used to calculate the permittivity using the relation, $\varepsilon = \frac{Cd}{A}$, where C is the capacitance of the crystal, d is the thickness and A is the area of the faces in contact with the electrodes. The dielectric constant of the crystals was calculated using the formula, $\varepsilon^1 = \frac{\varepsilon}{\varepsilon_0}$ and the a.c. conductivity of the grown crystals are calculated using the formula, $\sigma_{ac} = 2\pi f \varepsilon^1 \tan \delta$, where f is the frequency and tan δ is loss tangent. Fig. 2 shows the variation of a.c. conductivity with log f and Fig. 3 shows the variation of dielectric constant with log f of grown crystals.

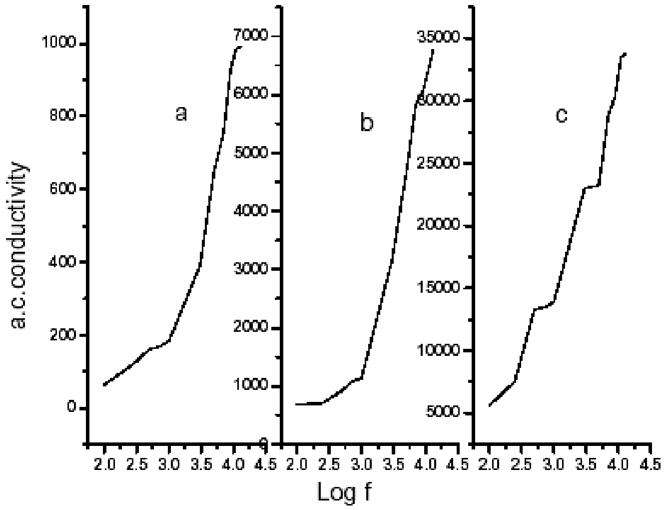

Fig. 2. Variation of a.c. conductivity with log f for (a) pure (b) copper doped (c) cadmium doped crystals

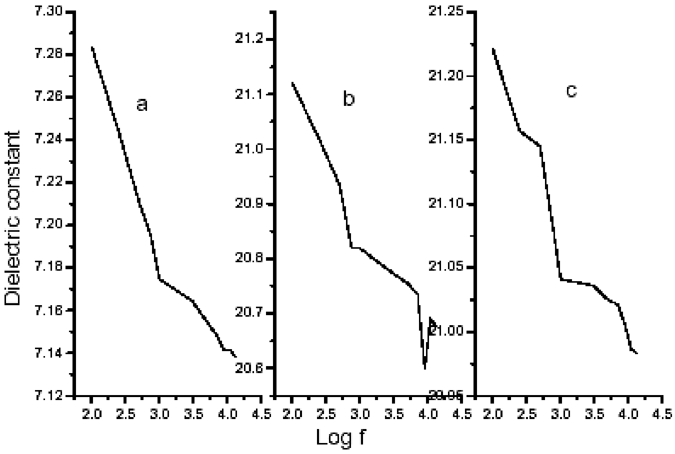

Fig. 3. Variation of dielectric constant with log f for (a) pure (b) copper doped (c) cadmium doped crystals

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