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Studies on the Growth and Characterization of Barium Doped Copper Cadmium Oxalate Dihydrate Single Crystals

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Abstract

Single crystals Barium doped copper cadmium oxalate (BCuCO) was grown from the silica hydrogel using a single diffusion technique. The grown crystals were characterized using energy-dispersive X-ray spectroscopy (EDX), single-crystal X-ray Diffraction studies, powdered X-Ray Diffraction, FTIR spectroscopy, UV-visible Spectrophotometer, and thermal studies. Energy-dispersive X-ray spectroscopy (EDX) confirmed the presence of Ba, Cd, and Cu elements in the lattice of BCuCO crystal. Single-crystal XRD reveals that the as-grown crystal belongs to the triclinic crystal system with the space group P_1. The FTIR spectroscopic studies confirmed the oxalate group, water molecule, formation of metal-oxygen bonding in BCuCO crystals. The UV-visible spectral studies reveal that the crystal is an insulator with wide bandgap and optical transparency in the visible region. The thermal stability of grown crystals, crystalline water molecules, and decomposition nature was determined using thermogravimetric analysis (TGA).

1. Introduction

Crystals are considered to possess distinct or diverse applications due to which the crystals are of higher demand and hence crystal growth is the field that is swiftly growing in the research. The conversion of one phase into another phase is involved in the process of crystal growth which is considered to be a heterogeneous chemical process [1, 2]. For the compounds having an immense melting point and which are insoluble in aqueous solution, the crystals can be synthesized from the melt at virtuous temperatures. Crystals can be grown from the gel technique if the material disintegrates before the melting point at atmospheric pressure and for which there is no availability of convenient solvent, then these crystals can be successfully grown from the gel technique. The management or regulation of nucleation is one of the problems of growth from aqueous solution.

Gel technique was the best method to synthesize the crystals which are insoluble or sparingly soluble. Gel method is an economical method out of which numerous types of crystals could be grown. Strain free and splendid or pure crystals can be grown from this method at a lower temperature [3-5]. The principle performances of the gel medium are turbulence suppression, chemical inertness, diffusion reagents at a restrained rate and nucleation control [6, 7]. Among the studied metal elements, cadmium and barium elements have attracted a great deal of interest because it has rather simple chemistry and coordination geometry [8]. The incorporation of alkaline metal elements to pure crystals is responsible for the specific changes of their physical properties. In this present work gel method is adopted to grow

crystals. We have laid our diligence towards the oxalate crystals since these crystals are having many applications in the field of optoelectronics and they can be synthesized with the help of silica gel method.

2. Material and Methods

2.1. Crystal Growth of BCuCO

Barium doped copper cadmium oxalate (BCuCO) crystals were grown using silica hydrogel at ambient temperature. Chemicals used for growing BCuCO crystals were Sodium Meta Silicate (Na_2SiO_3. $9H_2O$), Oxalic acid ($C_2H_2O_4$), Cupric chloride ($CuCl_2$), Cadmium chloride ($CdCl_2$) and Barium chloride ($BaCl_2$) of AR grade. Sodium metasilicate solution (SMS) was prepared by dissolving 22 g of Sodium metasilicate into 250 ml of distilled water with constant stirring and kept in dark and cool place. The SMS solution was diluted to attain specific gravity of nearly 1.042 g/cm^3. 0.5 M oxalic acid was prepared by dissolving 15.76 g in 250 ml of double-distilled water [3, 6]. SMS solution of specific gravity 1.042 g/cm^3 was mixed with 0.5 M oxalic acid in a beaker by adding SMS solution drop by drop with constant stirring in the ratio 5 ml : 4 ml. 9 ml of mixed solutions were collected in test tubes and allowed to set for four days. Once the gel set in the test tubes, the solution of Copper chloride and Cadmium chloride and Barium chloride (of 1ml: 1ml: 0.2ml) was poured to gel carefully through the walls of crystallizer to avoid gel breakage [9, 14]. The openings of the test tubes were tightly covered to prevent contamination of the gel surface by atmospheric impurities. Crystals grew within a week and well-shaped crystals were visible in 3 weeks. Grown crystals are shown in Figure 1.

Table1: Optimum condition for the growth of BCuCO crystal

Various Parameters	**Optimum Condition**
	BCuCO
Density of sodium meta silicate	1.042 g/cm^3
pH of gel	4.50
Concentration of $CdCl_2$ and $CuCl_2$	1M
Concentration of $BaCl_2$	0.5M
Gel setting period	8 days
Gel aging	48 hours
Period of growth	20 days
Quality	Transparent

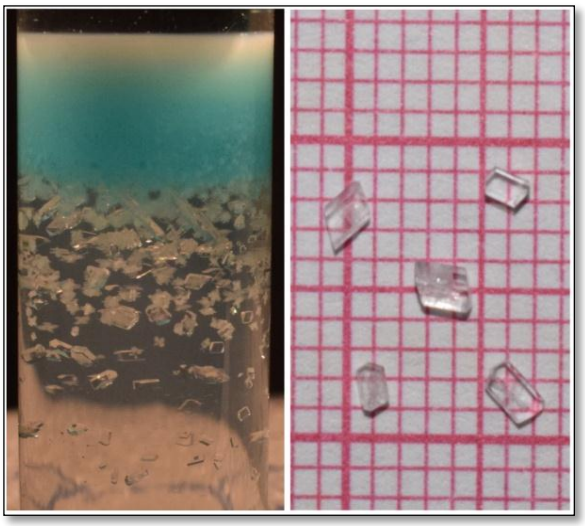

Figure 1: Growth of BCuCO crystals in silica gel and Photograph of grown crystals.

2.2. Characterization

The powder X-Ray Diffraction (PXRD) pattern of as-grown crystal was carried out by Rigaku MiniFlex600 X-ray diffractometer of X-ray wavelength 0.15406 nm (CuK_α) at a scan speed of 5˚/ minute. Single X-Ray Diffraction (SXRD) measurements were carried out using Bruker Kappa APEX II diffractometer, operated at maximum power of 50 kV and 40 mA. Fourier transform infrared (FTIR) spectrum of as-grown crystal was recorded using IR Prestige-21 SHIMADZU FTIR spectrometer in the region 400 - 4000 cm^{-1}. Field emission scanning electron microscope- Energy dispersive X-ray (FESEM-EDX) spectrum of as-grown crystals was analyzed using CARL ZEISS FESEM attached with the EDS system (Oxford Instruments) at the scanning image range is 2.73 kX to analyze the observed defects. Thermogravimetric analysis (TGA) and Differential thermal analysis (DTA) of grown crystals were carried out using the DSC-TGA TA (SDT-Q600) system in the nitrogen gas atmosphere. UV-Visible-NIR Absorption spectrum was recorded in the UV-Vis-NIR spectrophotometer (UV-1800 SHIMADZU) with a scanning speed of 480 nm/min between the wavelength ranges of 190 nm and 1100 nm.

3. Results and discussion

3.1. X-ray diffraction studies

The Powder X-Ray Diffraction (PXRD) pattern of BCuCO crystal is shown in Figure 2. The occurrence of highly resolved intense peaks at specific Bragg angles 2θ indicates the high crystalline nature of the grown crystals. From the Diffractogram, d- values for different *h k l* were computed using PowderX software and obtained (*h k l*) values for sharp peaks (without considering the small and overlapped peaks) are shown in the figure. The obtained d-spacing and miller indices (*h k l*) are in good agreement with the reported values [10, 11, 13]. From the single X-Ray diffraction studies, crystal parameters have been identified and tabulated in Table 2. The crystal parameters are in agreement with the calculated data of PXRD. The crystallite size was calculated using the Scherrer formula.

$$D_v = \frac{K\lambda}{\beta \cos\theta}$$

Where D_v is the average particle size, λ is wavelength of the radiation, K is the Scherrer constant and β is the FWHM (full width at half maximum) of the reflection peak that has the same maximum intensity in the diffraction pattern (integral breadth of the peak located at angle θ).

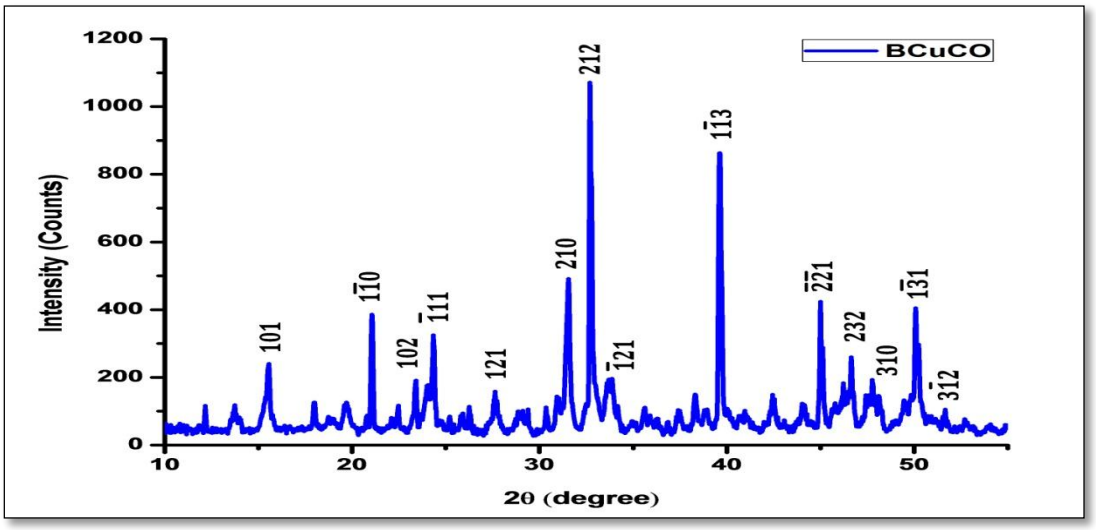

Figure 2: Powder XRD pattern.

Table 2: Crystal parameters of BCuCO crystals.

Crystal parameters	a Å	b Å	c Å	α°	β°	γ°	Volume Å^3	Space group	Crystal system	Grain Size Å
BCuCO	6.015	6.672	8.509	74.689	74.261	80.985	315.750	**P_1**	Triclinic	433.157

3.2. Functional Group Identification of BCuCO Crystal Using FTIR Spectrum

FTIR vibrational spectra of BCuCO crystal (except small peaks may be due to the presence of impurities) is shown in Figure 3. The spectra show broad absorption peaks at 3491.66 cm^{-1} due to O-H stretching vibrations of water [10]. The very strong bands at 1573.87 cm^{-1} were attributed to the C=O stretch of the carbonyl group and the peaks at 1312 cm^{-1} were assigned to C=O symmetric and O–C=O modes [11]. Due to the doping of Ba^{2+} earth metal ion into the copper cadmium lattice there exist many bands below 800 cm^{-1} represents metal-oxygen bonds (Ba-O) [12, 13]. The infrared spectral studies confirm the presence of water of crystallization and oxalate group in the grown crystal.

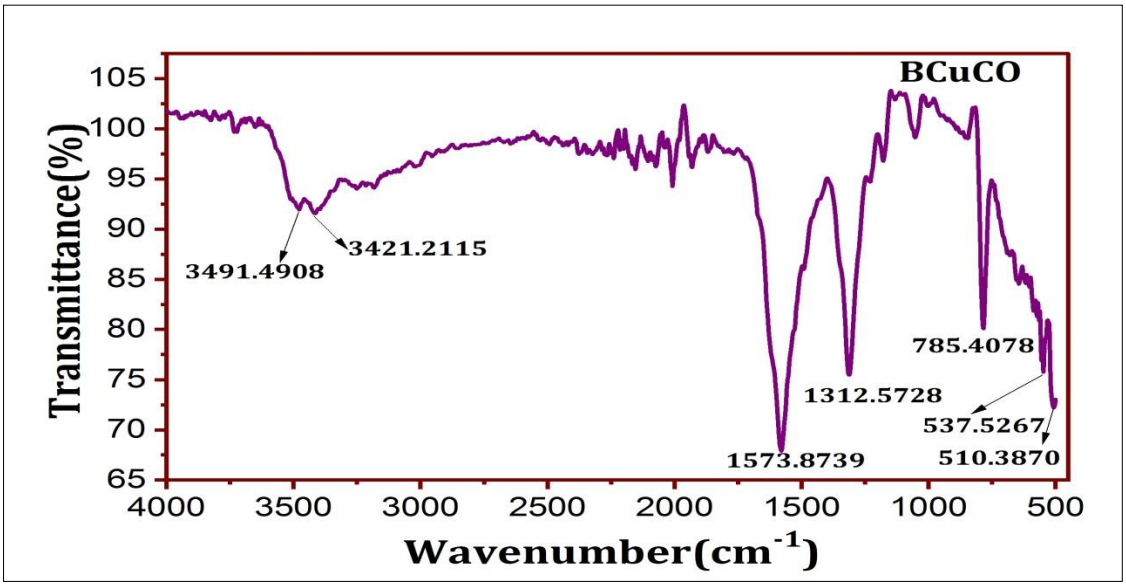

Figure 3: FTIR spectrum of the gel grown crystals.

3.3. FESEM- EDX studies

The fabrication of electronic devices for various applications needs defectless crystals, therefore the interpretation of plastic deformation, morphology of the crystals are important. The field emission scanning electron microscope (FESEM) image is shown in Figure 4. The FESEM image of width 100µm with magnification 100X recorded at EHT 5kV shows that the crystal topography contains agglutination of many polygonal structures with sharp edges. Those valley shaped dislocations between the grains are due to the plastic deformation caused by thermal stresses at the nucleation site [13]. The Energy-dispersive X-ray (EDX) spectrum is shown in Figure 5. The spectrum depicts the occurrences of expected major elements such as Cadmium, Copper, Barium, Carbon, and Oxygen of the title compound.

3.4. TGA/DTA Thermal analysis

Thermogravimetric (TGA) plots from Figure 6 shows two major steps. The first is due to the evaporation of water, which starts at 40˚C and ends at 250˚C, which results in the formation of anhydrous BCuCO crystal from BCuCO dihydrate crystal, resulting in the weight loss of 16.8303% [15, 16]. The next represent the decomposition of barium doped copper cadmium oxalate crystal into barium doped

copper cadmium oxide in the temperature range of 260˚C and 460˚C with 23.3622% weight loss, which shows the release of CO_2 and CO molecules as gases [14, 17].

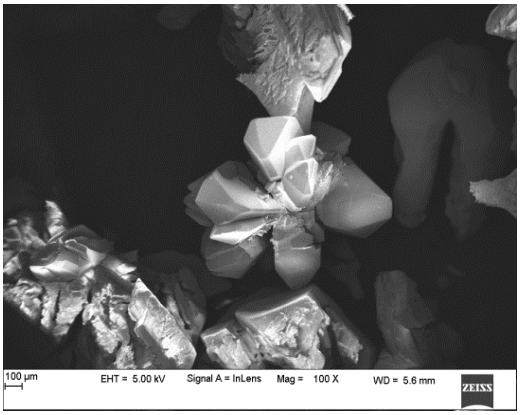

Figure 4: Morphology of BCuCO crystals.

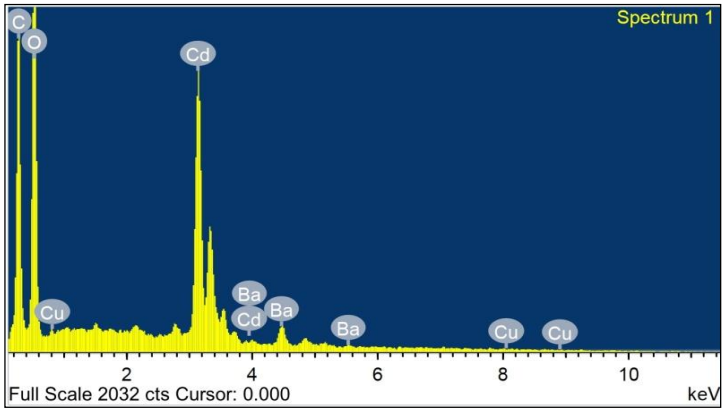

Figure 5: EDX spectrum of BCuCO crystals.

On the Differential thermal analysis (DTA) curve, there were two endothermic peaks at 108.0982˚C and 221.0064˚C due to the decomposition of BCuCO dihydrate into anhydrous BCuCO crystal. The exothermic peaks at 347.1117˚C and 451.4885˚C results in the formation of barium copper cadmium oxide due by the release of carbon monoxide and carbon dioxide [16, 17].

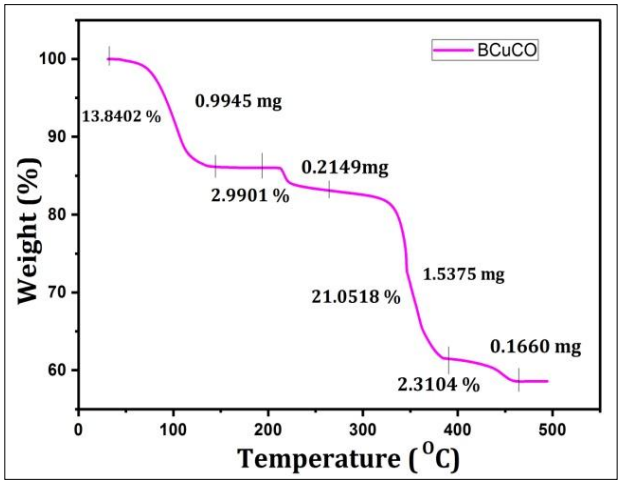

Figure 6: TGA plot of BCuCO crystal.

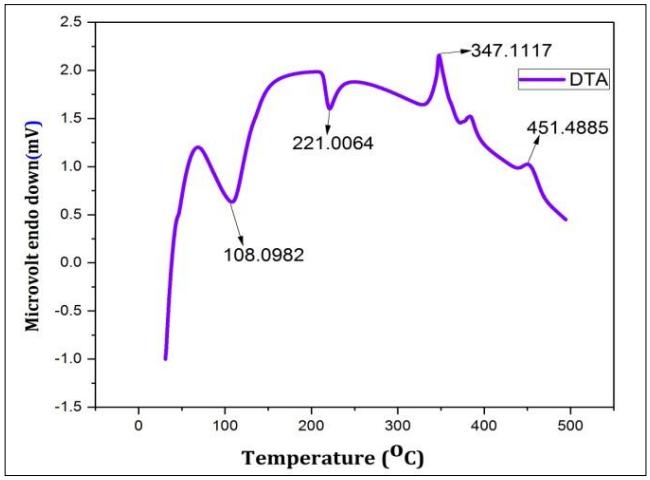

Figure 7: DTA plot of BCuCO crystal

3.5. UV-Visible NIR Studies

The absorbance spectrum of BCuCO crystal is active in the visible and ultra-violet region having the lowest cut off wavelength of 284.03 nm is shown in Figure 8.

The Tauc's [18] plot is shown in Figure 9. The extrapolation of the linear part of the graph gives the optical band gap energy, E_g =4.36 eV, and the crystal shows wide transparency in the visible region.

The relation between the refractive index (n) and the energy gap (E_g) was given by the expression [19, 20]

$$E_g . e^n = 36.3$$

This relation is suitable for the energy gap greater than 0 eV. Further studies on the refractive index (n) and reflectance (R) of the crystals are calculated by using the expression [14, 20],

$$R = \frac{(n-1)^2}{(n+1)^2}$$

The calculated band gap energy, high value of the refractive index and low value of reflectance are summarized in Table 3. The optical parameters of Barium doped CuCO crystal is compared with the parent CuCO crystals [14] shows that, there is a decrease in the energy gap and increase in the refractive index and reflectance. This variation is due to the incorporation of heavy metal ion barium.

Table 3: Calculated optical parameters of as grown BCuCO crystals

Compound	Wavelength (λ) nm	Energy gap (E_g) eV	Ref. Index (n)	Reflectance (R)
BCuCO	284.03	4.36	2.12	0.128

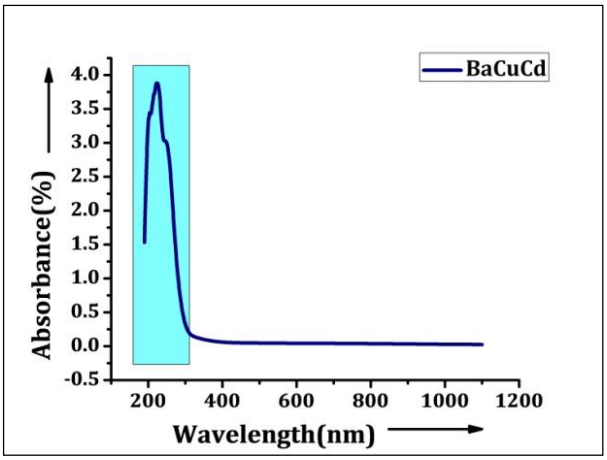

Figure 8: Absorption spectrum of BCuCO crystal.

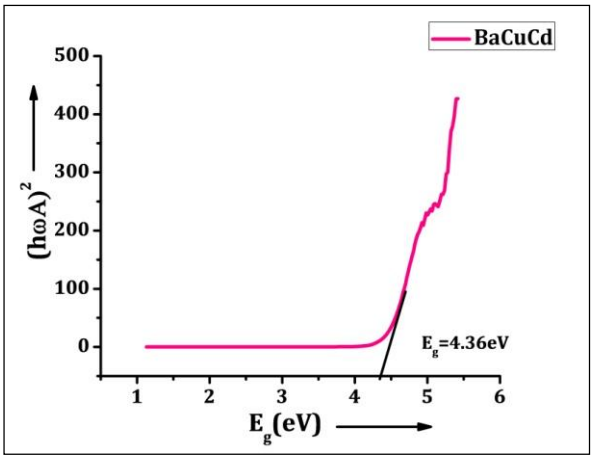

Figure 9: Tauc's plot of BCuCO crystal

Conclusion

Barium doped copper cadmium oxalate single crystals were grown by optimizing the growth parameters using the silica hydrogel single diffusion technique. The highly crystalline nature and the lattice parameters have been obtained from X-Ray diffraction; the grown crystal belongs to the triclinic crystal system with the P_1 space group. FTIR and EDX spectral studies explain the existence of expected functional groups, metal-oxygen bonding, and presence of all the added ions in the lattice of the as-grown crystal. The number of water molecules ($2.H_2O$) presents in the crystal lattice due to the crystallization process, decomposition temperature, and the thermal stability of crystals supporting its application in the fabrication of various electronic devices. The molecular weight of the crystal is calculated using EDX and TGA data and is found to be 238.93 g/mol. The energy bandgap, wide transparency nature, reflectance, and refractive index of the BCuCO crystals have been calculated. Due to the wide bandgap the material becomes an insulator, hence the as-grown crystals can be used as a dielectric material for the fabrication of the capacitor.

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