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Effect of Ba^{2+} Incorporation on Thermal and Optical Properties of Cobalt Cadmium Oxalate Single Crystals

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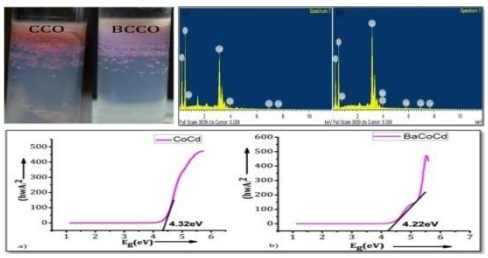
ABSTRACT

Single crystals of Ba^{2+} doped cobalt cadmium oxalate (BCCO) were grown by single diffusion silica hydro gel media. Specific gravity of Sodium Meta Silicate (SMS), gel setting time, pH of the gel, concentrations of Oxalic acid and concentration of supernatant solutions were varied to establish the optimum conditions for growth. Energy Dispersive X-ray (EDX) measurements predicted the matrix of Ba^{2+} ions with parental CCO crystal. Fourier Transform Infra-Red (FT-IR) spectral studies confirmed the presence of Oxalate group, water molecules and metal-oxygen link in BCCO crystals. Thermo Gravimetric Analysis (TGA) showed the thermal stability of the crystals in their anhydrous state. From UV visible Spectrophotometric studies, band gap energy measured was 4.22 eV for BCCO crystal.

Graphical Abstract



Keywords: BCCO, SMS, EDX, FT-IR, TGA, UV.

INTRODUCTION

The more ordered form of solids are crystals and these crystals are appropriate in understanding physical, chemical and optical properties of solids [**1, 2**]. In the field of semiconductor laser diodes and various optoelectronic devices the doped crystals are having great importance and they have vast application in it. The thermal stability and band gap energy found applications in optoelectronic industries can be explained by the Thermo gravimetric analysis (TGA) and optical characteristics of oxalates. One of the main properties of oxalate is that they are insoluble in water and which is useful in separating the transition elements from the mineral as oxalates precipitate. Quality and perfectness of the grown single crystals is the main advantage in growing oxalate crystals by single diffusion gel

method [3, 4]. In semiconductor industries importance is given to doping and mixing of impurities to intrinsic crystals by various crystallization processes. Nano crystals of Barium doped oxalate crystals show semiconducting properties find their applications in high temperature electronics [5]. More importance has been given to alkaline earth ion doped crystals since the dopant enhances their physical properties [6]. Ultimately, the present study mainly focused to study the growth of barium doped cobalt cadmium oxalate (BCCO) crystals, their Thermal and Optical properties.

MATERIALS AND METHODS

Crystal Growth: The crystal growth of BCCO was done using single diffusion silica hydro gel method. Na_2SiO_3 (SMS) solution with different specific gravity were prepared and acidified by 0.5 N oxalic acid to set the silica gel. After setting the gel, upper reactants (barium chloride, cobalt chloride and cadmium chloride) of desired molarities were poured over the gel surface without disturbing the gel. Nucleation starts within a minute and cations from the supernatant solution diffused into the gel through fine pores in the gel. A thick precipitate was formed, below which small crystals appeared and slowly starts to move down in the gel. The crystals become rectangular and gain maximum size in about 15 to 20 days. The experiment was repeated by varying the growth parameters. The specific gravity of the gel was varied between 1.02 to 1.06 and specific gravity of 1.04, 1.044 yields good single crystals of maximum size. pH of the gel were varied from 4 to 8. pH values below 5.25 yields good quality single crystals. Thickness of the blue precipitate increase, size of the crystals reduced with increase of pH above 5. Concentration of oxalic acid were varied from 0.2N to 0.8N, low molarities of oxalic acid reduces the number of crystals. Concentration of barium chloride, cobalt chloride and cadmium chloride were varied from 0.2N to 1.5N to observe the changes in crystallization. The number of crystals and size of the crystals were very less at higher concentration of the reactants. The optimum conditions for obtaining good quality crystals are recorded in table 1. The growth set up and grown crystals of CCO and BCCO are given in figure 1.

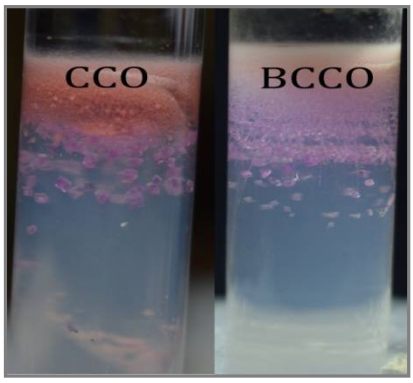


Figure 1. Growth of CCO and BCCO single Crystals:
formation in silica gel CCO, BCCO

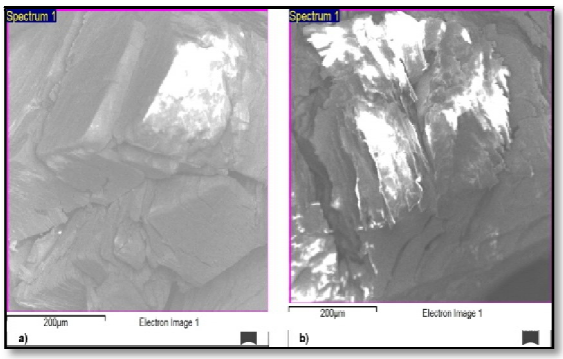
Table 1. Optimum condition for growth of CCO and BCCO crystal

Parameters	Optimum Condition CCO	Optimum Condition BCCO
Density of sodium meta silicate	1.04	1.044
pH of gel	4.5	4.8
Concentration of $CdCl_2$ and $CoCl_2$	1M	1M
Concentration of $BaCl_2$	0.5M	0.5M
Gel setting period	6 days	4 days
Gel aging	48 h	48 h
Period of growth	15 days	20 days
Quality	Transparent	Transparent

Characterization: Elemental composition of the grown crystals was determined using CARL ZIESS FESEM attached with EDS system (Oxford instruments). EDX analysis is used for chemical characterization of materials to detect chemical elements present in nanometers depth from the surface of crystal. Functional groups of crystals are identified using Fourier Transform Infrared Spectrophotometer (IRPrestige-21 SHIMADZU). FTIR analysis (using FTIR spectrophotometer within the wave number range 400-4500 cm^{-1}) is the spectroscopic technique used for analyzing the structural units of samples from their vibrational modes .Thermal properties of CCO and BCCO crystals are studied by TGA using DSC-TGA TA (SDT-Q600) instrument. TGA finds the percentage weight loss of a sample for the increase of temperature. Optical absorption studies are carried out using UV-Visible Spectrophotometer (UV-1800 SHIMADZU) in the spectral range 190-1200 nm.

RESULTS AND DISCUSSION

SEM/FESEM studies: The perfection of the grown crystals can be inferred to some extent by observing the surface morphology of the cut and polished samples using SEM/FESEM photographs. The observation of the cut and lapped wafers by naked eye indicates that the crystals grown had large grains and inclusions. The rectangle pattern of the crystal surface contains dislocations due to the high kink nucleation. The kink nucleation is principally controlled by the successful under saturation of the supernatant solutions. The dislocations may also be due to plastic deformation caused by thermal stresses.SEM/FESEM photographs of as grown crystals are shown in figure 2 and figure 3.



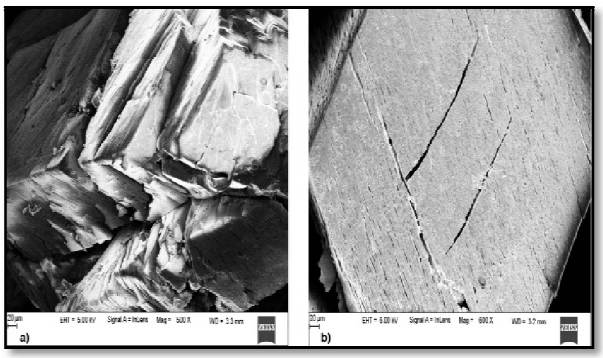


Figure 2. SEM images of (a) CCO and (b) BCCO crystals. **Figure 3**. FESEM images of (a) CCO and (b) BCCO crystals.

EDX Analysis: The EDX The spectrum confirms the presence of expected major elements like Barium, cadmium, cobalt, carbon and oxygen of the title compound. The elemental analysis of grown crystal has been done by EDAX in binding energy region within 0 to 10 KeV. The EDX pattern of CCO and BCCO crystals are shown in figure 4. Characteristic peaks observed in the spectra establish the incorporation of elements O, C, Co and Cd in CCO crystal and O, C, Co, Cd and Ba in BCCO crystal respectively. Atomic percentages of elements present in the crystals are listed in table 2.

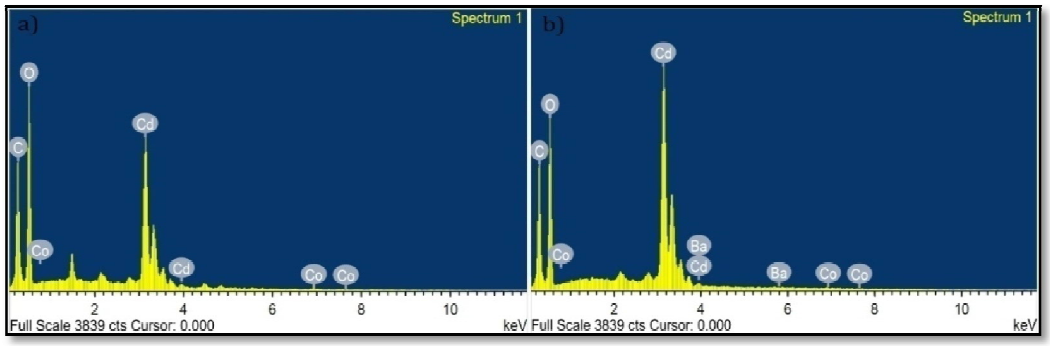


Figure 4. EDAX spectra of CCO and BCCO crystals.

Table 2. Chemical composition of CCO and BCCO crystals.

Crystal	Elements	Atomic(%)
CCO	C	31.12
	O	62.24
	Co	0.12
	Cd	6.52
BCCO	C	30.16
	O	60.33
	Co	0.06
	Cd	9.44
	Ba	0.01

Thermogravimetry Analysis (TGA): The TGA curve for CCO and BCCO crystal is shown in figure 5. The TG plot of CCO revealed that the decomposition occurs in two stages in the temperature range 60-380°C .The first step of thermal decomposition occurs in the temperature range of 60–130°C with measured weight loss of 21.81% (calculated loss: 21.24%) with the loss of three water molecules. The dehydrated CCO crystal further decomposed at 255-380 °C with a weight loss of 28.74% (calculated loss: 27.31%) loosing CO and CO_2 simultaneously. On heating above 380°C the crystal shows stability until 600°C. In the final stage, the material is reduced to its oxide state (>650 °C).

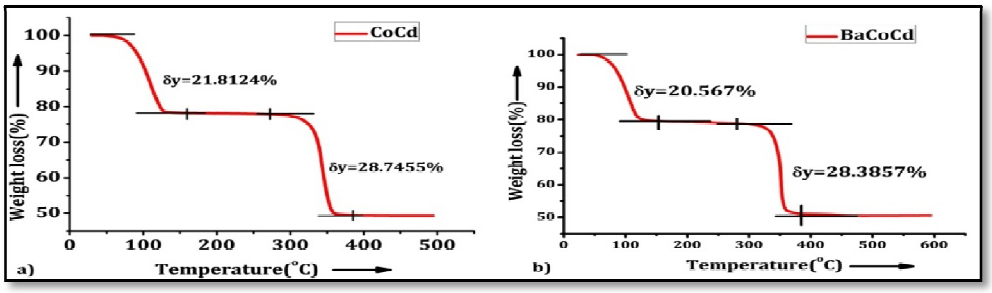


Figure 5. The TG plot of CCO and BCCO crystal.

In BCCO, the decomposition occurs in three stages in the temperature range 60-395°C. The first step of thermal decomposition occurs in the temperature range of 60–127°C with measured weight loss of 20.56% (calculated loss: 19.65%) with the loss of three water molecules. The second stage of decomposition occurs in the temperature range of 256°C-395°C with a weight loss of 28.38% (calculated loss: 27.32%).Third stage of decomposition occurs in the temperature range 400-420°C with a weight loss of 2.31% (calculated loss: 2.32%).

The DTA curve for gel grown CCO and BCCO crystals is as shown in the figure 6. In DTA curve, an endothermic peak is seen at 115.84°C and 109.09°C which is assigned as the melting point of the CCO and BCCO crystals and there is an exothermic at 345.68°C and 354.51°C in this region which corresponds to the phase transition of the as grown crystals.

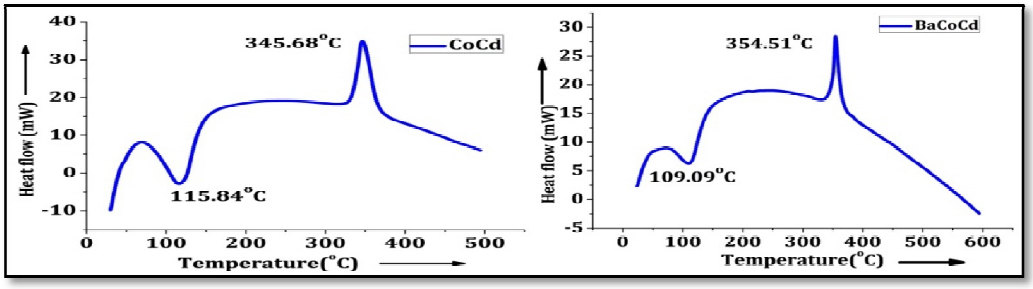


Figure 6. DTA curve of CCO and BCCO crystals.

FT-IR Analysis: FT-IR spectrum of CCO and BCCO crystals grown in silica gel is shown in figure 7. The infrared spectrum in the range of 400-4500 cm^{-1} show a strong band centered at about 3498.65 and 3497 cm^{-1} attributed to the water OH stretching and the water bending. The infrared bands observed below 1700 cm^{-1} in the pure cobalt cadmium oxalate trihydrate samples grown in silica gel are assigned to oxalate vibrational modes [7]. On the other hand, the band around 1300 cm^{-1} corresponds to the asymmetric stretching mode of C-O bond. The absorbed IR bands below 600 cm^{-1} are assigned to the metal oxide M-O bond [8, 9]. The infrared spectral studies confirm the presence of water of crystallization and oxalate group in the grown crystals. Detailed band assignment of some selected absorption bands/peaks observed in the FT-IR spectrum of CCO and BCCO are shown in table 3.

Table 3. FTIR results of CCO and BCCO crystals.

Wave numbers (cm^{-1})		Peak Assignments
CCO	BCCO	
3498.65,3430.13, 3189.74	3497, 3199.28	Symmetric and asymmetric stretching of OH group and water of crystallization
1598.69	1587.202	C = O stretching, O-H bending
1309.74	1318.81	C-C vibrations, C-O stretching
785.94,721.14	804.75,	O-H out of plane Bending
606.41,499.67	601.06,499.9	O-M stretching

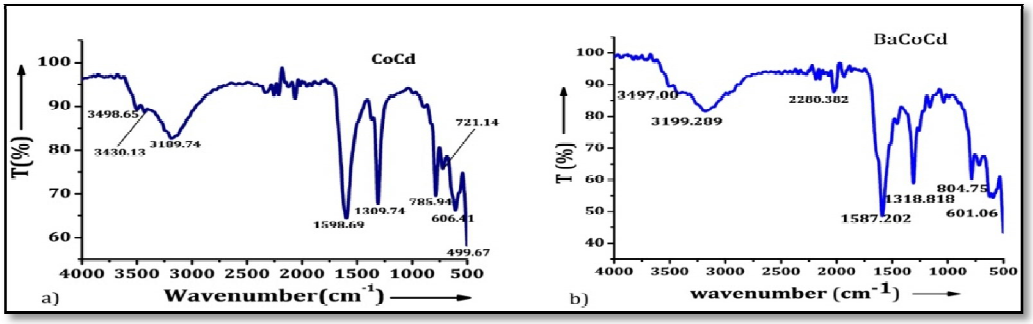


Figure 7. FTIR spectra of CCO and BCCO crystals.

UV-Visible NIR studies: UV-Vis spectrum of CCO and BCCO crystals were found to be active in the Visible and UV region having a significant absorption in the lowest cut off wavelength of 287 nm and 294 nm is shown in figure 8. The grown crystals shows absorption in the range 190 nm-300 nm (corresponds to UV region) with absorption maximum A_{max}=3.88 for CCO and A_{max}=3.86 for BCCO. Further for the entire visible region both the crystals shows maximum transparency, the variation of transmittance and wavelength is shown in figure 9.

In the high photon energy region, the energy dependence of absorption coefficient

$$\alpha = \frac{2.303A}{t}$$

Where α is absorption coefficient, A is absorption and t is the thickness of the cuvette (1cm). Energy for the given wavelengths were calculated by

$$E = h\nu = \frac{hc}{\lambda} \text{ eV}$$

Where h is Planck's constant (6.625×10^{-34} Js), ν is the frequency, c is speed of light and λ is the wavelength of absorption. The transmittance of the crystal was calculated by

Log T %=2-A

The Tauc's graph [**10-12**] plot between $(\alpha h\upsilon)^2$ and the photon energy ($h\upsilon$) is shown in figure 10. The extrapolation of the linear part of the graph gives the optical band gap energy value to be 4.32eV and 4.22eV, this wide band gap of CCO and BCCO crystals confirms the transparency in the visible range.

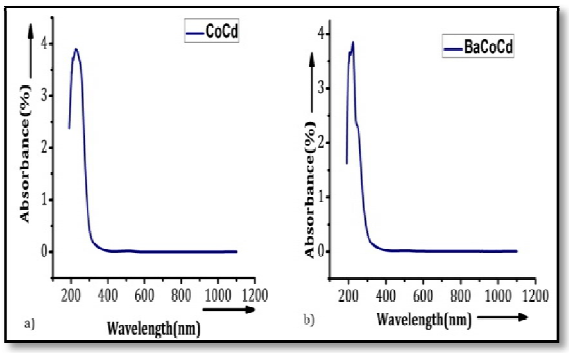


Figure 8. UV-Vis absorbance spectra of CCO and BCCO crystal**.**

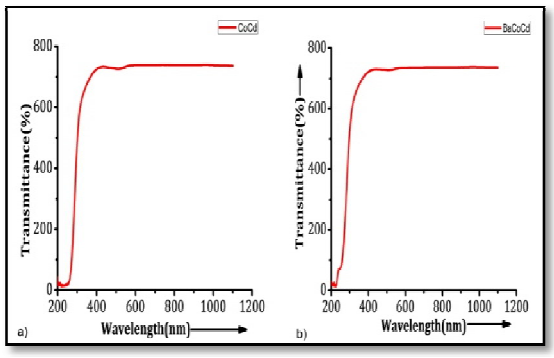


Figure 9. UV-Vis transmittance spectra of CCO and BCCO crystal.

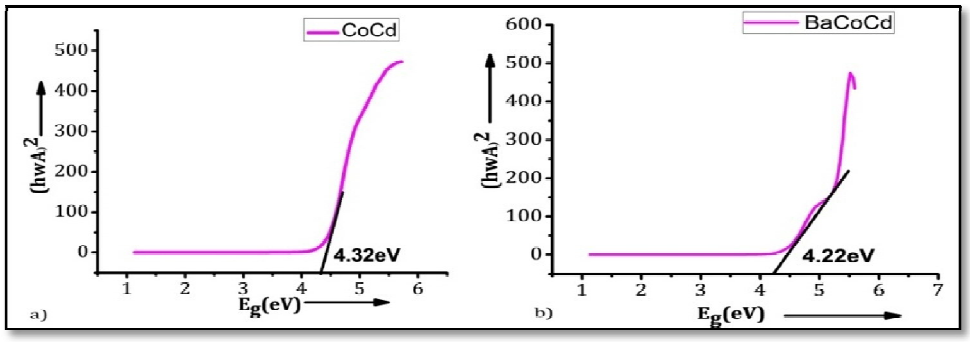


Figure 10. Tauc's plot of a) CCO and b) BCCO crystal.

APPLICATION

Optical transparency of gel grown CCO and BCCO crystals allows them to be used for information control in optical circuit, light valves and optical switching applications where the crystalline perfection and optical transparency is essential. As crystals behave as insulators, they can be used in IC fabrication.

CONCLUSION

Barium doped Cobalt Cadmium Oxalate single crystals were grown by the silica gel method. Size and quantity of grown crystals were changed by varying specific gravity of SMS solution. EDAX spectral studies confirm the presence of expected expected major elements and the incorporation of Ba^{2+} ion within the CCO lattice. FT-IR spectrum of CCO and BCCO crystals confirms the presence of water of crystallization, functional and metal-oxygen bonded groups. The thermal stability was studied by the TGA/DSC supporting its application in the electronic industries. UV visible spectrophotometric studies confirm that the crystal is an insulator.

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