International Journal of Scientific Research in Physics and Applied Sciences **Research Paper**
Vol.8, Issue.3, pp.01-05, June (2020) **E-ISSN:** 2348-3423
DOI: https://doi.org/10.26438/ijsrpas/v8i3.15

Studies on Growth, Magnetic and Spectroscopic Properties of Barium Doped Cobalt Cadmium Oxalate Crystals

P.S. Rohith[1], N. Jagannatha[2*]

[1,2]Dept. of Physics, FMKMC College, A Constituent College of Mangalore University, Madikeri-571201, Karnataka, India

[*]*Corresponding Author: jagannathnettar@mangaloreuniversity.ac.in, Tel.: +91-9448903732*

Available online at: www.isroset.org

Received: 24/May/2020, Accepted: 05/June/2020, Online: 30/June/2020

***Abstract*—** Barium doped cobalt cadmium oxalate (BCoCO) single crystals have been grown in silica hydro gel by optimizing the growth parameters. Obtained crystals were characterized using powder and single X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, Goy balance and UV-Visible spectroscopy. The crystal exhibit triclinic structure with unit cell parameters a=5.973Å, b=6.630 Å, c=8.442 Å, α= 74.68º, β=74.27º and γ = 81.17º. The presence of various functional groups was identified using FTIR spectroscopy. Magnetic susceptibility studies confirm the paramagnetic behaviour of the crystal. The energy bandgap, electrical susceptibility, real and imaginary parts of the dielectric constant of the as-grown crystals was calculated from the UV-Visible spectroscopy and reported.

***Keywords*—**BCoCO, triclinic, susceptibility, dielectric constant, UV-Visible spectroscopy.

I. INTRODUCTION

The compelling class of materials due to their uninterrupted and ceaseless recurrence of atoms and molecules around the specimen are considered as the single crystalline solids. Organic single crystals and also organo-metallic compounds are considered as influential materials for fundamental research in organo-electronics for the absence of grain boundaries, minimum existence of impurities, unique structure, excessively good surface crystallinity and exceptional interface quality. In various fields of microelectronics and optoelectronics, single crystals are of greater importance, therefore used as a structural material and the high temperature materials [1, 2]. With Lissegang's remarkable and renowned exploration of regular and repeated crystallization in gels, an organized or efficient study of crystal growth in the gel begins. For its integrity and efficiency in flourishing single crystals of few compounds, this technique has attained appreciable consideration [3, 4]. We consider this method to be more helpful for the solution growth due to its properties like composed dissemination, convection free and free from thermal strain [5]. Degree of saturation, solvent type, gel pH, doping agent and the variation in temperature of the growth is being the various process parameters which have an unquestionable influence to the crystal morphology [6]. On the growth of immense quality,defect-free single crystals, multitudinous researches are carried out in modern years since they play a crucial or indispensable role in of solid state lasers and optoelectronics [7].

For the growth of metal ions or mixture of metal ion oxalate crystals, plenty of publications are concerned.
Because of the exceptional chemical and physical properties and for the vast applications, alkaline earth elements based crystals have acquired extensive appreciation in modern years [8]. In modern days, it habituates abundant consideration to the role of alienated particles on the crystallization process. Sometimes, the physical properties of the crystals vary because of addition of impurities in definite ways. Hence many researches are drifted on the impact of addition of impurities on crystal growth at elementary levels [9].

To study the growth of good quality single crystal and for the formation of new materials which are highly crystalline, the nature of incorporated impurities, we consider the structure of crystals with impurity and its variation based on the growth circumstances being important. To gather the information on the growth of alkaline earth element (Barium) doped single crystal in gels at ambient temperature, an attempt is made in the present work.

The crystal structure, crystallinity, functional groups, magnetic behaviour and various optical constants of the as-grown crystals analysed using X-Ray diffraction (XRD), Fourier transform infrared (FTIR), Gouy balance and UV-visible spectroscopic techniques.

II. MATERIALS AND METHODS

Single diffusion gel technique is used in the crystallization process of BCoCO crystals.
Chemicals used to grow barium doped cobalt cadmium oxalate crystals are Sodium Metasilicate ($Na_2SiO_3.9H_2O$), Oxalic acid ($C_2H_2O_4.2H_2O$), Cobalt chloride ($CoCl_2.6H_2O$), Cadmium chloride ($CdCl_2.2.5H_2O$) and Barium chloride ($BaCl_2.2H_2O$) of AR grade.

The acidification of sodium metasilicate (SMS) by oxalic acid, the silica gel was set and hence the solution pH was brought to the chosen amount. After the gel is set, barium chloride (0.5M), cobalt chloride (1 M) and cadmium chloride (1 M) solution in the ratio (0.2ml : 2ml : 2ml) was poured over the surface of the gel along the sides of the test tube, without interrupting the gel [10]. There was a creation of semisolid–liquid phase, since the gel is semisolid, and the cations get disseminated into the gel from the supernatant in an accurately restrained way along with the elegant pores in the gel. The crystals gained ultimate size in 30 days; there is no further growth in the size of the crystals [11].

By varying the growth parameters like concentrations of the supernatant solutions, pH of the gel and density of the gel, the experiment was repeated. Between 1.03 and 1.06 $g.cm^{-3}$ the specific gravity of the gel was varied. The range between 1.036 to 1.046 $g.cm^{-3}$ is considered being the gel density at which great quality crystals with ultimate size were obtained. Above the gel density of 1.05 $g.cm^{-3}$ the grown crystal surface was noticed to be non-uniform. The gel pH was set at values 4 to 8 in steps of 0.5. At pH values below 5, great quality crystals were obtained. As there is an increase in the pH value, there is a reduction in the size of the crystal. From 0.1 to 0.7M the oxalic acid molarity was varied and for the supernatant solutions [barium chloride, cadmium chloride and cobalt chloride], the molarity was varied from 0.2M-1M to notice the variation in the process of crystallization [12, 13]. At the lower concentration of reactants, there is a reduction in the size of the crystals and the crystals gain larger size at greater reactant concentration [14, 15]. The great quality crystals were obtained at the optimum conditions as shown in the Table 1. Growth of crystal in test tube and fully grown crystals are shown in Figure 1.

Table 1. Optimum condition for the growth of BCoCO crystal.

Parameters	Optimum condition
Gel density	1.042 $g.cm^{-3}$
Gel pH	4.50
Concentration of $CdCl_2$ and $CoCl_2$	1M
Concentration of $BaCl_2$	0.5M
Gel setting period	96 hours
Gel aging	48 hours
Growth period	3 weeks

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°min^{-1}. Single X-Ray Diffraction (SXRD) measurements were carried out using Bruker Kappa APEX II diffractometer, operated at a maximum power of 50 kV and 40 mA.

Fourier transform infrared (FTIR) spectrum of BCoCO crystal was studied using IR Prestige-21 SHIMADZU FTIR spectrometer in the region 400 - 4000 cm^{-1}. UV-Visible-NIR Absorption spectrum was recorded in the UV-Vis-NIR spectrophotometer (UV-1800 SHIMADZU) with a scanning speed of 480 $nm.min^{-1}$ between the wavelength ranges of 190 nm and 1100 nm.

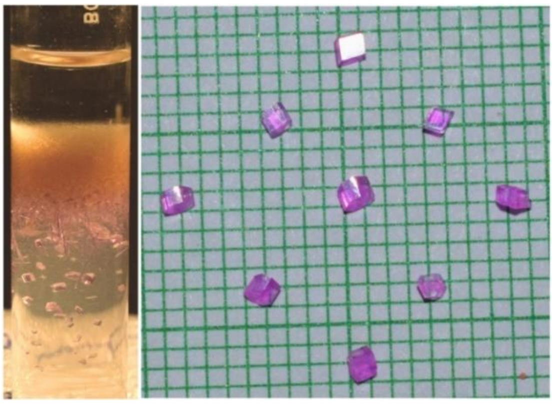

Figure 1. Process of crystal growth in test tube and grown crystals.

III. RESULTS AND DISCUSSION

Figure 2 shows the Powder X-Ray Diffraction (PXRD) pattern of BCoCO crystal. The crystallinity of the grown crystal is indicated by the presence of highly resolved sharp peaks at Bragg angles 2θ [16]. From the Diffractogram, d-values and corresponding miller indices (*hkl*) were computed using PowderX software and obtained (*h k l*) values are also shown in the figure 2.

The standard ICDD file corresponding to BCoCO crystal was not found. From the single X-Ray diffraction studies, crystal parameters have been identified and summarized in Table 2. The crystal parameters are in agreement with the calculated data of PXRD. The crystallite size was calculated using the Scherrer formula [17]

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

Where C_s is the average crystallite size, λ is wavelength of the X-ray radiation, K is the Scherrer constant and β is the FWHM (full width at half maximum) of the reflection peak, which has the same maximum intensity for the Bragg angle 2θ.

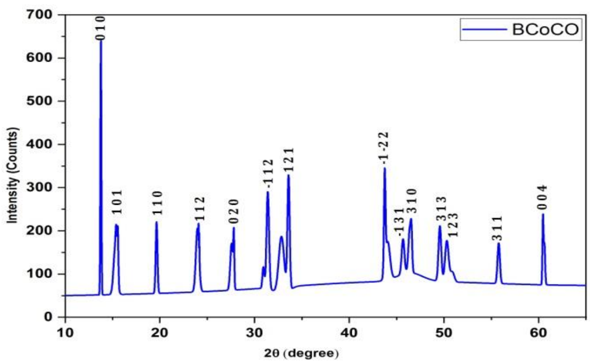

Figure 2. Powder XRD pattern.

Table 2. Crystal parameters of BCoCO crystal.

Crystal parameters	BCoCO
a (Å)	5.992
b(Å)	6.689
c(Å)	8.463
α °	74.88
Β °	74.44
γ °	81.31
Volume $Å^3$	314.3
Space group	P_1
Crystal system	Triclinic
crystallite Size (Å)	682.4108

Infrared spectrum of BCoCO crystal is depicted in Figure 3. The spectra show broad absorption peaks at 3497cm^{-1} and 3199.28 cm^{-1} owing to O-H stretching vibrations of water [18]. The very strong band at 1587.20 cm^{-1} were attributed to the C=O stretch of the carbonyl group. The vibrational peak at 1318.82 cm^{-1} were ascribe to C=O symmetric and O–C=O modes [19].

The incorporation of alkaline earth metal (Ba^{2+}) ion into the cobalt cadmium lattice leads to the appearance of many bands below 800 cm^{-1}, represents metal-oxygen bonds (Ba-O) [19-21]. The infrared spectral studies confirmed crystallization water and metal-oxygen bonding in the grown BCoCO crystal.

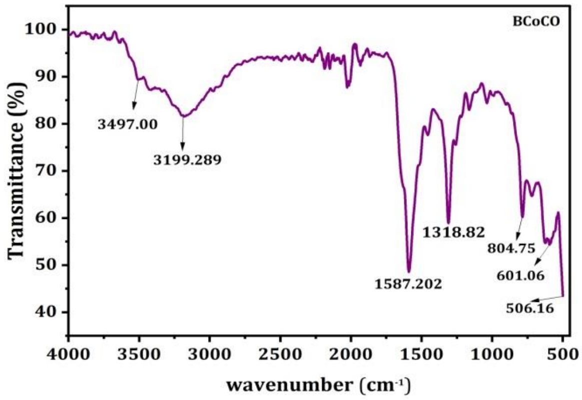

Figure 3. FTIR spectrum of the BCoCO crystal.

The magnetic susceptibility of gel grown BCoCO crystals have been determined by using the Gouy balance method. The gram susceptibility and molar susceptibility were calculated by analyzing the weight change due to the effect of applied magnetic field. The magnetic field strengths are varied from 0.1 to 0.5 Tesla and observed the changes in weight of the finely ground crystal sample in the test tube placed between the electromagnets. The effective magnetic moments of crystals were calculated using the equation

$$\mu_{eff} = 0.8942 \times \sqrt{\chi_m T}$$

Where, μ_{eff} is the magnetic moment of the metal ion in Bohr Magnetrons (B. M.) and T is the temperature.The calculated data are given in Table 3.

The susceptibility of grown crystal shows a positive value indicating that the grown crystals are paramagnetic in nature.

Table 3. Magnetic susceptibility data of BCoCO crystal.

Parameters	BCoCO
Gram susceptibility ($\chi_g \times 10^{-6}$)	0.53 $m^3.g^{-1}$
Molar susceptibility($\chi_m \times 10^{-6}$)	108.22 $m^3 mol^{-1}$
Magnetic moment	0.32
μ_{eff} (B.M)	0.56

The absorbance spectrum of barium doped cobalt cadmium crystal is active in the visible and ultra-violet region having the cut off wavelength of 241.83 nm, is displayed in Figure 4. The small peaks associated with optical absorption at around 230 nm as a result of excitation, may be due to the excitons. These excitons extremely influence the shape of the absorption spectra near the fundamental edge.

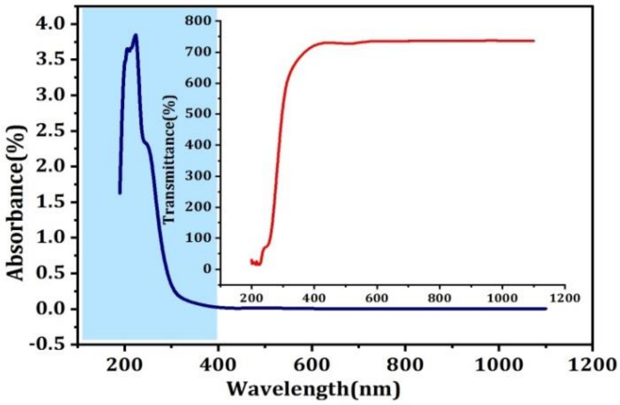

Figure 4. Absorption spectrum of BCoCO crystal.

The energy gap (E_g) of the grown crystal has been analysed from the absorption spectra using Tauc's relation [23]

$$(\alpha \hbar\nu)^{1/n} = C(E_g - h\nu)$$

Where C is a constant, E_g is the energy gap, h is the Planck's constant and ν is the incident photon frequency. The exponent 'n' depends on the direct and indirect allowed, direct and indirect forbidden transitions (n = 1/2, n = 2, n = 3/2 and n = 3 respectively).

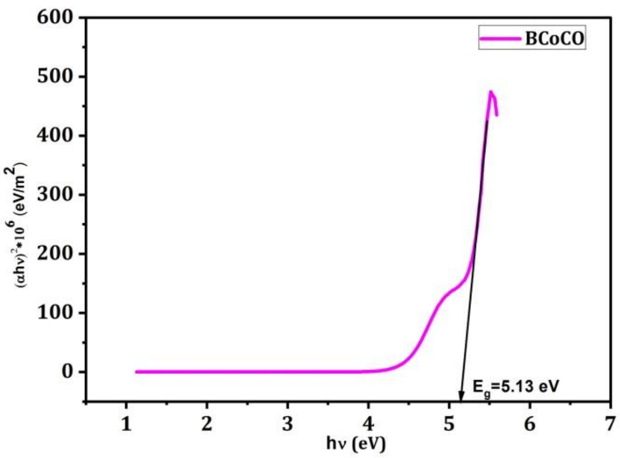

Figure 5. Tauc's plot of BCoCO crystal

The Tauc's plot is shown in Figure 5. The Tauc's graph gives the energy bandgap, E_g =5.13eV and the crystal shows wide transparency in the visible region is also shown in the inset of Figure 4.
The relation between the refractive index (n) and the energy gap (E_g) was given by the expression [24]

$$E_g.e^n = 36.3$$

The material with energy gap greater than 0 eV, this relation is suitable to determine the refractive index. Using the above relation, the refractive index of the crystals is found to be 1.96.
Further from the calculated value of refractive index (n), the reflectance (R) of the crystal is calculated by using the expression [25]

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

The reflectance value is 0.105 and is low.

The electric susceptibility (χ_e) of the grown crystal is determined using the relation [26, 27]

$$\varepsilon_r = 1 + \chi_e = n^2$$

Therefore,

$$\chi_e = \varepsilon_r - 1 = n^2 - 1$$

The electric susceptibility (χ_e) is found to be 2.83 and is greater than 1, which confirms that the material is highly able to polarize in response to the intense field.
The following relations are used to calculate the real (ε_r) and imaginary (ε_i) part of dielectric constant [28]

$$\varepsilon = \varepsilon_r - i\varepsilon_i$$

Where,

$$\varepsilon_r = n^2 - k^2$$

$$\varepsilon_i = 2nk$$

Where k is the extinction coefficient; calculated from the values of absorption coefficient (α) and wavelength (λ) using the equation

$$k = \frac{\lambda\alpha}{4\pi}$$

The calculated values of extinction coefficient, real and imaginary parts of the dielectric constant are 1.046×10^{-5}, 3.83 and 4.096×10^{-5} respectively.

IV. CONCLUSION

Barium doped cobalt cadmium oxalate single crystals were grown by optimizing the growth parameters using single diffusion technique. The highly crystalline nature and the lattice parameters have been obtained from X-Ray diffraction studies; the grown crystal belongs to the triclinic crystal system with the P_1 space group.

FTIR spectral studies explain the existence of various functional groups of oxalate compound, M-O bonding and water of crystallization. Low positive value of susceptibilities confirms the paramagnetic behaviour of the grown crystal.
The energy bandgap, wide transparency nature, reflectance, and refractive index of the BCoCO crystals have been calculated. Due to the wide bandgap E_g =5.13eV, the material becomes an insulator, hence the grown crystals can be used as a dielectric material for the fabrication of the capacitor.

The dielectric constants and electric susceptibility values are also suggests that the material is greater ability of polarization in response with the light radiation; hence the grown BCoCO crystal can be used in optoelectronic device applications.

ACKNOWLEDGEMENT

The authors are thankful to The Principal, FMKMC College Madikeri, The Director USIC Mangalore University, and The Director STIC Cochin for providing laboratory, characterization facilities and technical support to carry out the work.

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AUTHORS PROFILE

P. S. Rohith is a post graduate and pursuing Ph.D from Mangalore University, Mangalagangothri, has Eight years of experience of teaching Physics to postgraduate students of FMKMC College. He has published eight research papers in National and International Journals of repute, attended and presented papers in more than fifteen national and international conferences.

Dr. N. Jagannatha is an Associate professor in F.M.K.M.C. College Madikeri, a constituent college Mangalore University, Mangalagangotri, has twenty seven years of experience in teaching Physics to graduate and postgraduate students. He has published forty research papers in National and International Journals of repute, attended and presented papers in more than fifty national and international conferences.

