Journal of Physics and Chemistry of Materials **Research Paper**
Vol.7, Issue.2, pp.01-04, June (2020) **E-ISSN:** 2348-6341

Spectroscopic Studies on Zinc Barium Oxalate Crystals Grown by Gel Method

Mangala M. Sanjeevannanavar[1], Jagannatha N.[2*], Rohith P.S.[3]

[1,2,3]Dept. of physics, FMKMC College, A constituent college of Mangalore University, Madikeri-571201, Kodagu, Karnataka, India

[*]*Corresponding Author: jagannathnettar64@gmail.com, Tel.: +91-9448903732*

Available online at: www.isroset.org

Received: 25/May/2020, Accepted: 06/June/ 2020, Online: 30/June/2020

***Abstract*—** In the present paper, Zinc mixed Barium Oxalate (ZnBaO) crystals were grown successfully by silica hydrogel technique. The optimum conditions were established by varying various parameters such as specific gravity of Sodium Meta Silicate (SMS), concentration of the oxalic acid ($C_2H_2O_4.2H_2O$) solution, pH of the gel, gel setting time, concentration of reactants like zinc chloride ($ZnCl_2$) and barium chloride ($BaCl_2.2H_2O$) etc. Field Emission Scanning Electron Microscope (FESEM) characterization shows the existence of various layers in the grown crystals. Elemental analysis studied by Energy Dispersive X-ray Analysis (EDAX). It determines the percentage composition of elements present in the grown crystals. The study of EDAX confirms the grown crystal has Zn^{2+}, Ba^{2+}, C and O elements. The vibrational analysis of grown crystals identified by FTIR and laser Raman spectroscopy reveals the functional groups like O-H band, C-H band, C=O, C-C bands and metal oxide bands present in the grown crystals. The study of UV-Visible spectrum reveals optical constants like energy bandgap, absorption coefficient, refractive index, reflectance, electrical polarizability and cutoff wavelength of the grown crystal. These constants considered to characterizing materials which are used in various applications like fabrication of optoelectronic devices.

***Keywords*—** *Zinc Barium Oxalate, Silica hydrogel, FESEM, EDAX, FTIR.*

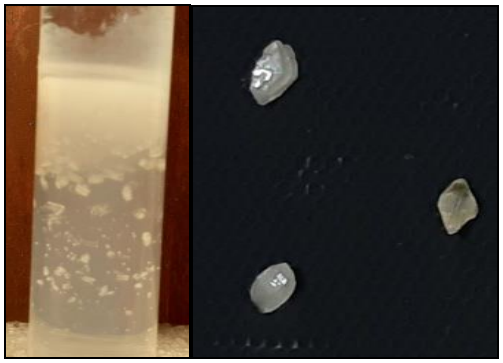
I. INTRODUCTION

Present day single crystals are backbone of modern technology. They are of great importance for their application in the field of electrical and optical devices. Growths of single crystals were very famous due to wide applications in the field of ceramics, physics, chemistry, metallurgy, mineralogy, medicine and engineering [1]. In the present work good quality crystals have been achieved by the gel technique. Gel technique method is efficient and simple method to grow single crystals in ambient temperature. Now days many researchers showing interest in study of oxalate single crystals. The oxalate compound hold vital role in the areas of optoelectronic devices, solid state lasers, remote sensing and medical diagnostic etc [2]. They behave as a precipitating agent [3]. Oxalate crystals are utilized in many technologies like ferroelectric, superconducting materials, magnetic and luminescent devices [4]. They are used in many linear and nonlinear mechanical devices. Nonlinear optical properties have great attention in the areas of optical communication, signal processing, light modulators, random access and switchable nonlinear devices [5]. The present paper describes the zinc barium oxalate crystals were grown in silica gel technique in the room temperature. Growth of crystals in gel technique was inexpensive and insoluble in water [6]. Zinc and Barium ions have attracted a much interest because it has simple chemistry and coordination geometry. Growth parameters and their effects on Zinc Barium oxalate crystals were optimized. Characterizations of as-grown crystals were investigated by FESEM, EDAX, FTIR, Raman spectrometer and UV-Visible spectrometer. The FTIR and Raman spectrometer were used to identify the different functional groups [7]. Optical constants of ZnBaO crystals were determined by the UV-Visible spectrometer.

II. METHODOLOGY

Zinc Barium Oxalate single crystals were grown by silica gel technique. The chemicals used for growth were Sodium Meta Silicate (Na_2SiO_3), Oxalic acid ($C_2H_2O_4.2H_2O$), Zinc chloride ($ZnCl_2$) and Barium Chloride ($BaCl_2.2H_2O$). The crystallization apparatus consists of glass test tubes of length 15cm and diameter 2.5cm. In silica gel technique, gel was prepared by mixing of Sodium Meta Silicate solution of 1.038 $g.cm^{-3}$ specific gravity with 0.5M oxalic acid solution. The solution of oxalic acid was prepared by dissolving 15.759 g of oxalic acid with 250ml distilled water. Mixed solution was poured into various test tubes. After 4 to 5 days gel was set. Mixture of an aqueous solution of Zinc chloride ($ZnCl_2$) and Barium chloride ($BaCl_2.2H_2O$**)** was poured slowly along the sides of the test tubes. Concentration of Zinc chloride and Barium chloride was 0.5M. After 24 days crystals were found inside the gel

contained test tubes. The grown crystals Zinc Barium Oxalate are shown in Figure 1.



(a) (b)

Figure 1. a) Growth of ZnBaO crystals b) Extracted ZnBaO crystals

III. RESULTS AND DISCUSSION

3.1.Growth parameters

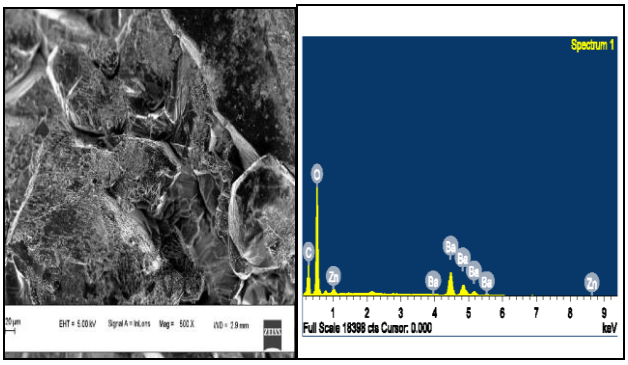
The growth parameters of zinc barium oxalate crystals optimized by various parameters like specific gravity of the gel, concentration of oxalic acid, pH of the gel, concentration of zinc chloride, concentration of barium chloride [8]. Optimization conditions achieved to grow good quality single crystals. The ZnBaO crystals were grown in different specific gravities like 1.03g.cm^{-3}, 1.038g.cm^{-3}, 1.04g.cm^{-3}, 1.04g.cm^{-3} and 1.049g.cm^{-3}. As specific gravity varies size of the crystals also varies. The nucleation rates of grown crystals were varied with different pH values [9]. The pH of the gel was 3.50. The concentration of the reagents varied with 0.2M, 0.5M and 1M. The concentration below 0.5M no nucleation observed because less amount of reactants diffused through the gel in the formation of crystals [10]. The nucleation starts above 0.5M concentration. Optimized conditions for grown crystal shown in the Table 1.

Table 1.Optimized growth parameters of ZnBaO crystal

Parameters	**Optimization conditions**
Specific gravity of SMS	1.038 g.cm^{-3}
pH of the gel	3.5
Concentration of oxalic acid	0.5M
Concentration of $ZnCl_2$	0.5M
Concentration of $BaCl_2.2H_2O$	0.5M
Gel setting time	4 to 5 days
Period of growth	24 days

3.2. FESEM AND EDAX

The morphology of the sample ZnBaO was examined by using FESEM technique. It reveals the information about its internal structure and surface morphology. The flat surface of the crystals contains few rock and valley shaped dislocations due to the high kink nucleation [11, 12]. The crystals were grown by layer deposition**,** Shown in Fig 2. The spectrum of EDAX confirms the presence of Zinc, Barium, Carbon and Oxygen elements. Atomic and weight percentage of grown crystals were confirmed by EDAX spectrum [13] shown in Table 2.



(a) (b)

Figure 2. a) FESEM image of ZnBaO crystal b) Electron spectra of ZnBaO crystal

3.3 Fourier Transformation Infrared Spectrometer

The FTIR spectrum was recorded in the range 0 to 4000cm^{-1}. It reveals and analyses the presence of functional groups in the grown crystals [14]. The peaks 3965.56cm^{-1}, 3708.34cm^{-1}, 3587.45cm^{-1}, 3345.68cm^{-1}, 3013.02cm^{-1} were stretching vibrations of the water molecules [15]. The bands in the region 2892.14cm^{-1}, 2362.15cm^{-1}, 2287.71cm^{-1}, 2168.83cm^{-1}, 2031.42cm^{-1}, 1925.06cm^{-1} were due to vibrations of the hydrogen bonding [16]. The sharp and intense band at 1593.31cm^{-1} indicates presence of C-O group. The sharp and intense band at 1320.6cm^{-1} was due to asymmetric stretching mode of C=O bond. The absorption bands at 1195.86cm^{-1}, 1018.88cm^{-1} were due to C-H bending. The IR bands between 837.10cm^{-1} to 414.46cm^{-1} were due to Metal oxide bond. The FTIR spectrum confirms the presence of water crystallization and the oxalate group in the grown crystals. Figure 3.

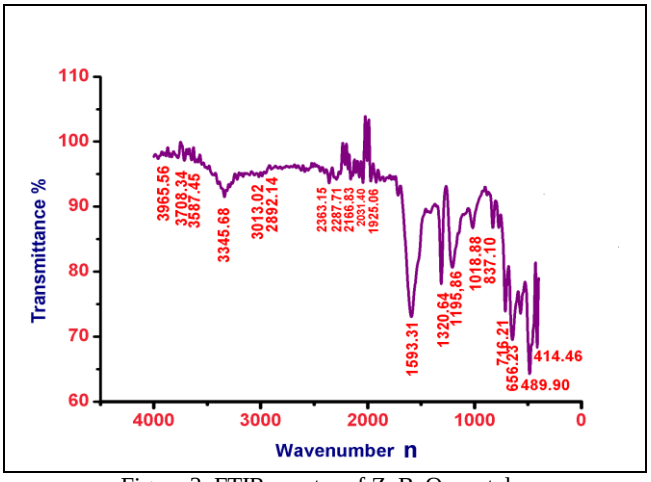


Figure 3. FTIR spectra of ZnBaO crystals

3.4. Raman spectrum

Laser Raman spectroscopy is a type of vibrational spectroscopy. It is an optical technique capable of identify the molecules present in the compound. The Raman spectrum was analyzed by the Horiba scientific instrument with a 532nm excitation source in the region 0 to 4000cm^{-1} is shown in Figure 4. The modes below 600cm^{-1} are single phonon modes; spectrum shows five phonons [17]. The frequency shifts observed in wavenumbers. The Raman spectrum of grown crystal shows 12 lines. In the Raman spectra O-H stretching in the region 3000cm^{-1} to 3600cm^{-1}. O-H stretching modes of the grown crystals were observed at the peak 3349.82cm^{-1} [18]. The wide symmetric vibration band of C-H assigned at the peak 2793.84cm^{-1} [19]. The peaks 2110.81cm^{-1} and 1713.41cm^{-1} identifies the carboxyl group C=O. The sharp peak anti-symmetric modes of CH_2 scissoring observed at 1459.30cm^{-1} and deformation symmetric stretching of CH_2 band assigned at 1205.19cm^{-1}[20]. The sharp peaks at 888.19cm^{-1} and 729.46cm^{-1} was assigned to C-C vibration bending modes of grown crystal [21]. The sharp peaks at 490.63cm^{-1}, 205cm^{-1}, 141cm^{-1}, 109.47cm^{-1} and 61.71cm^{-1} were assigned to metal-oxide bands [22].

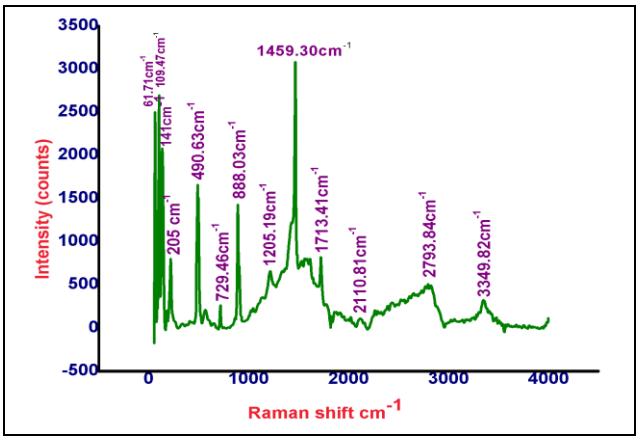


Figure.4. Raman spectra of ZnBaO crystals

3.5. UV-Visible spectrum

Optical absorption spectrum was recorded with performing wavelength ranging from 200nm to 1100nm. The grown crystals have absorbance in the entire UV-Visible region is 1.3819 at the wavelength 212.199nm and cut off wavelength is 238.194nm. Figure 5. The lower cut off wavelength suggests wide optical transmission [23]. From Tauc's plot the optical band gap energy values to be 5.490eV, shown in Figure 6. It shows the transparency in the visible region [24]. Absorption coefficient of the material is calculated by the relation $\alpha = 2.303A/t$. (A=1.3819, t=1mm) Hence $\alpha = 3.1825$.

Refractive index is determined using equation given by Reddy et al.

$$E_g e^n = 36.3$$

Hence $n = 1.8888$

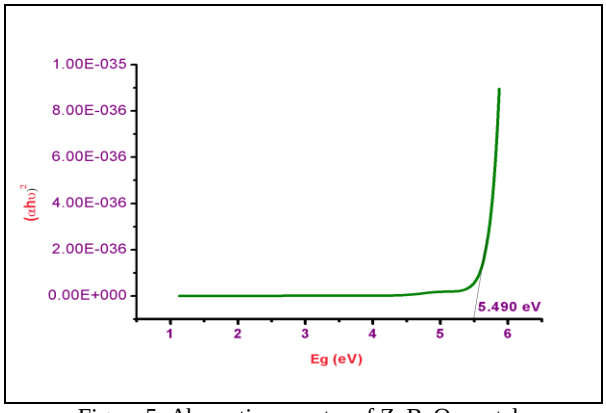


Figure.5. Absorption spectra of ZnBaO crystals

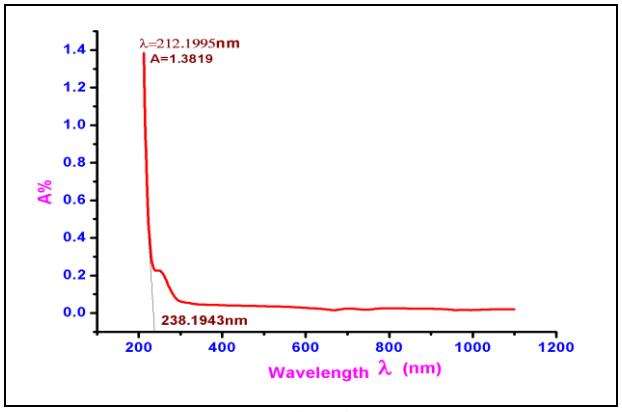


Figure.6. Tauc's plot of ZnBaO crystals

The electrical susceptibility (χ_e) is calculated using the relation [25],

$$\chi_e = \epsilon_r - 1$$
$$\chi_e = n^2 - 1 \qquad (\epsilon_r = n^2)$$
$$\chi_e = 2.5678$$

The electrical susceptibility is greater than 1, hence the material is polarized.

IV. CONCLUSION

Zinc Barium Oxalate crystals were grown successfully using silica hydro gel technique. Grown crystals are optimized by various parameters like specific gravity of Sodium Meta Silicate (SMS), concentration oxalic acid ($C_2H_2O_4 2H_2O$) solution, pH of the gel, gel setting time, concentration of reactants like zinc chloride ($ZnCl_2$) and barium chloride ($BaCl_2.2H_2O$). FESEM characterization reveals surface morphology of crystals. EDAX spectrum confirms the presence of Zinc, Barium, Carbon and oxygen elements. The fundamental vibrational properties of crystals were understood by laser Raman spectroscopy. Presence of functional groups O-H, C-H, C=O, CH_2, C-C bands were analysed and recorded by using FTIR spectrum and laser Raman spectroscopy. UV-Visible spectrum determines the cut off wavelength, energy band gap, absorption coefficient, Refractive index, reflectance and electrical polarizability of grown crystals. Crystals has good transmittance and polarized.

ACKNOWLEDGMENT

Authors are grateful to purse laboratory Mangalore University and UPE University of Mysore Manasagangothri, Mysore for providing research facilities during the course of this work. Authors are also thankful to Mangalore University for providing scholarship facility

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AUTHORS PROFILE

Mangala M Sanjeevannanavar is a post graduate and pursuing Ph.D from Mangalore University, Mangalagangotri, has two years of experience of teaching Physics to postgraduate students of FMKMC College. She has published two research papers in National and International Journals of repute, attended and presented papers in more than eight 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.

P. S. Rohith is a post graduate and pursuing Ph.D from Mangalore University, Mangalagangotri, 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.

