RESEARCH ARTICLE

SAMRIDDHI Volume 14, Issue 1, 2022 Print ISSN: 2229-7111 Online ISSN: 2454-5767

Synthesis and Spectral Characteristics of CoO mixed $ZnO\text{-}Bi_2O_3\text{-}B_2O_3$ Glasses

Bejjipurapu Chandrasekhar[1,3], Gunnam Nagarjuna[2], Sopinti Ramesh[1], B.V. Raghavaiah[3]*

[1]Department of Physics, Acharya Nagarjuna University, Nagarjuna Nagar, Guntur, 522510, Andhra Pradesh, India

[2]Department of Chemistry, SRR & CVR Government Degree College (A), Vijayawada, 520 004, Krishna District, Andhra Pradesh, India

[3]Department of Physics, RGUKT-Ongole Campus, Rajiv Gandhi University of Knowledge Technologies–AP, Ongole, 523001, Andhra Pradesh, India

Abstract

The conventional melt-quench process synthesized bismuth borate glasses containing ZnO and CoO. CoO is introduced up to a maximum of 0.8 mol% by replacing boric acid. All the prepared samples were tested by x-ray diffraction and scanning electron microscopy techniques. Characterization methods confirm the non-crystalline behavior of samples. The density of the samples was found to increase while molar volume diminishes against the content of cobalt oxide. UV-visible spectra have shown the necessary bands of divalent and trivalent cobalt ions. Infrared spectra display all characteristic vibrational bands of different molecular groups. Increasing structural degree of disorder is evidenced from the analyses of results, and details are presented.

Keywords: Bismuth, Borate glasses, Cobalt, Infrared, UV-visible absorption.

SAMRIDDHI : A Journal of Physical Sciences, Engineering and Technology (2022); DOI: 10.18090/samriddhi.v14i01.7

Introduction

Recently, a large amount of concentration has been paid to explore the spectral features of cobalt ions in different glass systems due to their significant visible and infrared emission that makes them potential materials for non-linear optical absorbers and fast switching devices.[1-3] When cobalt ions are added with heavy metal oxide like bismuth oxide enables them as prominent candidates for non-linear optical devices. Bi_2O_3 has the characteristic electron pair arrangement that opens pathways for large susceptibility coefficients, in turn, suitability for optical switches solid-state ionic devices.[4,5] Cobalt ions exhibit divalent and trivalent states, where divalent states give characteristic pink color to the glass samples. Based on the occupation symmetry of 'Co' ions in the fundamental borate structure would result in other colors. B_2O_3 is considered a very good network developer among various glass formers and could form glasses at low temperatures with high transparency.[6] The borate glass network allows cobalt and zinc ions and causes structural changes by conversion of BO_3 to BO_4along with non-bridging oxygens (NBOs). The structural degree of disorder is very much linked with oxygens and leads to changes in physical and spectroscopic properties of $ZnO\text{-}Bi_2O_3\text{-}B_2O_3$: CoO glasses. Limited numbers of studies are available on spectroscopic features of cobalt ions in zinc bismuth borate glass network. However, most of the investigations were focused on spectral features of 'Co' ions in borate glasses, silicate glasses without zinc oxide.[4,7] Hence, the current investigation is focused at the preparation of $ZnO\text{-}Bi_2O_3\text{-}B_2O_3$glasses doped with cobalt oxide and further characterization by XRD, SEM, absorption, and infrared studies to explore the usability of samples for optical switches applications because of their structural degree of disorder against replacement of zinc oxide by cobalt oxide. Attention is given to cobalt ions' oxidation conditions and their occupational symmetry in the borate glass system.

Corresponding Author: B.V. Raghavaiah, Department of Physics, RGUKT-Ongole Campus, Rajiv Gandhi University of Knowledge Technologies–AP, Ongole, 523001, Andhra Pradesh, India, e-mail: bv_raghavaiah@rediffmail.com

How to cite this article: Chandrasekhar, B., Nagarjuna, G., Ramesh, S., & Raghavaiah, B.V. (2022). Synthesis and Spectral Characteristics of CoO mixed $ZnO\text{-}Bi_2O_3\text{-}B_2O_3$ Glasses. *SAMRIDDHI : A Journal of Physical Sciences, Engineering and Technology,* 14(1), 44-47.

Source of support: Nil

Conflict of interest: None

Experimental Methods

A specific glass composition $ZnO\text{-}Bi_2O_3\text{-}B_2O_3$: CoO has been selected. Composition specifications of samples with their

nomenclature are presented below. The glasses exhibited transparency up to 0.8 mol% of CoO; thereafter, glass nature was present but opaque in nature.

ZC_2: 19.8 ZnO- 25Bi_2O_3-55 B_2O_3: 0.2 CoO
ZC_4: 19.6 ZnO- 25 Bi_2O_3-55 B_2O_3: 0.4 CoO
ZC_6: 19.4 ZnO- 25 Bi_2O_3-55 B_2O_3: 0.6 CoO
ZC_8: 19.2 ZnO- 25 Bi_2O_3-55 B_2O_3:0.8 CoO

AR grade chemicals of Bi_2O_3, H_3BO_3, ZnO, and CoO powders in suitable amounts (all in mol%) had been very well jumbled using a mortar and liquefied in a platinum crucible withinside the temperature variety of 900 to 980°C in a PID temperature managed furnace for approximately1 hour. The resultant bubble-free melt was then poured in a brass mold and subsequently annealed at 300°C. After the annealing process, the samples prepared were ground and optical polished to the dimensions of 1 cm × 1 cm × 0.2 cm. Samples' solid-state nature is tested using an X-ray diffractometer with CuK_α radiation. Scanning Electron Microscope is used to verify the morphology of glasses. With Archimedes' principle and using o-xylene (99.99% pure), densities of samples were measured. Infrared transmission spectra were recorded on a JASCO-FT/IR–5300 spectrophotometer up to a resolution of 0.1 cm^{-1} in the spectral range 400–2000 cm^{-1}usingpotassium bromide pellets (300 mg) containing pulverized sample (1.5 mg). These pellets were pressed in a vacuum die at ~680MPa. The absorption spectra spanning from 300 to 1800 nm were carried out with a spectral resolution of 0.1 with a UV–vis–NIR spectrophotometer.

Results and Discussion

Before proceeding to spectroscopic properties, material features are calculated using experimental density values. Average molecular weight, density, cobalt ion concentration increase with the content of cobalt oxide. It could be due to the replacement of zinc oxide by cobalt oxide, whose molecular weight is higher than that of ZnO. The increase in density is associated explicitly with the cross-linkages with boron groups and other available transition metals along with interstitial positions/vacancies.[7,8] In another way, the interionic distance and polaron radius exhibited decrement with the rising content of CoO (Table 1). XRD patterns of ZnO-Bi_2O_3-B_2O_3: CoO glasses are shown in Figure 1. All X-ray scans of ZnO-Bi_2O_3-B_2O_3: CoO glasses have exhibited similar patterns, including a significant wide band from 20° to 30° that assures the non-crystalline behavior of glasses. Scanning electron microscopic pictures show no voids. However, tiny crystal granules are presented that could be due to the process of gradual cooling from a molten state to normal condition. The SEM images of two samples are presented in Figures 2 and 3.

UV-Visible-NIR spectra of all glass samples in the range 350 to 1800 nm are carried out. An interesting observation is that the absorption edges of all samples exhibited redshift against CoO content. Every sample has shown relevant bands; one small band in the range 520 to 550 nm assigned to $^4T_{1g}(F) \rightarrow {}^2T_{1g}(H)$ Co^{2+} ions occupied octahedrally, second peak is in the range 590 to 605 nm attributed to $^4A_2(^4F) \rightarrow {}^4T_1(^4P)$ and third peak in the range 1400 to 1450 nm attributing to transition $^4A_2(^4F) \rightarrow {}^4T_1(^4F)$ of divalent cobalt ions.[8] Another noteworthy observation is the very small absorption peak from 710 to 725 nm that could be due to transition $^5T_2 \rightarrow {}^2E$ corresponding octahedrally occupied trivalent cobalt ions.[9]

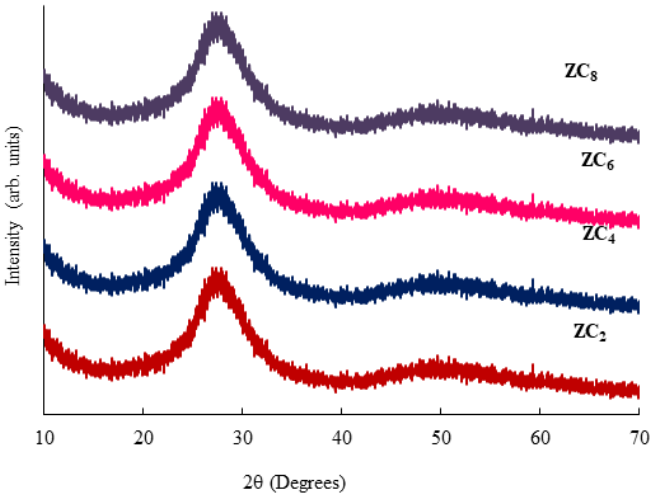

Figure 1: XRD patterns of ZnO-Bi_2O_3-B_2O_3: CoO glasses.

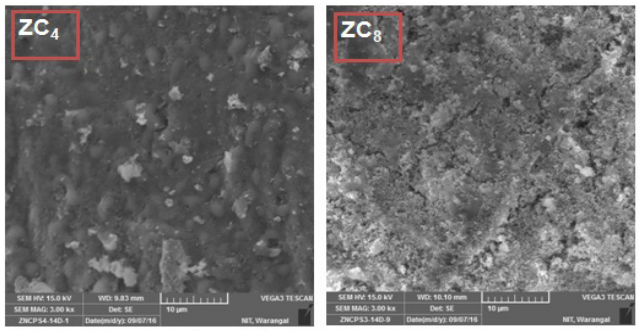

Figure 2: SEM images of ZC_4 and ZC_8 glasses.

Table 1: Experimental physical features of ZnO-Bi_2O_3-B_2O_3: CoO samples.

Glass	*Avg. Mol. Wt.*	*Density (g/cm^3)*	*Conc. of 'Co' ions N_i ($10^{21}/cm^3$)*	*Inter ionic distance of 'Co' ions $r_{i\,(A°)}$*	*Polaron radius $_{RP\,(A°)}$*
ZC_2	171.37	4.701	3.31	0.67	0.27
ZC_4	171.69	4.703	6.59	0.53	0.21
ZC_6	172.01	4.704	9.88	0.46	0.18
ZC_8	172.33	4.706	13.15	0.42	0.17

Table 2: IR spectral positions of $ZnO\text{-}Bi_2O_3\text{-}B_2O_3$: CoO glasses.

	Borate groups (cm^{-1})			
Glass	*BO_3*	*BO_4*	*B-O-B/B-OBi*	*Co-O groups (cm^{-1})*
ZC_2	1398	1072	731	---
ZC_4	1393	1079	733	659, 561
ZC_6	1386	1084	736	651, 553
ZC_8	1382	1087	739	640, 549

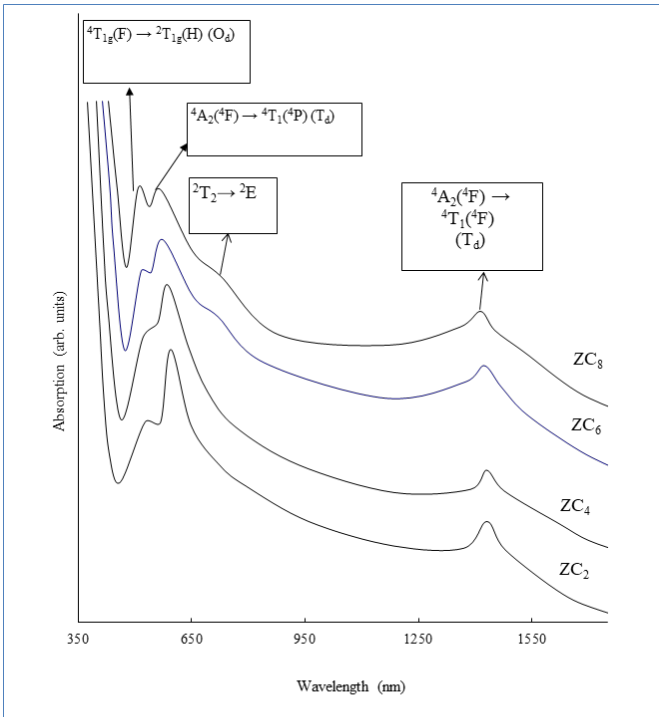

Figure 3: Optical absorption spectra of $ZnO\text{-}Bi_2O_3\text{-}B_2O_3$: CoO glasses recorded at room temperature.

The subsequent two bands were found to decrease at the expense of the first band.

An increasing dopant of CoO has resulted in a decrease in the half-width and the intensity of the bands in the range 590 to 1500 nm, whereas the 550 nm band has risen. These variations confirm the slow conversion of "Co" ions from the triangular pyramid to octahedral regularity. These ions, along with zinc ions, act as modifiers leading to NBOs, causing a blue shift in the bandgap.

Figure 4 depicts the infrared transmittance spectra of $ZnO\text{-}Bi_2O_3\text{-}B_2O_3$: CoO glasses. All the samples have evidenced the characteristic bands corresponding to all possible cross-connections among various structural clusters in the glass system. Pertaining to borate groups, BO_3 units in the range 1382 to 1398 cm^{-1}, BO_4 units in the range 1072 to 1087 cm^{-1}, and B-O-B bending vibrations & B-O-Bi in the range 731 to 739 cm^{-1} are observed.[10] Two tiny bands in the regions 549 to 561 cm^{-1} and 640 to 659 cm^{-1} are observed and attributed to Co-O linkages. The intensity of BO_3, B-O-B / B-O-Bi linkages, and Co-O bands is found to increase while the BO_4 band is found to decrease. The information on vibrational bands is

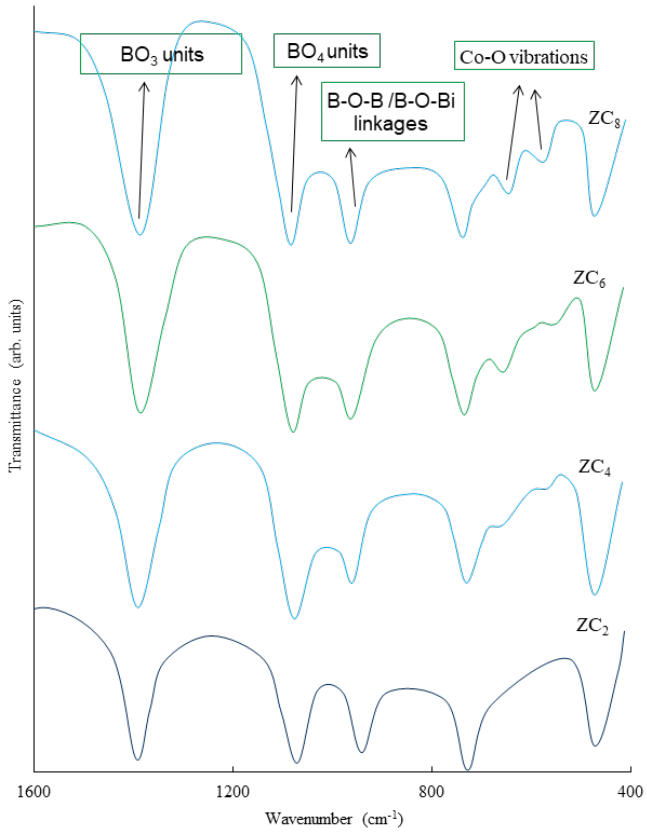

Figure 4: IR spectra of $ZnO\text{-}Bi_2O_3\text{-}B_2O_3$: CoO glass samples.

summarized in Table 2. When the content of CoO is low, i.e., 0.2 mol% (Sample ZC_2), no bands corresponding to Co^{III}-O bands are seen. Another band is located in the range 470 to 480 cm^{-1} that could be due to impurities or zinc oxide-related vibrational bands.

Conclusion

Preparation of $ZnO\text{-}Bi_2O_3\text{-}B_2O_3$: CoO glasses were done using the melt quenching method. The XRD studies show the broad halo, which is a characteristic non-crystalline nature. The scanning electron microscopic images indicated irregular shaping of samples. The IR studies have evidenced the presence of different borate, cobalt and bismuth linkages. From the analyses of IR results, it is very clear that the symmetrical structural vibrational groups diminished with the increasing dopant of CoO. The optical absorption spectra confirm conversational occupational symmetry and the

presence of cobalt ions' oxidation states. All the studies were directed to the fact of cobalt ions changing from tetrahedral to octahedral surroundings that might be the reason for more structural degree of disorder.

References

[1] Abhiram. J., Rajaramakrishna. R.,Rajashekara. KM, Jagannath. G., Vinayak. P., Venugopal RaoS., EraiahB., JagadeeshaA.V., Jakrapong, K., and Suchart, K.2020, Investigation on non-linear optical properties of gold nanoparticles doped fluoroborate Glasses for optical limiting applications,J. Non-Crys. Solid., 538, 120010.

[2] Johnson. B.,Chand. N. R. K., Sudhakar. B. K., and Srinivasa Rao. G., 2016, Chemical durability, thermal stability and spectroscopic studies of the influence of Ni^{2+} ions in oxyfluorophoshate glasses, J. Mat. Sc.: Mat. Ele., 27, pp 8833-8847.

[3] Abdelghany. A.M., El- Damrawi.G., Oraby. AH, andMadshal. MA, 2018, Optical and FTIR Structural Studies on CoO-Doped Strontium Phosphate Glasses, *J. Non-Crys.Solid.*, 499,pp153-158.

[4] Vinaya Teja. P.M., Rajyasree. Ch., Srinivasa Rao. P., Ramesh Babu. A., Tirupataiah. Ch., And Krishna Rao. D, 2012, Structural and electrical properties of ZnF_2-Bi_2O_3-GeO_2 glasses doped with CoO, J. Mol. Str., 1014, pp 119-125.

[5] Arti Yadav, Dahiya. MS, Hooda. A., Agarwal. A. and Khasa., 2018, Nano-Crystalline phase evolution and structural modification in Co/V substituted Li_2O-Bi_2O_3-B_2O_3 glasses, AIP Conf. Proc., 1953,090008.

[6] Satyanarayana. T., Gandhi. Y., Valente, A., Kityk. IV and Veeraiah. N., 2011, Influence of titanium ions on spectroscopic properties of TeO_2-Sb_2O_3-B_2O_3: TeO_2 glass ceramics, Phys. Status Solidi C-John Wiley & Sons, 11-12, pp 3082-3086.

[7] Satyanarayana. T., Valente, M.A., Nagarjuna. G., and Veeraiah. N., 2013, Spectroscopic Features of manganese doped tellurite borate glass ceramics, J. Phys. Chem. Solids, 74, pp 229-235.

[8] Sallum. O.I., Abdel Galil. A., Moussa. NL, 2021, Optimizing of optical and structure Characters of borate glasses by different concentration of CoO: Electron beam irradiation dosimetry, Mater, Chem. Phys., 269, 124767.

[9] Satyanarayana. T., Kityk. I.V., Piasecki. M., Brik. M. G., Gandhi. Y., and Veeraiah. N. 2009, Structural investigations on PbO-Sb_2O_3-B_2O_3: CoO glass-ceramics by means of spectroscopic and dielectric studies. J. Phy. Cond. Mat. (IOP-London), 21, 245104.

[10] Ravi Kumar. G., Srikumar. T., Rao. M. C., Venkat Reddy. P., and Srinivasa Rao. Ch., 2018, Influence of cobalt ions on spectroscopic and dielectric properties of Sb_2O_3 doped lithium fluoroboro phosphate glasses, Mater. Res. Exp., 5, 035203.