IOSR Journal Of Applied Physics (IOSR-JAP)
e-ISSN: 2278-4861.Volume 15, Issue 5 Ser. I (Sept. – October. 2023), PP 29-34
www.Iosrjournals.Org

Effect Of Al_2O_3 On The Optical And Physical Characteristics Of Cdo-Zno-B_2O_3 Glasses

B.Sreenivas[1], P. Hima Bindu[1*]
[1]*Department of Physics, University College of Science, Osmania University, Hyderabad-500007, Telangana, India*

Abstract
A Glass composition of quaternary oxide constituents of different Al_2O_3 content with a composition (80-x)B_2O_3-xAl_2O_3-10CdO-10ZnO*; (x=0 to 20 mol % with a step of 5 mol %) was fabricated by conventional melt quenching method. The primary structural disorderness confirmed by X-ray diffraction analysis. The non-crystalline nature of the produced glasses were verified as the absence of crystalline peaks in X-ray diffraction spectra. The density of the glass system decreased from* 4.410 g.cm^{-3} to 3.138 g.cm^{-3}*with the increase of Al_2O_3content. Optical absorption spectroscopic studies were carried out on the glass system. The Cut-off wave length (λ_c) varied between 378 nm-500 nm whereas, the optical band gaps (E_{opt}) decreased with the addition of Al_2O_3 in the glass network. The role of NBOs on the physical and optical properties was also discussed.*
Keywords: *Density, X-ray diffraction study, optical properties*

Date of Submission: 06-09-2023 Date of Acceptance: 16-09-2023

I. Introduction

B_2O_3 based glasses are of scientific and technical interest due to their low melting point, chemical durability, low cation size, thermal stability and high transparency. B_2O_3 is an excellent glass former among various inorganic oxides and it convert its units from BO_3 to BO_4 very easily when network modifiers like Al_2O_3 etc. were added to the borate host matrix. B_2O_3 based glass matrix undergoes the structural changes when alkali oxides like Al_2O_3 and Ag_2O are added which leads to the creation of non-bridging oxygens (NBOs)[**1-3**]. The crystals and glassy materials containing borates, the boron atom is generally co-ordinated with either three or four oxygen atoms, that forms [BO_3] pyramidal or [BO_4] tetrahedral structural units which are fundamental.

These [BO_3] and [BO_4] units can randomly form either the supposed superstructure or B_xO_y structural groups like diborate, tetraborate, pentaborate, boroxal-ring. Glasses incorporated with ZnO and CdO are of particular attention various areas of optical and electronics based materials [**4-6**]. Addition of Al_2O_3 to a glass matrix causes excess negative charge and also influences the symmetry of glass network. Al_2O_3 containing borate glasses widely used for battery applications due to their higher order ionic conductivity [**7-8**]. Borate glasses have gained significant attention in recent years due to their unique optical and magneto-optical(MO) properties[**9-10**]. In general, these glasses show high transparency of (UV) to the mid-infrared (MIR)spectral region, making them promising for optical applications such as fiber optics, amplifiers, and lasers[**11–12**].The other advantage of borate glasses is their good glass-forming ability[**13**] and relatively easy preparation at mild temperatures[**14]**.

The density (ρ) can play a significant role on the structural variations due to the addition of alkali, alkaline earth oxides into the borate glass network. It also explores the tightness of the glass structure. It closely associated with the co-ordination number of the atoms and dimensions of the glass network. Density related physical properties such as molar volume (V_m), molecular weight (M), Oxygen packing density (OPD) etc. have been calculated and studied here. Optical absorption spectroscopy used to study the excited states of molecules or atoms. The present paper deals with the influence of Al_2O_3on the physical and optical properties of CdO-ZnO containing borate glass system. The role of non-bridging oxygens on the density related parameters and optical parameters have been discussed in the paper.

II. Material And Methods

Preparation of glasses

Al_2O_3 added glasses with a chemical composition (80-x)B_2O_3-xAl_2O_3-10CdO-10ZnO (BACZ), where x values lies from 0 to 20 mol% with 5 variation were synthesized by rapid melt-quench route. AR grade B_2O_3, CdO(Sigma), ZnO (AR grade) and Al_2O_3 were taken for preparation of the glass samples. About 15 grams of oxides powder are taken in a crucible made of porcelain, and melted at 1250^{o}C for 1hr. The powder melted and

formed liquid. The liquid in the crucible was agitated/swirled frequently for 1 hr to form a homogeneous liquid melt. The crucible with melt was emptied on a steel plate which is at 250ºC and hard-pressed using another steel disc which is also at same temperature which resulted in the formation of glasses. The prepared glassy samples were annealed at around 200ºC for 24 hrs for removal of thermal stress and strain and also to avoid cracking of glass samples. The glass samples thus obtained were good transparency. The glass formation was confirmed with the transparency and uniformity.

Characterisation of glasses

Using Archimedes' principle density measurements was carried out on Vibra-HT analytical balance in which xylene used as immersion liquid with random error ±0.002. UV-Vis-NIR spectra were recorded on Spectrophotometer (Shimadzu) in the range 200nm-1000nm with spectral resolution 2nm for all the synthesized glasses and uncertainty is almost ±0.5 nm. X-ray diffraction spectra of the glasses recorded on a PAN analytical X-pert PRO model diffractometer in the Bragg's angle range 10^0-80^0.

III. Results and Discussion

X-Ray Diffraction

The X-ray diffraction (XRD) analysis was performed on a specific set of glasses with varying compositions of (80-x)B_2O_3-xAl_2O_3-10CdO-10ZnO. The x values fixed for the samples were 0, 5, 10, 15 and 20 mol %. The results of the analysis are presented in **Figure 1**, which shows the XRD patterns of all the glasses. The absence of sharp Bragg's peaks in the XRD patterns indicates that the glasses are amorphous in nature. This is because the XRD technique is primarily used to identify crystalline structures, and the absence of any sharp peaks in the pattern suggests that there is no long-range order in the atomic arrangement of the glass. Therefore, the glasses prepared in this study do not exhibit any crystalline behavior and are confirmed to be amorphous.

Density, Molar volume and Oxygen Packing Density(OPD)

The density of the prepared glasses in the present study was measured using Archimedes principle. **Figure.2** illustrates how the density of BACZ glasses varies when B_2O_3 is replaced with modifier concentrations of Al_2O_3. In (80-x)B_2O_3-xAl_2O_3-10CdO-10ZnO glasses, the density decreased with increasing Al_2O_3 content. The density varies from 4.410 g.cm^{-3} to 3.138 g.cm^{-3}. This decrease in density with the addition of Al_2O_3 can be attributed to several factors: Firstly, Al_2O_3 has a lower atomic weight compared to B_2O_3, CdO, and ZnO. Therefore, the substitution of B_2O_3 with Al_2O_3 leads to a decrease in the average atomic weight of the glass, resulting in a lower density. Secondly, Al_2O_3 has a larger atomic radius compared to B_2O_3, CdO, and ZnO [**24,25**]. This substitution leads to an increase in the average bond length between atoms, which reduces the packing density of the glass and contributes to the overall decrease in density. Finally, the incorporation of Al_2O_3 into the glass network may also lead to the formation of voids or structural defects in the glass, which can further contribute to the decrease in density [**26,27]**. Overall, the decrease in density with increasing Al_2O_3 content in (80-x)B_2O_3-xAl_2O_3-10CdO-10ZnO glasses can be attributed to a combination of these factors. Nassar et al. [**28**] explored the impact of Aluminium ions on B_2O_3-Al_2O_3 glasses. They observed that substituting B_2O_3 with Al_2O_3 resulted in a reduction in glass density, as the concentration of BO_4 groups decreased and boroxol groups have formed. The introduction of aluminium ions into the B_2O_3glasses caused a shift in the structural units from BO_4 to BO_3, ultimately leading to a decrease in density. In the case of Al_2O_3 series glasses, the experimental density decreases with the addition of modifiers while the molar volume increases. These glasses follow the general trend of molar volume with density. However, in the case of BACZ glasses, density decreased and molar volume increased with an increase in Al_2O_3 content.

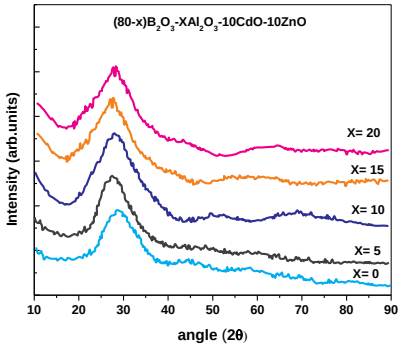

Figure 1: XRD patterns of BACZ glass samples.

Table 1: Density , Molar volume and oxygen Packing density (OPD) of present glasses

Glass Compostion	X	Molar weight	Density ($g.cm^{-3}$)	Molar volume (m^3/mol)	OPD (g-atom/1)
80 B_2O_3-10CdO-10ZnO	0	76.67	4.410	17.39	149.55
75 B_2O_3- 5 Al_2O_3- 10 CdO-10 ZnO	5	78.291	3.395	23.06	112.76
70 B_2O_3- 10 Al_2O_3-10 CdO-10 ZnO	10	79.908	3.349	23.86	108.96
65 B_2O_3- 15 Al_2O_3-10 CdO-10 ZnO	15	81.525	3.231	25.23	103.04
60 B_2O_3- 20 Al_2O_3-10 CdO-10 ZnO	20	83.142	3.138	26.49	98.13

It is also possible to find Al_2O_3-B_2O_3-CdO glass compositions where both the density and molar volume decrease with increasing Al_2O_3 content. The change in glass structure with increasing Al_2O_3 content can again cause this behavior. Jiao Han et al [**29**] investigated physical properties of the calcium boro silica glasses a function of Al_2O_3 content and observed that both glass density and molar volume decreases due to structural changes in the glasses. Ahmed et al., [**30**] reported physical properties of Al_2O_3-B_2O_3-CdO glasses. In that, as the Al_2O_3 content increases, the glass structure shifts from a network of B-O and Cd-O polyhedra to a network of Al-O polyhedra, resulting in a decrease in both density and molar volume. Singla et al., [**31**] investigated the effect of Al_2O_3 content on the properties of Aluminium borate glasses. They found that as the Al_2O_3 content increased from 0 to 50 mol%, the density of the glass decreased from 4.30 g/cm^3 to 4.02 g/cm^3.In the present glasses, if the concentration of network modifiers increases, the oxygen packing density of oxygen atoms in the glass network may decrease due to changes in the local atomic arrangement and the bonding between atoms. This may lead to an increase in the molar volume of the glass, as more free volume becomes available. All the physical parameters were shown in **Table.1**.

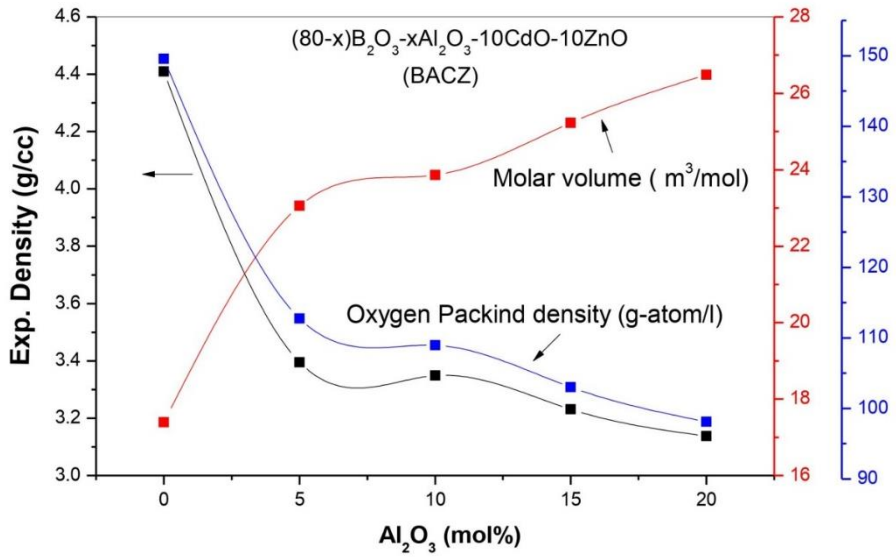

Figure 2: Density and molar volume of BACZ glasses

Optical Studies

Cut off wavelength

The cutoff wavelength is an important parameter in the optical properties of glasses as it provides information about the transparency range of the material. The cutoff wavelength is crucial in the design and selection of optical components. By understanding the cutoff wavelength, one can choose glasses that are suitable for specific applications. For instance, in ultraviolet (UV) applications, glasses with a low cutoff wavelength are preferred, while in infrared (IR) applications, glasses with a high cutoff wavelength are desired. The cutoff wavelength can be determined by identifying the point at which the absorption decreases significantly by drawing tangents in the absorption spectra.

The following equation was used to get the optical absorption co-efficient (ν) at the fundamental absorption edge.

$$\alpha(\nu) = \left(\frac{1}{d}\right) log\ log\ \left(\frac{I_o}{I_t}\right) \qquad (1)$$

Here, incident and transmitted beam strengths are denoted by I_0 and I_t, respectively. d represents the glass sample's thickness in this case. Log (I_0/I_t) is an element that matches absorbance.

In the glass composition (80-x) B_2O_3-xAl_2O_3-10CdO-10ZnO, the increase in cutoff wavelength from 408.66 nm to 500.02 nm when the Al_2O_3 content increases can be attributed to several factors, including changes in the electronic structure, optical properties, and the refractive index of the glass [**33**].The addition of Al_2O_3 to the glass composition introduces different elements and their electronic structures. The energy levels and electronic transitions of Al_2O_3 may contribute to the absorption properties of the glass at different wavelengths. As the Al_2O_3 content increases, there could be a shift in the energy levels or electronic transitions, resulting in a change in the cut-off wavelength [**34**].

Figure.3 depicts the optical spectra. By plotting $(\alpha h\nu)^n$ as a function of hν, where B is a constant related to the extent of the band tailing and h*ν* is the incident photon energy, one can determine the optical energy band gap E_g for all electronic transitions. The value of n, determines the type of transition [**35**]. Generally in glasses the type of transition is indirect allowed (n=1/2). The optical band gap energy E_g is obtained by extrapolating the absorption coefficient to zero in the $(\alpha h\nu)^n$ versus h*ν* plots for n=1/2. **Figure.4** depicts Tauc plots showcasing the band gap energies of glasses comprising (80-x)B_2O_3-xAl_2O_3-10CdO-10ZnO.

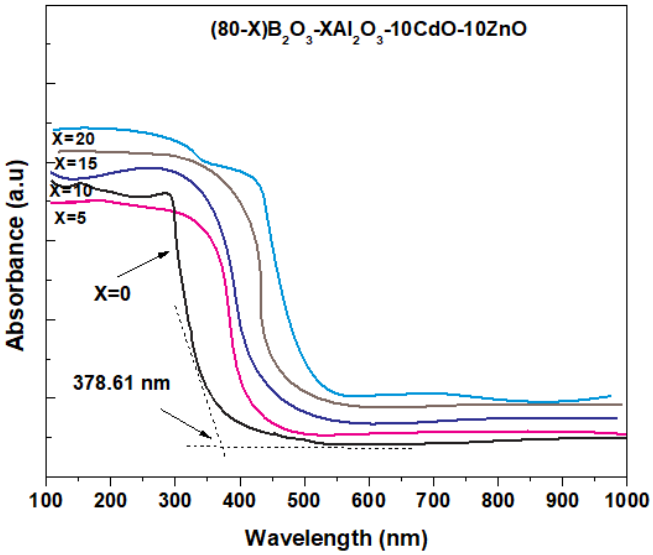

Figure 3: Optical Absorption spectra of BACZ glasses

Optical Energy band gap

The optical band gap of present glasses are calculated from the Urbach plots using following relation,

$$(\alpha h\nu)^n = B(h\nu - E_g) \qquad (2)$$

The extracted values are obtained from **Table.2**, indicating that the band gap energies exhibit decreasing trend as the Al_2O_3 content in the glasses is raised. The addition of Al_2O_3 may introduce new NBOs or modify the existing ones in the glass structure. These changes can affect the electronic structure, leading to a decrease in the band gap energy[**32]**. If the Al_2O_3 NBOs have energy levels closer to the valence or conduction bands, they can facilitate electron transitions, resulting in a smaller band gap. The interaction between Al_2O_3 and other constituents in the glass can result in NBO hybridization. This can modify the energy levels and bonding characteristics, influencing the band gap energy. Hybridization between Al_2O_3 NBOs and those of other elements in the glass can lead to a decrease in the band gap. Sing et al.[**33**] conducted a study on the optical properties of Al_2O_3-PbO-B_2O_3 glasses. Their findings revealed a decrease in energy band gaps as the Al_2O_3 content increased, ranging from 3.28 eV to 2.78 eV. Furthermore, the introduction of zinc content resulted in an increased availability of oxygen ions within the glass network, leading to a transformation from trigonal [BO_3] to tetrahedral [BO_4] configurations. Consequently, this alteration caused a contraction in the glass network, ultimately shifting the absorption edge to lower energy levels [**36**]. In a separate investigation, Lin et al.[**37**] examined the optical properties of Aluminium borate glasses. They observed a similar trend of decreasing optical energy band gaps with increasing Al_2O_3 content. This phenomenon was attributed to structural changes occurring within the glass network, specifically the conversion of [BO_3] units to BO_4] units.

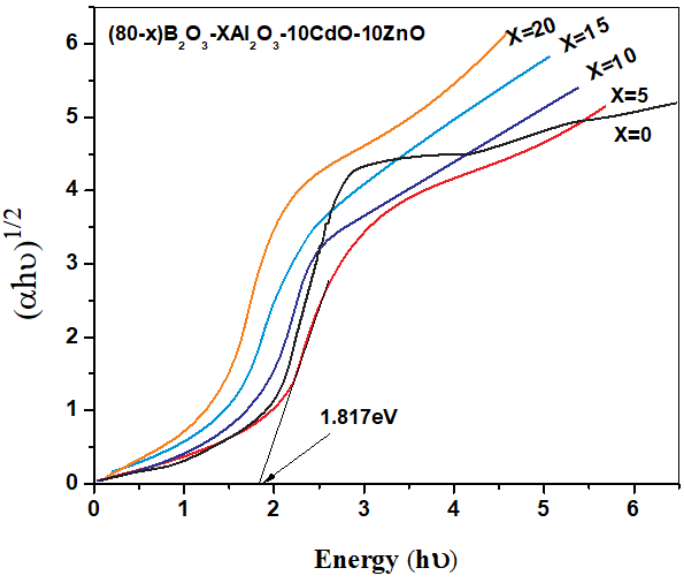

Figure 4: Tauc plots of (80-x)B_2O_3-xAl_2O_3-10CdO-10ZnO (BACZ) glasses

Urbach energy

The Urbach energy ΔE was used to calculate the creation of defect concentration in the glass structure. The well-known Urbach law [**38**] describes the relationship between α(ν) and ΔE

$$\alpha(\nu) = B \exp\left(\frac{h\upsilon}{\Delta E}\right)$$

B is a constant, while E expressed as Urbach energy.

All glass samples demonstrated Urbach plots depicting ln(α) versus hυ. The inverse slope of the linear segments within the Urbach plots was calculated to determine the Urbach energy (E). The Urbach energy serves as a measure of disorder in non-crystalline materials, where lower values indicate a less glassy nature. To obtain the Urbach energy values, Urbach ΔE plots were constructed by plotting ln(A) versus hν. **Figure 5** illustrates the Urbach energy of BACZ glasses. The graph shows that as the Al_2O_3 content increased, the Urbach energy decreased. The energy range recorded in this study ranges from 2.715 eV to 2.435 eV. The addition of Al_2O_3 promotes the creation of strong covalent bonds within the glass matrix, increasing the overall structural integrity. This enhanced structural order reduces the presence of localized states or defects resulting in a decrease in Urbach energy. Moreover, Al_2O_3 has a smaller ionic radius compared to B_2O_3, CdO, and ZnO. This difference in ionic radii can induce stress or strain in the glass structure when Al_2O_3 is incorporated. The presence of stress or strain can further limit the formation of defects or localized states, leading to a decrease in Urbach energy. The calculated energy values are presented in **Table.2.**

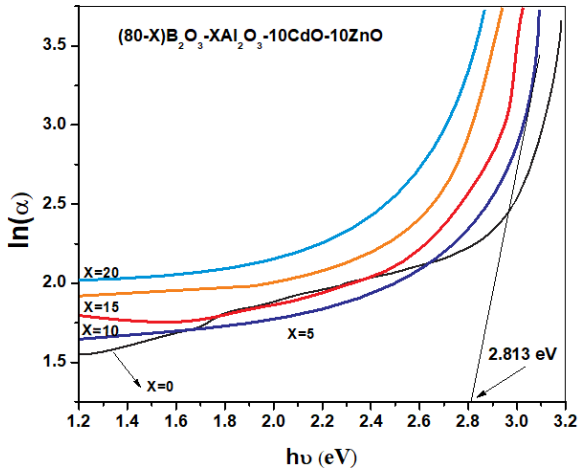

Figure 5: Urbach energy of (80-x)B_2O_3-xAl_2O_3-10CdO-10ZnO glasses.

Table 2: Optical Parameters of BACZ glasses

X	Cut off Wavelength (nm)	Energy band gap (eV)	Urbach Energy (eV)
0	378.61	2.145	0.368324
5	408.66	1.817	0.355492
10	419.45	1.611	0.36049
15	441.04	1.338	0.389105
20	500.02	1.157	0.410678

IV. Conclusion

The glass composition was successfully prepared by melt quench route. XRD results confirmed the amorphous nature of the glasses. The density was decreased with additive Al_2O_3.The UV-Vis.spectra confirmed the creation of NBOs as its shift towards higher wavelength. The indirect band gap values decreased with increasing Al_2O_3 content. The NBOs are responsible for changes occurred in the optical properties. The Refractive index increased with additive Al_2O_3. The increment of Urbach values confirms more randomness in the glass by adding Al_2O_3 due to NBOs.

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