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The role of NBOs on Optical and Physical properties of Na_2O added Sb_2O_3-ZnO-B_2O_3 glasses

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Abstract
Glass series of quaternary inorganic constituents of different Na_2O content with a composition $xNa_2O.10Sb_2O_3.20ZnO(70-x)\ B_2O_3$; where x=0, 5,10,15 and 20 mol% was prepared by conventional melt quenching method and investigated by X-ray diffraction, UV Absorption spectra. Absence of sharp peaks in XRD spectra confirms the amorphous nature of the system. The physical parameters such as density and molar volume have been investigated. Optical absorption spectroscopic studies revealed that, the cut-off wave length increased from 301 nm-352 nm and optical band gap decreased from 4.05 to 3.75eV by the addition of Na_2O in the glass network. The density of the glass system increased from 3.42 g/cm^3 to 3.72 g/cm^3 with the increase of Na_2O content. The Urbach energy (ΔE) increased from 0.35 to 0.78eV and the refractive index increased from 2.15 to 2.29. The role of NBOs on the physical and optical properties has been discussed.
Keywords: *Molar volume, X-ray diffraction, Optical properties, Refractive index, Non-Bridging Oxygens (NBO).*

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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. It converts its units from BO_3 to BO_4 easily when network modifiers like Li_2O, Na_2O etc, were added to the borate host matrix. It undergoes the structural changes when alkali oxides like Li_2O and Na_2O are added, which leads to the creation of non-bridging oxygens (NBOs)[**1-3**]. In borate glasses, boron is 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 structural groups like diborate, tetraborate, pentaborate, boroxal-ring. Glasses incorporated with ZnO and Sb_2O_3 are of particular attention in various areas of optical and electronic-based materials [**4-6**]. Addition of Li_2O to a glass matrix causes excess negative charge and also influences the symmetry of glass network. Lithium borate glass materials are technologically sound, widely used for solid electrolytes due to their fast-ionic conduction and used in optical lenses for their practical applications [**7-8**]. The density (ρ) plays 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.
Optical absorption spectroscopy is used to study the excited states of molecules or atoms.
The present paper deals with the influence of Na_2O on the physical and optical properties of antimony zinc borate glass system. The role of non-bridging oxygens on the density related parameters and optical parameters have been discussed in this paper.

II. Material and Methods

Preparation of glasses

The chemical composition of glass system is xNa_2O-$10Sb_2O_3$-20ZnO-(70-x) B_2O_3($0 \leq x \leq 20$) are synthesized by rapid melt-quench route. AR grade of B_2O_3, Sb_2O_3, Na_2O and ZnO from Sigma Aldrich were procured for the preparation of glass samples. The calculated amount of starting materials is taken in a crucible made of porcelain and melted at 1050^{o}C for 1hr. The obtained liquid in the crucible was swirled thoroughly for 1 hr to form a homogeneous molten liquid. It is poured on a steel plate which is at 200^{o}C and hard-pressed using another steel disc which is also at 200^{o}C. The prepared glass system is annealed at around 200^{o}C for 12 hrs to avoid thermal strains and cracks of glass samples. The obtained glass is observed with the transparency and uniformity. The synthesized glass samples are ground and optically polished to the required dimensions for further studies.

The synthesized glass compositions are labelled as
$70B_2O_3$-20ZnO-10 Sb_2O_3 is BZSNa-1
$65B_2O_3$-20ZnO-10 Sb_2O_3-$5Na_2O$ is BZSNa-2
$60B_2O_3$-20ZnO-10 Sb_2O_3-$10Na_2O$ is BZSNa-3
$55B_2O_3$-20ZnO-10 Sb_2O_3-$15Na_2O$ is BZSNa-4
$50B_2O_3$-20ZnO-10 Sb_2O_3-$20Na_2O$ is BZSNa-5.

2.2 Characterisation of glasses

Using Archimedes' principle, density measurements are carried out on Vibra-HT analytical balance in which xylene is used as an immersion liquid. UV-Visible-NIR spectra are recorded on Spectrophotometer (Shimadzu) in the range 200nm-800nm with spectral resolution of 2nm for all the synthesized glasses. X-ray diffraction spectra was recorded on Philips Xpert-Pro spectrometer with an angle range between 10^0 and 80^0.

III. Results and Discussion

X-ray diffraction studies (XRD)

The X-ray diffraction patterns of BZSNa-1 to BZSNa-5 glass system are shown in Fig. 1. Absence of sharp peaks in all the synthesized glass system indicates that they are amorphous in nature.

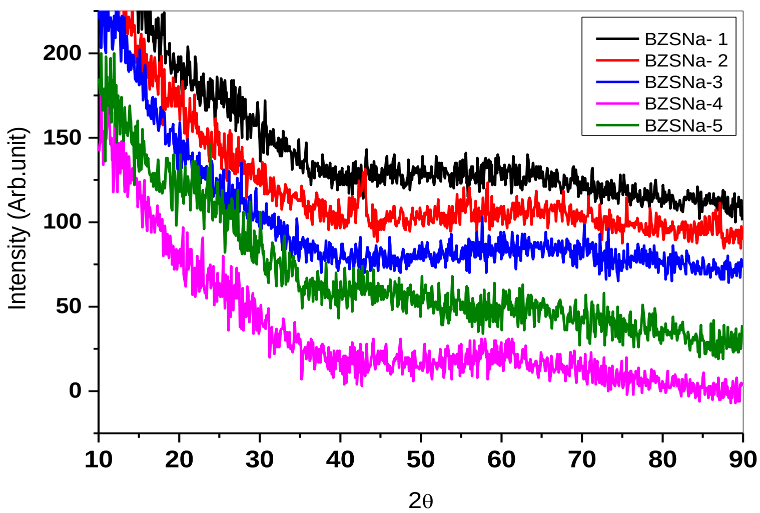

Fig 1. XRD spectrograms of BZSNa glass system

Physical Properties:

The Density of synthesized glasses was found to increase from 3.42 to 3.72 g/cm^3 and molar volume decreased from 41.77 to 34.25 cm^3/mol with the increasing modifier Na_2O content. It is evident that the increase in density with addition of Na_2O is due to the higher molecular weights of the network constituents ZnO and Sb_2O_3. Density and molar volume are inversely proportional to each other. The graph is plotted between the variation of measured density and molar volume with increasing Na_2O as shown in Fig. 2.

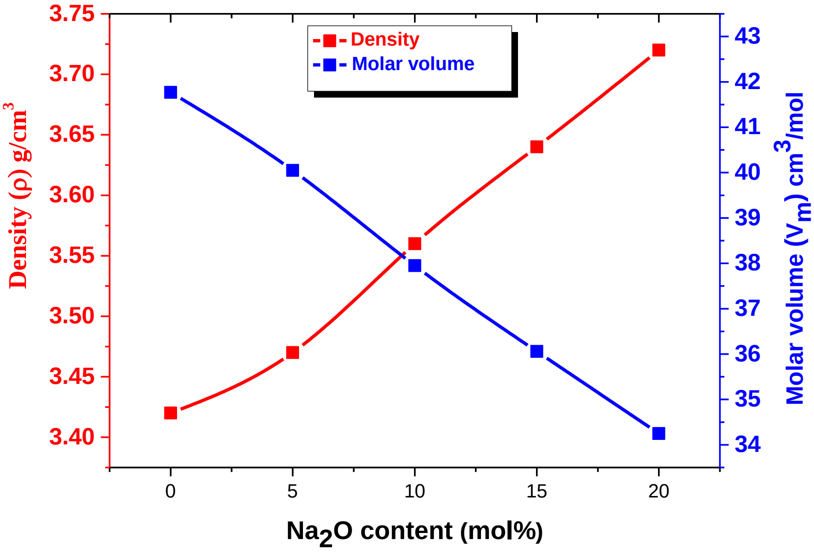

Fig .2 Variation of density (ρ) and molar volume (V_m) with Na_2O.

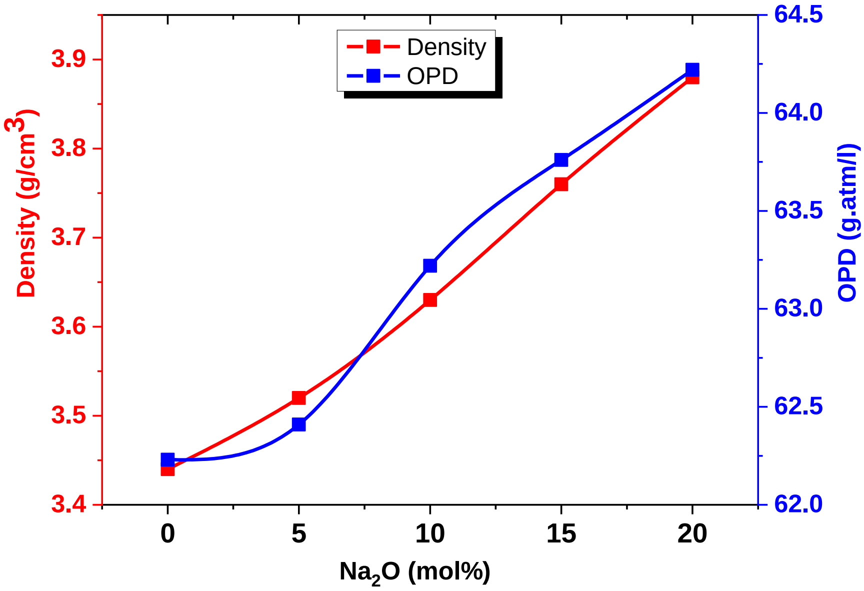

Fig 3. Variation of density and oxygen packing density with Na_2O%.

The molar volume (Vm), is a function of molecular weight and density of the studied glasses. Molar volume of the glasses decreased with the increase in Na_2O mole percentage. It is due to the breaking of continuous boron group networks when Na_2O enters into glass network [**9-10**]. Oxygen packing density (OPD) of the glass samples is increased due to increase in oxygen atoms in glass network. Molar volume and OPD increases with Na_2O mole percentage as shown in **Fig. 3.** All the physical parameters of present glass system are tabulated in **Table 1.**

Table.1 Physical and optical parameters of BZSNa series

Properties	BZSNa-1	BZSNa-2	BZSNa-3	BZSNa-4	BZSNa-5
Density (g/cm^3)	3.42	3.47	3.56	3.64	3.72
Molecular weight (g/mol)	142.87	139	135.1	131.28	127.42
Molar volume (cm^3/mol)	41.77	40.05	37.95	36.06	34.25
OPD (g atm/1.)	62.23	62.41	63.22	63.76	64.22
Cut off wavelength (nm)	301	309	323	339	352

Indirect band gap(eV)	4.05	3.96	3.92	3.81	3.75
Direct band gap(eV)	4.16	3.99	3.95	3.87	3.79
Urbach energy(eV)	0.40	0.45	0.53	0.58	0.69
Molar refraction(cm^3/mol)	22.89	22.27	21.18	20.16	19.45
Refractive index	2.15	2.18	2.19	2.197	2.29
Electronic polarizability ($\times10^{-24}$ cm^3)	9.09	8.89	8.38	7.98	7.7

Optical Absorption Spectra

The Optical spectra of the prepared glass system is shown in figure 4. The sharp absorption edge shifted to higher values of wavelengths with Na_2O mole percentage. The cut-off wavelengths lie in between 301 nm to 352 nm. The non-bonding oxygen atoms increases as a function of modifier addition, which leads to more randomness in the glass system [**11-12**]. The values of indirect band gap of BZSNa glass-system calculated from the **Fig 5** and it was observed that these values decreased from 4.05eV to 3.75 eV with Na_2O content due to increase in non-bridging oxygens [**13-14**]. The Optical band gap energy is maximum (4.05eV) for the pure sample.

The value of refractive index determines the suitability of the material for opto-electronic device applications. The pure sample has the minimum value and increased with the addition of modifier. The increase in refractive index may be due to the appearance of NBOs in the network. Electronic polarizability decreased from 9.06 to 7.7 in the order of 10^{-24} cm^3 non-linearly.

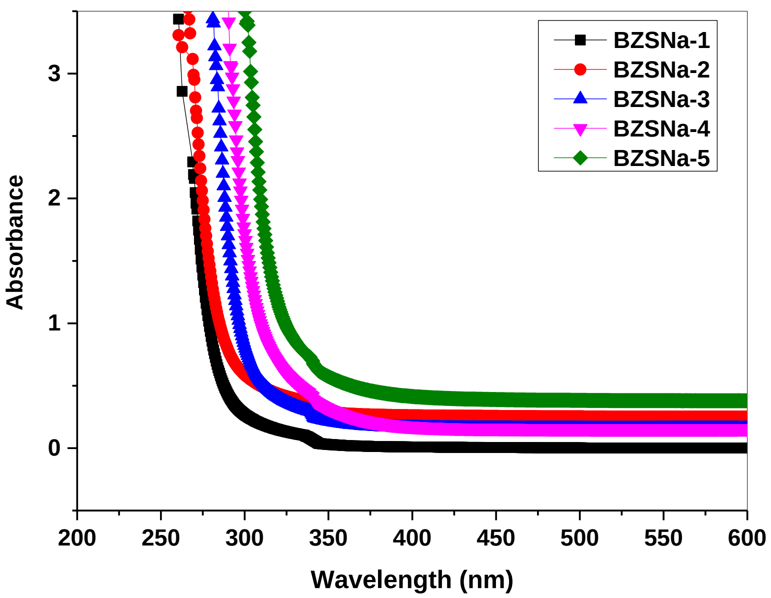

Fig. 4 Optical Absorption Spectra of BZSNa series

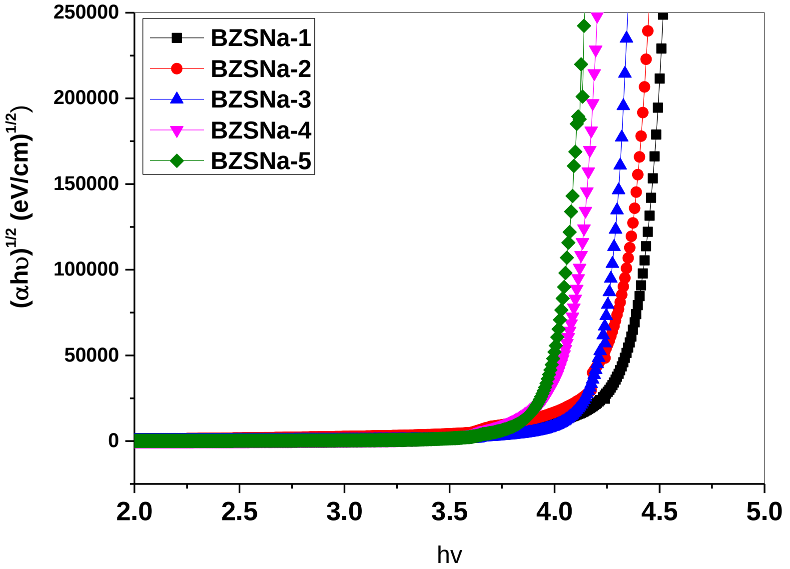

Fig. 5 Tauc plots for indirect band gap of BZSNa series

The direct band gap of the present glass system is calculated from the **Fig. 6**. It was found that direct optical band gap of pure sample is 4.16eV. By the addition of Na_2O, it is decreased to 3.79eV. Refractive index of these glasses increased from 2.15 to 2.29 with addition of Na_2O.

Urbach Energy

Natural logarithm of absorption coefficient is the parameter which explains the randomness of glassy network. According to Urbach's rule, optical absorption coefficient near the absorption edge is an exponential function of photon energy [15]. The range of Urbach plots of BZSNa series monotonically enhanced with the addition of modifier content Na_2O as shown in **Fig.7**. The values of ΔE evaluated from the reciprocal slope of the plots between absorbance and photon energy. The values of cut-off based and other parameters of the BZSNa series are given in the **Table 1.** The ΔE is the minimum for pure sample and it is raised with the addition of network modifying oxides which causes the creation of more disorderness in the form of NBOs. The range of ΔE values of BZSNa series lies between 0.40 and 0.69 with the increase of Na_2O mole percentage. The number of NBOs are responsible for increasing the randomness of the glass network [16-**18**]. The decrease in E_{opt} values shows more tails in the localized states and as a result Urbach energy has been increased.

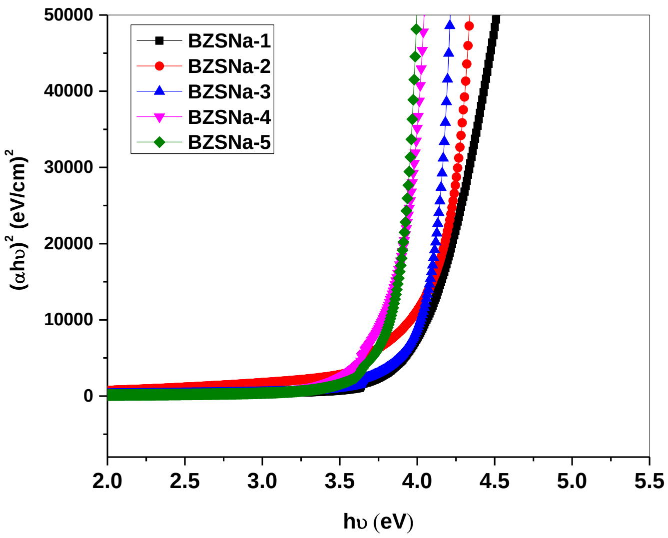

Fig. 6 Tauc plots for direct band gap of BZSNa series

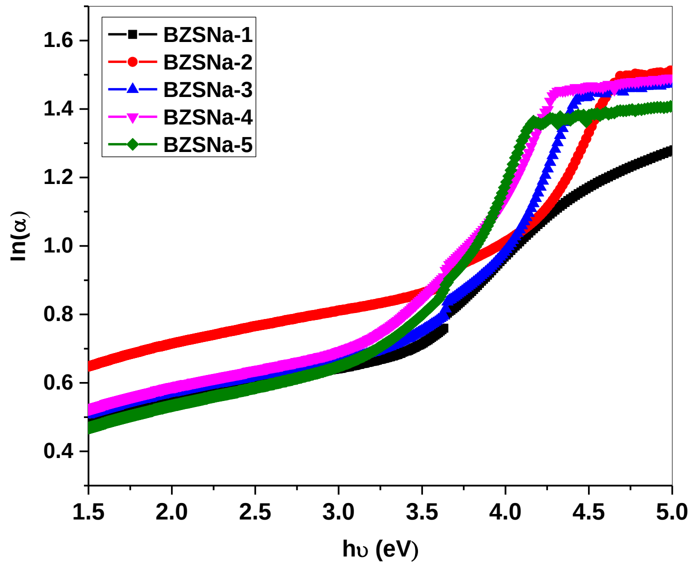

Fig. 7 Urbach plots of BZSNa glass series

IV. Conclusion

The selected glass composition is prepared by melt quench route. XRD results confirmed the amorphous nature of the glass system. Optical and Physical properties of studied glass sample depend on glass composition. Increase in density and decrease in molar volume are due to increase in NBOs with Na_2O mole percentage. The UV-Visible spectra confirmed the creation of NBOs as cut off wavelength shifts towards higher values. The indirect band gap values decreased with increasing Na_2O content. With the addition of Na_2O, number of NBOs increases in glass network, which in turn cause increase in refractive index values. The increase in Urbach energy is owing to the more randomness in glass structure with the addition of Na_2O.

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