Compositional dependence of optical band gap and refractive index in lead and bismuth borate glasses

Saisudha B. Mallur, Tyler Czarnecki, Ashish Adhikari and Panakkattu K. Babu
Department of Physics, Western Illinois University, Macomb, Illinois-61455, USA

Abstract

We prepared a series of lead and bismuth borate glasses by varying PbO/Bi₂O₃ content and studied refractive index and optical band gap as a function of glass composition. Refractive indices were measured very accurately using a Brewster's angle set up while the optical band gaps were determined by analyzing the optical absorption edge using the Mott-Davis model. Using the Lorentz-Lorentz method and the effective medium theory, we calculated the refractive indices and then compared them with the measured values. Bismuth borate glasses show better agreement between the calculated values of the refractive index and experimental values. We used a differential method based on Mott-Davis model to obtain the type of transition and optical band gap (E_{opt}) which in turn was compared with the value of E_{opt} obtained using the extinction coefficient. Our analysis shows that in both lead and bismuth borate glasses, the optical band gap arises due to direct forbidden transition. With increasing PbO/Bi₂O₃ content, the absorption edge shifts toward longer wavelengths and the optical band gap decreases. This behavior can be explained in terms of changes to the Pb-O/Bi-O chemical bonds with glass composition. We obtained a new empirical relation between the optical band gap and the refractive index which can be used to accurately determine the electronic oxide polarizability in lead and bismuth oxide glasses.

KEYWORDS: A. Glasses, B. Optical properties, D. Dielectric properties

1. Introduction

Lead and bismuth borate glasses represent two interesting glass forming systems which exhibit a considerable range of variation in optical properties as a function of glass composition [1-7]. The influence of $\text{PbO/Bi}_2\text{O}_3$ on the structure of these glasses is unique since they can act as network formers as well as network modifiers [8-11]. The effect is also seen on the glass transition temperature. With the addition of PbO from 30 mol% to 70 mol% the glass transition temperature decreases from 500 °C to 275 °C [12]. In addition, these glasses have large refractive indices, strong absorption in the ultraviolet region, good radiation shielding properties and wide transmission range which make them suitable as host glasses for lasing rare earth ions. The highly polarizable nature of heavy metal cations is responsible for the high linear refractive index of these glasses which also make them promising materials for use in the field of nonlinear optics. Structural groups like boroxol, pentaborates, and diborates containing three and four coordinated borons, and ring- and chain-type metaborate groups containing nonbridging oxygen (NBO), are found to be present in lead and bismuth borate glasses for different $\text{PbO/Bi}_2\text{O}_3$ concentrations which can strongly influence the physical and optical properties [11,13]. Hence studying the optical properties, in particular, the refractive index and optical band gap of lead and bismuth borate glasses and how these properties vary with glass composition is of great interest for practical applications.

In the present work, we investigated the compositional dependence of optical properties of $\text{PbO-B}_2\text{O}_3$ and $\text{Bi}_2\text{O}_3\text{-B}_2\text{O}_3$ for a broad range of glass compositions. We measured density (ρ), refractive index (n) and optical band gap (η) and determined the average electronic oxide polarizability of these glasses. We used Lorentz-Lorenz (LL) method and effective medium

theory (EMT) to calculate the refractive index n and then the experimental values of the refractive index were compared with the calculated values. Refractive indices calculated using EMT and LL methods show better agreement with the experimental results for the case of bismuth borate glasses than for lead borate glasses.

Optical absorption spectra were analyzed using the Mott-Davis model [14] to determine η . In order to determine the type of optical transition, we used the relation between the imaginary part of dielectric constant (ϵ_2) and extinction coefficient (K). Our analysis shows that in both lead and bismuth borate glasses, the absorption edge arise due to indirect forbidden transitions. E_{opt} for both glass systems is found to decrease with increasing PbO/Bi₂O₃ content which is explained in terms of the Pb-O and Bi-O covalency. Finally, for our binary oxide glass systems with different PbO/Bi₂O₃ composition, we obtained an empirical relation between the optical band gap and the refractive index. This empirical relation is capable of accurately reproducing our electronic oxide polarizability calculated from n and E_{opt} .

2. Experimental

We prepared binary lead borate glasses with the composition $x\text{PbO}:(100-x)\text{B}_2\text{O}_3$ with $x = 30\text{-}70$ mol% and binary bismuth borate glasses with the composition $x\text{Bi}_2\text{O}_3:(100-x)\text{B}_2\text{O}_3$ with $x = 30\text{-}60$ mol%. x was varied in steps of 10 mol% giving 5 glass samples for the lead borate system (PbB30-PbB70) and 4 glass samples for the bismuth borate system (BiB30-BiB60), respectively. The raw materials were thoroughly mixed and melted in the range 800 – 1000 °C. The melt was air quenched by pouring it on a thick brass plate and covering it immediately with another brass plate. The glass samples thus obtained were annealed at 400°C for 3hrs to remove thermal strains. Annealed glass samples were polished using a lapping machine (Inland

SwapTop) to obtain well reflecting flat surfaces. The sample density was measured by the Archimedes' method using xylene. The refractive index of the glasses is measured by the Brewster angle method using a PASCO set up (OS-8170) with a diode laser as the source. When unpolarized light of 650 nm wavelength is incident on the surface of the sample at the Brewster angle ($\theta = \tan^{-1} n$, where n is the refractive index of the glass) the reflected light is rendered linearly polarized with the electric vector transverse to the plane of incidence. The reflected light passes through a polarizer and is detected by a light sensor. The angle of reflection is measured by a rotary motion sensor mounted on a spectrophotometer table (OS-8539). The intensity of the reflected polarized light versus reflected angle is graphed and a parabolic fit to this data then provides a very accurate determination of the Brewster's angle, which is used to calculate the refractive index of our glass samples [15]. The accuracy of these measurements is around ± 0.01 . It may be pointed out that the refractive index does not vary significantly with wavelength and, hence, we have measured n at a single wavelength for each sample using a diode laser as the source. Optical absorption spectra of the glasses in the UV-VIS region were recorded at room temperature on polished samples of size $1\text{cm} \times 1\text{cm} \times 1\text{mm}$ using a Varian/Cary 5G spectrometer in the wavelength range 190 – 1000 nm. The resolution of this spectrometer is ± 0.02 nm.

3. Results and Discussion

3.1. Refractive Index

Dimitrov et al. [4] have reported variation of refractive index of $\text{PbO}:\text{B}_2\text{O}_3$ glasses with PbO content varying from 30 mol% to 70 mol% and Honma et al. [16] for $\text{Bi}_2\text{O}_3:\text{B}_2\text{O}_3$ glasses with Bi_2O_3 content varying from 30 to 60 mol% using ellipsometric measurements. Their refractive index values vary from 1.67 to 2.00 for lead borate glasses and 1.84 to 2.10 for bismuth borate

glasses with increasing PbO/Bi₂O₃ content. In our binary lead borate glasses and bismuth borate glasses, the refractive indices measured using the Brewster's angle method shows that n varies from 1.66 to 1.92 for lead borate glasses and from 1.92 to 2.21 for bismuth borate glasses. Table 1 lists the experimental refractive indices measured by Brewster's angle method.

Refractive index in glasses is usually expressed by the Lorentz-Lorenz equation [17]

$$R_m = \left(\frac{n^2 - 1}{n^2 + 2} \right) \frac{M}{\rho} = \left(\frac{n^2 - 1}{n^2 + 2} \right) V_m \quad (1)$$

where R_m is the molar refraction, M is the molar mass, ρ is the density, V_m is the molar volume, and n is the refractive index. The molar refraction can be expressed as a function of polarizability (α_m) of a molecule as [17, 18]:

$$R_m = \frac{4\pi\alpha_m N_A}{3} \quad (2)$$

$$R_m = 2.52\alpha_m \quad (3)$$

where N_A is the Avogadro's number and α_m is expressed in Å³. In the first approximation, α_m and R_m can be considered as additive quantities. For an oxide system with chemical formula A_pO_q it can be expressed by the relation [6]:

$$R_m = pR_i + qR_{O^{2-}} = 2.52(p\alpha_i + q\alpha_{O^{2-}}) \quad (4)$$

where R_i and $R_{O^{2-}}$ are the ionic refraction and α_i and $\alpha_{O^{2-}}$ are the polarizabilities of the cation and the oxide ion, respectively.

Since the molar refraction is an additive quantity, we can assume that for our binary system

$$R_{m,t} = \sum_i f_i R_{m,i} \quad (5)$$

where $R_{m,t}$ is the molar refraction of the binary glass, f_i is molar fraction and $R_{m,i}$ is the molar refraction of the i th oxide. As a first approximation using α_i and $\alpha_{O^{2-}}$ reported for simple oxides we calculated α_m and $R_{m,t}$ values [6,19]. Then using equation (1), the refractive index by LL method (n_{LL}) is calculated.

Maxwell-Garnett theory [20] and Bruggeman model [21] are two major EMTs in use today which can be extended to calculate the refractive index of multicomponent mixtures [22]. Maxwell-Garnett theory is quite successful in predicting features of a two-component system when one of the components occupies only a small fraction of the total volume but becomes inaccurate when the two components have comparable volumes. The Bruggeman model is a better EMT for such systems [22]. This model describes the refractive index of a two-component composite material by considering it as an inter-dispersed medium of the two constituent materials. One can apply the geometric parameters of the Bruggeman model to the general expressions for the optical constants of composites to arrive at an explicit prediction for a two-component system as:

$$\frac{\varepsilon_a - \varepsilon_{eff}}{\varepsilon_a + 2\varepsilon_{eff}} V_a + \frac{\varepsilon_b - \varepsilon_{eff}}{\varepsilon_b + 2\varepsilon_{eff}} V_b = 0 \quad (6)$$

where ε_a and ε_b are the dielectric constants and V_a and V_b are the volume fractions of the two components a and b , respectively. ε_{eff} is the effective dielectric constant of the mixture. In general, for dielectric constant of a mixture (ε_m), equation (6) can be written as

$$\sum_i \left(\frac{\varepsilon_i - \varepsilon_m}{\varepsilon_i + 2\varepsilon_m} \right) V_i = 0 \quad (7)$$

where $\varepsilon_i = n_i^2$ is the dielectric constant of the i th component whose volume fraction is V_i . Using the known values of refractive indices $n(\text{PbO}) = 2.51$, $n(\text{B}_2\text{O}_3) = 1.64$ [6] $n(\text{Bi}_2\text{O}_3) = 2.50$, [23], known values of the densities of binary components $\rho(\text{PbO}) = 9.53 \text{ g/cm}^3$, $\rho(\text{Bi}_2\text{O}_3) = 8.90 \text{ g/cm}^3$, $\rho(\text{B}_2\text{O}_3) = 2.46 \text{ g/cm}^3$ and experimentally measured values of densities of our glasses, we calculated ε_m as a function of glass composition, which was then used to calculate the refractive index.

The experimental refractive index values (n_{exp}), the refractive index values calculated according to LL equation (n_{LL}), and according to EMT (n_{EMT}) are presented in the Table 1 and plotted in Figures 1(a) and 1(b) for lead and bismuth borate glasses, respectively. In lead borate glass, the calculated refractive indices are about 10-15% larger than the experimental values, whereas in bismuth borate glasses both EMT and LL methods give better overall agreement between calculated and experimental values. To understand the difference between lead borate and bismuth borate glasses, we must examine the details of the structural changes that occur as a function of $\text{PbO/Bi}_2\text{O}_3$ concentration. In lead borate glasses, addition of PbO converts 3-coordinated boron (B_3) to 4-coordinated boron (B_4). The fraction of B_4 reaches a maximum around 45-50 mol% of PbO concentration and with further addition of PbO , back conversion of B_4 to B_3 takes place with the formation of NBO. For PbO concentrations above 65 mol%, most of the oxygen bonded to the boron atoms are NBO [11]. Similar changes are observed in bismuth borate glasses also. Addition of Bi_2O_3 to B_2O_3 , results in the conversion of B_3 to B_4 with the fraction of B_4 reaching a maximum around 40 mol% of Bi_2O_3 . With further addition of Bi_2O_3 , back conversion of B_4 to B_3 takes place resulting in the formation of NBO. Thus both lead and bismuth borate glasses show significant changes to the boron coordination with changing glass composition. However, there is a fundamental difference between these two types of glasses.

Due to the higher polarizability of Bi atoms, Bi_2O_3 can form a glass with a trace of B_2O_3 whereas PbO cannot. It appears that Bi_2O_3 can form its own network not needing the presence of borate groups for network interconnection [24] whereas PbO needs the presence of B_2O_3 to form the glass network [11]. Thus in bismuth borate glasses, varying the Bi_2O_3 content does not significantly alter the immediate surroundings of the Bi_2O_3 molecules as much as it happens with PbO in lead borate glasses. In the theoretical calculation of the refractive index by both LL and EMT methods, only changes of R_m and V_m with composition are taken into account whereas changes in the metal ion and oxide ion polarizability are neglected. But from the discussion above, it is clear that PbO undergoes a larger alteration to its immediate chemical environment compared to Bi_2O_3 when the glass composition is varied. Therefore, the assumption that the average cation electronic polarizability is a constant for PbO is likely to be inaccurate resulting in the difference between the experimental and calculated values of n for PbO - B_2O_3 glasses.

Figure 1. Variation of n_{exp} , n_{LL} , n_{EMT} of (a) lead borate glasses with PbO content (b) bismuth borate glasses with Bi_2O_3 content.

Table 1. Glass composition, density (ρ), molar volume (V_m), experimental refractive index (n_{exp}), refractive index by Lorentz-Lorenz method (n_{LL}), refractive index by effective medium theory (n_{EMT}) of lead and bismuth borate glasses

Glass Composition	Physical Parameters				
	ρ (g/cm ³)	V_m (cm ³ /mol)	n_{exp}	n_{LL}	n_{EMT}
PbB30	4.232±0.004	27.34±0.11	1.66±0.03	1.84±0.02	1.87±0.03
PbB40	4.589±0.002	28.56±0.06	1.72±0.03	1.91±0.04	1.93±0.04
PbB50	5.068±0.006	28.89±0.2	1.76±0.03	1.99±0.05	2.02±0.03
PbB60	5.519±0.005	29.31±0.2	1.81±0.03	2.08±0.05	2.11±0.04
PbB70	6.032±0.007	29.36±0.3	1.92±0.04	2.17±0.03	2.20±0.04
BiB30	5.511±0.008	34.21±0.3	1.922±0.05	2.02±0.05	2.00±0.06
BiB40	6.260±0.003	36.45±0.12	2.03±0.06	2.13±0.04	2.10±0.04
BiB50	7.039±0.005	38.04±0.2	2.13±0.03	2.28±0.04	2.19±0.05
BiB60	7.609±0.007	40.40±0.3	2.21±0.04	2.37±0.04	2.27±0.03

3.2. The optical band gap

The study of optical absorption in the ultraviolet region is a useful technique to understand the electronic band structures of glasses. In the optical absorption spectrum of glasses, one can observe a rapid rise in the absorbance toward lower wavelengths. The rapid rise of absorption coefficient is referred to as the fundamental absorption edge (UV “cut off”). Beyond this UV “cut off” value, glasses will be opaque to electromagnetic radiation. Most of the oxide glasses are opaque at wavelengths shorter than 200 nm when the photon energy becomes greater than the optical band gap that exists between the valence and conduction bands. In glasses, measuring this band gap can provide information regarding structural alterations and the nature of chemical bonds in the matrix. The width of the localized states in the band gap which arises due to the disorder in the matrix can also be determined from the analysis of the optical absorption spectra.

Basically, two types of transitions can occur at the fundamental absorption edge of both crystalline and non-crystalline materials - direct transitions and indirect transitions. For the direct optical transitions, it is essential that the wave vector for an electron remains the same as it absorbs a photon. On the other hand, the indirect transitions will also involve simultaneous interaction between the electron and lattice vibrations (phonons). In this case, the wave vector of the electron can change in an optical transition due to the absorption/emission of a phonon. In other words for indirect transitions, the minimum of the conduction band lies in a different k -space direction compared to the maximum of the valence band.

The optical absorption edge of binary lead borate and bismuth borate glasses is shown in Figures 2(a) and 2(b), respectively. As the concentration of $\text{PbO/Bi}_2\text{O}_3$ increases, the position of

the fundamental absorption edge shifts from 344 to 458 nm in lead borate glasses and from 400 to 460 nm in bismuth borate glasses. For comparison, in lead silicate glasses the absorption edge was found to shift from 340 to 400 nm with increasing PbO content [25]. The absorption edge of these glasses is not as sharp as in crystalline compounds due to the disorder in the matrix. The shifts in the optical absorption edge to longer wavelengths indicate that the E_{opt} values decrease with increase in PbO/Bi₂O₃ content which is explained below.

Analyzing the behavior of the optical absorption coefficient α , near the fundamental absorption edge is a standard method for investigating optically induced electronic transitions in many materials. We can obtain experimental optical band gap directly by using relation between absorption coefficient and extinction coefficient which is given by [26]

$$\kappa = \frac{\alpha\lambda}{4\pi} \quad (8)$$

The extinction coefficient is plotted as a function of energy $h\nu$ (Figs 3(a) and 3(b)). By extrapolating the linear region of the extinction coefficient to zero, we obtained the experimental optical band gaps for different glass compositions as listed in Table 2.

Mott and Davis [14] suggested the following form for the absorption coefficient $\alpha(\nu)$ as a function of photon energy

$$\alpha(\nu) = B(h\nu - E_{opt})^m / h\nu \quad (9)$$

Here, for direct transitions we have $m = 1/2$ or $3/2$ depending on whether the transition is allowed or forbidden and for indirect transitions, $m = 2$ or 3 depending on whether the transition is allowed or forbidden, B is a constant, and E_{opt} is the optical band gap. The type of transition can

be obtained from the value of m . In order to determine the unique value of m , we followed the differential method [27]. We rewrite equation (10) as follows.

$$\frac{d[\ln(\alpha h\nu)]}{d[h\nu]} = \frac{m}{h\nu - E_{opt}} \quad (10)$$

The differential curve $\frac{d[\ln(\alpha h\nu)]}{d[h\nu]}$ versus $h\nu$ has a discontinuity at a particular energy value ($h\nu = E_{opt}$) which gives the optical band gap E_{opt} . In order to find the type of transition, the E_{opt} values are calculated by extrapolation of the linear parts of $(\alpha h\nu)^{1/m}$ vs. $h\nu$ curves to $(\alpha h\nu)^{1/m} = 0$ for different values of m (Table 2). By comparing the value from the differential curve with the optical band gap obtained using different values of m , we find good agreement with E_{opt} values for $m = 3/2$. Hence we can conclude that for lead and bismuth borate glasses the optical band gap arises due to the direct forbidden transition. Thus the experimental optical band gap obtained directly from the extinction coefficient matches well with the Mott-Davies relation for $m = 3/2$ transition. Figures 4(a) and 4(b) show the plot of $(\alpha h\nu)^{2/3}$ vs. $h\nu$ for various PbO/Bi₂O₃ contents. E_{opt} is found to decrease from 3.52 to 2.74 eV for lead borate glasses and from 3.10 to 2.78 eV for bismuth borate glasses with increasing concentration of the metal oxide as shown in Figures 5(a) and 5(b). In lead borate glasses, there is a slope change in E_{opt} vs. composition curve around 50 mol% of PbO indicating a significant electronic alteration around that composition, whereas a similar change occurs in bismuth borate glasses around 30-40 mol% of Bi₂O₃.

The origin of optical band gap in lead silicate glasses is well established [28]. According to this work, E_{opt} of binary lead borate glasses represents the excitation energy of electrons from the hybridized orbitals of 6s lead and 2p non-bridging oxygens states to the conduction band (6p states of lead forms the conduction band). The E_{opt} depends on the energy level of the upper

valence band edge which is determined by the separation of 6s lead and 2p oxygen states. A theoretical study of the energy bands based on ionic model, indicates that the separation between 6s lead and 2p oxygen states is very sensitive to the charge on the oxygen ion [29]. As the ionicity of the oxygen decreases, the energy of the 6s lead state decreases and the 2p oxygen state increases, so the hybridization of these two states increases. This implies that an increase in the covalent character of the Pb-O bond decreases the optical band gap. Such an increase in covalency of Pb-O bond with PbO content in lead borate glasses has been suggested by far infra-red spectrum [30]. From NMR results [13, 31], it is found that the chemical shift of B₃ units changes with PbO concentration. This change shows that the PbO units which are formed due to the addition of PbO to B₂O₃, bridge preferentially to B₃ units. This results in the formation of Pb-O-B linkages, which arise as a result of the increasing covalency of the Pb-O bond. This increase in covalency of the PbO bond is a consequence of the high polarizability of Pb ions and the directional nature of the PbO bond which effectively reduces the optical band gap. In bismuth borate glasses the reduction of E_{opt} with Bi₂O₃ content is also due to an increase in the covalent nature of Bi-O bond. The covalency of Bi-O bond is larger compared to Pb-O bond due to the highly polarizable and directional nature of Bi-O bond. Hence, the E_{opt} values in bismuth borate glasses are smaller compared to their lead borate counterparts.

The optical absorption edge of many amorphous semiconductors is characterized by the tail of the absorption edge where the absorption coefficient $\alpha(\nu)$ rises exponentially with photon energy $h\nu$ as

$$\alpha(\nu) = A \exp\left(\frac{h\nu}{\Delta E}\right) \quad (11)$$

ΔE (Urbach energy) represents the width of the band tails of localized states in the band gap. The values of ΔE are calculated from the slopes of the linear plots of $\ln \alpha$ vs. $h\nu$ in the lower photon energy region and are listed in Table 2 for both lead borate and bismuth borate glasses. The values of ΔE vary from 0.29 to 0.21 eV for lead borate glasses and 0.23 to 0.19 eV for bismuth borate glasses. Large ΔE values for these glasses are due to the disorder and the wide distribution of local electric field intensities in the glass matrix compared to the crystalline systems where $\Delta E \sim 0.046\text{-}0.066$ eV as reported by Mott and Davis [14].

Figure 2. Optical absorption edge of (a) lead borate glasses (b) bismuth borate glasses

Figure 3. Plot of extinction coefficient vs. $h\nu$ for (a) lead borate glasses (b) bismuth borate glasses

Figure 4. Plot of $(\alpha h\nu)^{2/3}$ vs. $h\nu$ for (a) lead borate glasses (b) bismuth borate glasses

Table 2. Variation of E_{opt} for lead and bismuth borate glasses with glass composition

Optical Bandgap E_{opt} (eV)	Glass Composition				
	PbB30	PbB40	PbB50	PbB60	PbB70
E_{opt} from k (Experimental)	3.59±0.04	3.30±0.05	3.12±0.04	2.95±0.05	2.80±0.03
E_{opt} from Differential Curve	3.50±0.05	3.25±0.04	3.05±0.03	2.89±0.04	2.76±0.04
Direct allowed transition $m=1/2$	3.83±0.03	3.50±0.04	3.28±0.03	3.13±0.04	2.95±0.05
Direct forbidden transition $m=3/2$	3.52±0.03	3.20±0.04	3.01±0.04	2.90±0.03	2.74±0.04
Indirect allowed transition $m=2$	3.36±0.03	3.03±0.04	2.90±0.03	2.81±0.04	2.63±0.04
Indirect forbidden transition $m=3$	3.11±0.03	2.79±0.04	2.72±0.04	2.59±0.04	2.46±0.03
Urbach energy ΔE	0.291±0.002	0.233±0.003	0.232±0.004	0.204±0.002	0.213±0.001
	BiB30	BiB40	BiB50	BiB60	
E_{opt} from k (Experimental)	3.19±0.03	3.03±0.03	2.91±0.03	2.83±0.04	
E_{opt} from Differential Curve	3.07±0.04	2.91±0.05	2.84±0.04	2.77±0.02	
Direct allowed transition $m=1/2$	3.33±0.04	3.16±0.03	3.06±0.04	2.98±0.05	
Direct forbidden transition $m=3/2$	3.10±0.03	2.93±0.05	2.86±0.04	2.78±0.03	
Indirect allowed transition $m=2$	3.01±0.04	2.82±0.04	2.75±0.03	2.70±0.03	
Indirect forbidden transition $m=3$	2.76 ±0.03	2.64±0.04	2.55±0.03	2.51±0.02	
Urbach energy ΔE	0.230±0.003	0.201±0.004	0.191±0.004	0.193±0.00

Figure 5. Compositional dependence of experimental optical band gap and optical band gap from Mott-Davis Model for $m = 3/2$ transition (a) lead borate glasses (b) bismuth borate glasses

3.3. Optical band gap and refractive index based electronic polarizability of the oxide ion

It is known that the nonlinear optical response of a material when exposed to intense light is closely related to its electronic polarization. The macroscopic polarization itself is governed by the electronic polarizability of its individual components. Assuming that molar refractivity (R_m) and polarizability (α_m) are additive quantities, Dimitrov and Sakka [6] obtained the relationship given by equation (4). Combining this relationship with Lorentz-Lorenz equation (1) leads to

$$\alpha_{O^{2-}}(n) = \left[\left(\frac{V_m}{2.52} \right) \left(\frac{n^2 - 1}{n^2 + 2} \right) - \sum_i p \alpha_i \right] q^{-1} \quad (12)$$

Where $\left(\frac{n^2-1}{n^2+2}\right) = \frac{R_m}{V_m}$ from equation (1)

For simple oxides, Dimitrov and Sakka used the following linear relationship suggested by Duffy [6,32]

$$E_{opt} = 20(1 - R_m / V_m)^2 \quad (13)$$

Vithal et al [33] extended their work to simple binary oxides. They found an empirical relation very close to Duffy's relation which is given as

$$\sqrt{E_{opt}} = 1.23(1 - R_m / V_m) + 0.98$$

Plotting E_{opt} vs. $(1 - R_m / V_m)$ gave us the following empirical relations

$$E_{opt} = 6.73(1 - R_m / V_m)^{1.46} \quad (14)$$

$$E_{opt} = 4.4(1 - R_m / V_m)^{0.56} \quad (15)$$

for lead borate glasses with PbO content (Figure 6a) and for bismuth borate glasses with Bi₂O₃ content (Figure 6b), respectively. Thus we obtained two new empirical relations between E_{opt} and $(1 - R_m / V_m)$. These relations explain the compositional dependence of E_{opt} for lead and bismuth borate glasses.

Substituting equations (14) and (15) in place of $\left(\frac{n^2-1}{n^2+2}\right)$ in equation (12) we get for lead borate glasses

$$\alpha_{O^{2-}}(E_{opt}) = \left[\left(\frac{V_m}{2.52} \right) \left(1 - \left(\frac{E_{opt}}{6.73} \right)^{0.68} \right) - \sum_i p\alpha_i \right] q^{-1} \quad (16)$$

and for bismuth borate glasses,

$$\alpha_{O^{2-}}(E_{opt}) = \left[\left(\frac{V_m}{2.52} \right) \left(1 - \left(\frac{E_{opt}}{4.4} \right)^{1.79} \right) - \sum_i p \alpha_i \right] q^{-1} \quad (17)$$

Using the relations (16) and (17), the average electronic oxide polarizability can be calculated from the optical band gap E_{opt} , molar volume V_m and cation polarizability α_i . We also calculated $\alpha_{O^{2-}}$ from n values using equation (12). Results of these two independent calculations are given in Table 3. Duffy's empirical relation is obeyed by a large number of simple oxides. However, for our binary oxide glass systems with different PbO/Bi₂O₃ composition, we find that $\alpha_{O^{2-}}$ calculated using our empirical relations (15) and (16) match better with $\alpha_{O^{2-}}$ obtained from the refractive index values.

Figure 6. Variation of E_{opt} with $1-R_m/V_m$ (a) in lead borate glasses (b) in bismuth borate glasses

Table 3. Glass composition, molar refraction, molecular polarizability (α_m), electronic oxide polarizability ($\alpha_{O^{2-}}(n)$), electronic oxide polarizability ($\alpha_{O^{2-}}(E_{opt})$) of lead borate and bismuth borate glasses

Glass Composition	Physical Parameters				
	R_m	$I-R_m/V_m$	α_m (10^{-24} cm^3)	$(\alpha_{O^{2-}})(n)$ (10^{-24} cm^3)	$(\alpha_{O^{2-}})(E_{opt})$ (10^{-24} cm^3)
PbB30	10.09±0.1	0.631±0.007	4.001	1.215	1.155
PbB40	11.32±0.2	0.604±0.006	4.492	1.382	1.385
PbB50	11.91±0.12	0.588±0.005	4.726	1.458	1.508
PbB60	12.67±0.18	0.568±0.006	5.028	1.585	1.610
PbB70	13.83±0.15	0.529±0.005	5.488	1.846	1.749
BiB30	16.16±0.15	0.528±0.008	6.413	1.835	1.806
BiB40	18.58±0.21	0.491±0.007	7.374	2.055	2.083
BiB50	20.58±0.19	0.459±0.009	8.168	2.219	2.225
BiB60	22.80±0.16	0.436±0.006	9.046	2.412	2.388

4. Conclusions

Using an accurate method to measure the Brewster's angle, we investigated the compositional dependence of refractive index for $\text{PbO-B}_2\text{O}_3$ and $\text{Bi}_2\text{O}_3\text{-B}_2\text{O}_3$ glasses for a broad range of glass compositions. We also calculated the refractive index by two theoretical methods (Lorentz-Lorenz and Bruggeman's effective medium theory). We found that in lead borate glasses, the calculated refractive indices are larger than the experimental values, whereas in bismuth borate glasses both EMT and LL methods give better overall agreement between calculated and experimental values. In lead borate glasses PbO undergoes a larger alteration to its immediate chemical environment compared to Bi_2O_3 when the glass composition is varied. Therefore, assuming constant values for the average cation electronic polarizability of PbO is likely to be incorrect which leads to the difference between the experimental and calculated values of n for $\text{PbO-B}_2\text{O}_3$ glasses. With increasing $\text{PbO/Bi}_2\text{O}_3$ content, the optical absorption edge shifts to longer wavelengths indicating significant changes to the electronic band structure of these glasses. We obtained optical band gap for our systems using Mott-Davis model from the optical absorption edge measurements. In order to find the type of transition, optical band gap is obtained by the differential method using Mott-Davis model and compared with the experimentally obtained value. We found that in both lead borate and bismuth borate glasses, the absorption edge arises due to direct forbidden transitions ($m = 3/2$). The E_{opt} is found to decrease from 3.52 to 2.74 eV for lead borate glasses and from 3.10 to 2.78 eV in bismuth borate glasses with increasing concentration of the metal oxide. The reduction of E_{opt} with $\text{PbO/Bi}_2\text{O}_3$ content is due to the increase in the covalent nature of Pb-O/Bi-O bond. The electronic oxide polarizability in lead borate glasses and bismuth borate glasses were calculated on the basis of two different

properties, linear refractive index (n) and the optical band gap (E_{opt}) by using a new empirical relation between E_{opt} and n . Both values show very good agreement.

Acknowledgement

The authors would like to acknowledge a start-up grant from the University Research Council, Western Illinois University. Optical absorption measurements were carried out at the Frederick Seitz Materials Research Laboratory Central Facilities, University of Illinois, which are partially supported by the U.S. Department of Energy under grants DE-FG02-07-ER46453 and DE-FG02-07-ER46471.

References

- [1] I. Opera, H. Hesse, and K. Betzler, *Opt. Mater.*, 26 (2004) 235-237.
- [2] X. Zhao, X. Wang, H. Lin, and Z. Wang, *Physica B*, 390 (2007) 293-300.
- [3] O. Sanz, E. Haro-Poniatowski, J. Gonzalo, & J. M. Fernández Navarro, *J. Non-Cryst. Solids*, 352 (2006) 761-768.
- [4] V.V. Dimitrov, S. Kim, T. Yoko and S. Sakka, *J. Ceramic. Soc. Japan*, 101 (1993) 59-63
- [5] V.V. Dimitrov and S. Sakka., *J. Appl. Phys.* 79 (1996) 1741-1745
- [6] V. Dimitrov, S. Sakka, *J. Appl. Phys.* 79 (1996) 1736-1740
- [7] Joanna Pisarska, *Opt. Mater.* 31(2009)1784–1786
- [8] M.B. Saisudha and J. Ramakrishna, *Phys. Rev. B.*, 53 (1996) 6186-6196
- [9] M.B. Saisudha, K.S.R. Koteswara Rao, H.L. Bhat and J. Ramakrishna, *J. Appl. Phys.* 80, (1996) 4845-4853
- [10] M.B. Saisudha and J. Ramakrishna, *Optical Materials*, 18 (2002) 403-417
- [11] B.N. Meera, A.K. Sood, N. Chandra Bhas, and J. Ramakrishna, *J. Non-Cryst. Solids* 126, (1990) 224-230

- [12] I. Avramov, Ts. Vassilev, I. Penkov., J. Non-Cryst. Solids, 351 (2005) 472–476
- [13] P. J. Bray, M. Leventhal, and H. O. Hooper, Phys. Chem. Glasses 4 (1963) 47-66
- [14] N.F. Mott and E.A. Davis, “Electronic processes in non-crystalline materials”, 2nd edn (Oxford University Press, Oxford, 1977)
- [15] Cristian Bahrim and Wei-Tai Hsu, Am. J. Phys. 77 (2009) 337-343
- [16] T. Honma, Y. Benino, T. Komatsu, R. Sato, V. Dimitrov, Phys. Chem. Glasses, 43 (2002) 32-40
- [17] E. A. Moelwyn-Hughes, Physical Chemistry, Pergamon, London 1961
- [18] H. Rawson, Properties and Applications of Glass, Elsevier, Amsterdam 1980.
- [19] V. Dimitrov, T. Komatsu, J. Solid State Chemistry 163 (2002) 100-112
- [20] C. Maxwell-Garnet, Philos. Trans. R. Soc. Cand. 203 (1904) 385, ibid 205 (1906) 237
- [21] D. A. G. Bruggeman, Ann. Phys. (Leipzig) 24 (1935) 636-679
- [22] R.J. Gehr, G.L. Fischer, R.W. Boyd, J. Opt. Soc. Am. B, 14 (1997) 2310-2314
- [23] P. B. Clapham, Br. J. Appl. Phys. 18 (1967) 363-366
- [24] A. Vegas, F.H. Cano and S. Garcia-Blanco, J. Solid St. Chem., 17 (1976) 151-155
- [25] B.M. Cohen, D.R. Ulmann and R.R. Shaw., J. Non-Cryst.Solids, 12 (1973) 177-188
- [26] Seung-Gu Lim, Stas Kriventsov, and Thomas N. Jackson et al, J. Appl.Phys., 91 (2002) 4500-4505
- [27] A. Masuno, H. Inoue, J. Yu, Y. Arai., J. Appl.Phys 108 (2010) 063520-1
- [28] I.S. Reshetnikova and V. N. Shapovalov., Optica and Spectroscopy, 75 (1993) 749-752
- [29] A.H. Kahn and A.J. Leyendecker., Phys. Rev A., 135 (1964) 1321-1325
- [30] P.Tarte and M.J.Portier., The structure of non-crystalline materials, P.H.Gaskell (Ed.) (1977) 227.

- [31] M. Leventhal and P.J. Bray., Phys.Chem.Glasses, 6 (1965) 113-125
- [32] J. A. Duffy, J. Solid State Chem., 62 (1986) 145-157
- [33] M. Vithal, P. Nachimuthu, T. Banu, and R. Jagannathan., J. Appl. Phys. 81 (1997) 7922-7926