Optical properties of alkaline earth borate glasses

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Abstract

Borate glasses containing fixed concentrations of heavy metal oxides (MO= ZnO, PbO, TeO_2, Bi_2O_3) and alkaline earth oxides (R= Mg, Ca, Sr, Ba) are prepared by melt quenching technique. The optical band gap values are estimated from the optical absorption spectra using absorption spectrum fitting (ASF) method. The values of electronic polarizability, optical basicity and interaction parameters of the glass were discussed. The increment of refractive index values in each series is attributed to the substitution of alkaline earth oxides of increasing mass. Optical band gap (E_{opt}) values decreased with the replacement of RO oxides in the glass matrix. The cut-off wavelengths have shown a red shift with composition. The decrease in optical band gap values and consequently increase in Urbach's energies confirms more extension of the localized states within the band gap. As a result there shall be an increase in the disorder of the glass network. The variation in optical parameters is owing to substitution of RO oxides in $MO-B_2O_3$ glass network.

Keywords: alkaline earth borate glasses, optical band gap, Urbach energy, refractive index, electronic polarizability, molar refraction

1. Introduction

Borate rich glasses containing heavy metal oxides have got special interest due to their possible applications as laser hosts, lamp phosphors and other photonic devices (Khattak et al., 2005; Murugavel et al., 2007). Heavy metal oxide glasses also find applications in the field of optical fibers, optoelectronic devices; radiation shields, surgical lasers and their glass ceramic counter parts have wide range of applications (Rajasree et al., 2011; Sharma et al., 2007, Limkitjaroenporn et al., 2010). Boric acid (H_3BO_3) form stable glasses with alkaline earth oxides (R= MgO, CaO, SrO, BaO) and heavy metal oxides (MO= ZnO, PbO, TeO_2, Bi_2O_3). The alkaline earth borate glasses containing heavy metal oxides show good solubility of rare-earth ions. Glasses containing PbO exhibit low glass transition temperature (T_g) and high refractive index (Dimitrov et al., 1996). Glasses containing TeO_2 show interesting non-linear optical properties (Yousef et al., 2007), good chemical durability, and low melting point (Sanghi et al., 2004; Singh et al., 2008; Agarwal et al, 2003). Alkaline earth oxides improve glass forming capability while heavy metal oxides give rise to good optical properties such as second harmonic generation. Both alkaline earth and heavy metal oxides could act as glass network formers (GNF) or glass network modifiers (GNM) depending on their composition in the glass. Mostly at low concentration they occupy network modifier positions and at higher concentration they occupy network former positions (Yasser et al., 2008; Veeranna Gowda and Anvekar, 2004; Doweidar et al., 1999).

The electronic polarizability is one of the most important parameter for the application of glasses as optical and electronic materials. The non-linear response to the incident light exhibited by glassy materials is a function of electronic polarizability of the constituents in the glass matrix. The ability of glass formation, glass forming region, stability, chemical durability of the glass

forming oxide materials like B_2O_3, SiO_2, GeO_2, P_2O_5, As_2O_3 etc, can be enhanced by adding metal oxides such as ZnO, TeO_2, PbO, Bi_2O_3 etc, which are called conditional glass modifiers.

The present glass samples when doped with appropriate rare earth ions may be potential candidates for luminescent host materials and non-linear optical applications. Many authors reported various properties of $MO-B_2O_3$ glasses. But there are limited reports on optical properties of $MO-B_2O_3$ glasses containing alkaline earth oxides. This paper reports optical band gap, refractive index, electronic polarizability, optical basicity and interaction parameters of $RO-MO-B_2O_3$ glasses.

2. Experimental Techniques

Glass systems with the composition $RO-MO-B_2O_3$ in the ratio 1:4:5 (R=Mg, Ca, Sr, Ba and MO= ZnO, PbO, TeO_2 and Bi_2O_3) are prepared by melt quenching technique. The mole percentage of each constituent in the glass composition is maintained as constant and only alkaline earth oxides are progressively substituted from MgO to BaO in the $MO-B_2O_3$ glass matrix. The effect of alkaline earth oxides on $MO-B_2O_3$ glass network was studied. Four series of glasses were prepared by progressive substitution of alkaline earth oxide in $MO-B_2O_3$ glass network. Each series was labeled as ZB, PB, TB and BB glasses for each of the MO employed namely ZnO, PbO, TeO_2 and Bi_2O_3, respectively.

The analar grade H_3BO_3, zinc oxide (ZnO), lead monoxide (PbO), tellurium oxide (TeO_2), bismuth oxide (Bi_2O_3), magnesium oxide (MgO), calcium carbonate ($CaCO_3$), strontium oxide (SrO) and barium carbonate ($BaCO_3$) are taken as starting materials. The appropriate mole percent of these materials after grinding are taken in porcelain crucible and introduced into an electrical furnace maintained at 1000^0C. The mixture is melted for about 30-40 minutes and melt was shaken frequently to achieve homogeneity. The melt was quickly poured onto a hot stainless steel plate (maintained at 373K) and pressed with a steel rod. The fresh samples are annealed at the temperature 373K to relieve internal stresses. The glass formation was not observed in the composition $10MgO-40TeO_2-50B_2O_3$ around 1000^0C even after heating for a long time. The glasses formed are clear, transparent with light yellowish tint. The compositions of the glass samples are given in table.1. The bubble-free glass samples of thickness 0.25 to 1mm are employed in optical absorption measurements. The optical absorption spectra are recorded on Shimadzu UV-VIS-NR-3100 spectrophotometer in the wavelength range 250nm to 800nm at room temperature. The refractive index values of the glass samples are determined from the optical band gap (E_{opt}) values.

3. Results and Discussion

3.1 . Optical band gaps and Urbach Energy

The optical absorption spectra of the glass samples are shown in Figure.1. The power law region is clearly observed in absorption spectra. It is clear from Figure1 that the fundamental absorption edges are not sharp. This is a characteristic feature of amorphous glass samples. The absorption of intensity of incident light by the glass sample follows the famous Beer-Lambert-Bouguer law. In the near absorption edge, the optical absorption coefficient $\alpha(\omega)$ of a glass sample of thickness 't' (average thickness of 0.75mm)can be calculated from the relation:

$$\alpha(\omega) = \frac{1}{t}\ln(\frac{I_o}{I_T}),\tag{1}$$

where $ln (I_o/I_T)$ is the absorbance, I_0 and I_T are the intensities of incident and transmitted light respectively. The optical absorption of disordered materials $[\alpha(\omega) \geq 10^4 cm^{-1}]$ follows Tauc's rule (Tauc, Mott and Davis power law) (Davis, 1970; Mott and Davis, 1971)

$$\alpha(\omega) = \frac{Const}{\hbar\omega}(\hbar\omega - E_{opt})^r\tag{2}$$

where 'r' can take values ⅓, ½, 2, 3 for direct forbidden, direct allowed, indirect allowed, indirect forbidden transitions respectively. Here E_{opt} is the optical energy band gap and $\hbar\omega$ is the incident photon energy.

$$[\hbar\omega\alpha(\omega)]^{\frac{1}{2}} = Const(\hbar\omega - E_{opt})\tag{3}$$

It is observed that the measured absorption data best fits to equation (3) for $r =2$, which corresponds to indirect allowed transitions. A graph between $(\alpha h\nu)^{½}$ and $(h\nu)$ is called Tauc's plot. The Tauc's plots for the glass samples are shown in Figure 2. For fundamental absorption edge in lower incident photon energy ($\hbar\omega$) between 10^2-10^4 cm^{-1}, absorption coefficient $\alpha(\omega)$ follows Urbach law given by

$$\alpha(\omega) = B\exp(\frac{\hbar\omega}{\Delta E})\tag{4}$$

where B is a constant and ΔE is the Urbach's energy. The Urbach energy values are calculated from the slopes of linear regions of the plots $ln\alpha(\omega)$ vs $\hbar\omega$ (Figure 3 shows these curves for BB series of glasses). The wavelength values corresponding to the absorption edge, where the intensity reaches the maximum value in optical absorption spectra are taken as cut-off wavelengths ($\lambda_{cut-off}$). The cut-off wavelength ($\lambda_{cut-off}$), optical band gap values (E_{opt}) and Urbach energy (ΔE) values of the present glass samples are given in table.1. The optical band gap values (E_{opt}) of the present glass systems are in agreement with values of similar glass systems reported in the literature (Singh et al., 2008). There errors due to the extrapolation method in the estimation of energy band gaps and Urbach energies are around ±0.05ev and ±0.005eV respectively.

In order to obtain 'optical band' gap or 'Tauc gap', measurement of absorption coefficient (α) of the sample as a function of the photon energy versus the absorbance, the reflectance and the film thickness is required. However, Escobar-Alarcon et al. and Dariush Souri and Shomalian proposed absorption spectrum fitting (ASF) method to determine the optical band gaps when
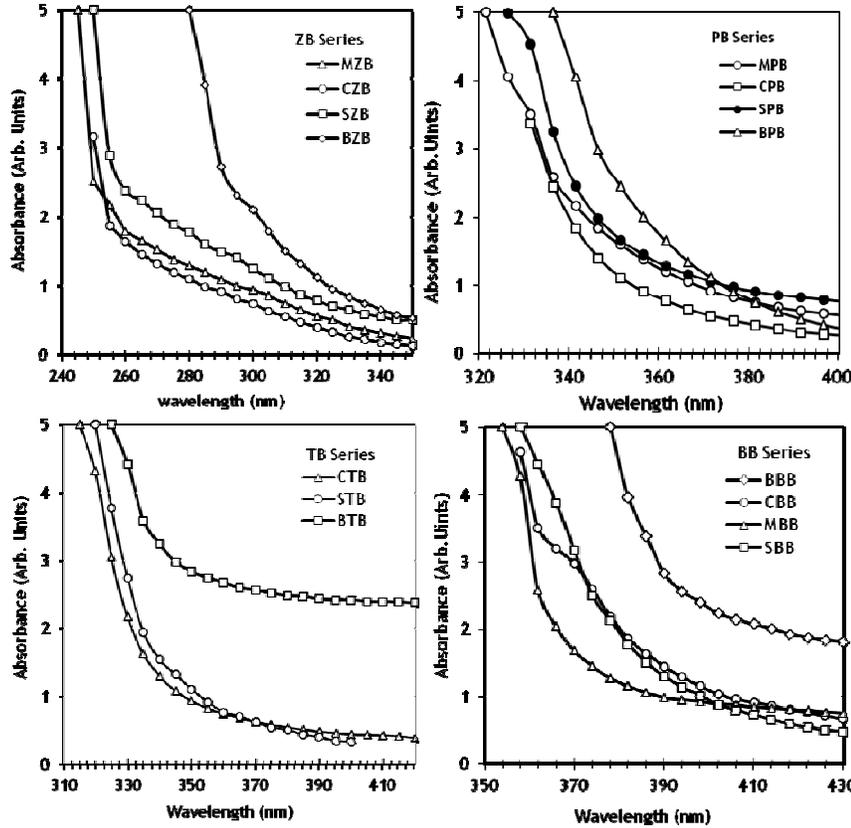

Figure 1. Optical absorption spectra of RO-MO-B$_2$O$_3$, where R= Mg, Ca, Sr, Ba and MO= ZnO, PbO, TeO$_2$, Bi$_2$O$_3$ glass samples

absorbance measurements are alone made. The equation (2) can be rewritten as a function of wavelength (Alarcon et al., 2007; Souri and Shomalian, 2009; Souri and Salehizadeh, 2009),

$$\alpha(\lambda) = Const \ (hc)^{r-1}\lambda\left(\frac{1}{\lambda} - \frac{1}{\lambda_g}\right)^r \qquad (5)$$

where λ_g, h and c are wavelength corresponding to the optical gap, Plank's constant and the velocity of the light, respectively. Incorporating the Beer–Lambert's law in the above equation, the absorbance $a(\lambda)$ can be expressed,

$$a(\lambda) = K_1\lambda\left(\frac{1}{\lambda} - \frac{1}{\lambda_g}\right)^r + K_2 \qquad (6)$$

where $K_1 = [Const \ (hc)^{r-1}t/2.303]$ and K_2 is a constant which takes into account the reflection of the incident light lost, assuming that the fraction reflected or dispersed is small. Using equation (6) optical band gap can be calculated from the absorbance spectrum fitting (ASF) method without the need of thickness of the glass sample. The value of band gap can be determined by extrapolating the linear region of $(a/\lambda)^{1/r}$ vs. $(1/\lambda)$ curve at $(a/\lambda)^{1/r} = 0$. The best fitting is observed for $r = 2$, and the value of band gap $\left(E_{opt}^{asf}\right)$ in eV, can be obtained from the parameter λ_g using the expression

$$E_{opt}^{asf} = \frac{1239.83}{\lambda_g} \qquad (7)$$

The variation of $(a/\lambda)^{1/r}$ vs. $(1/\lambda)$ was shown in figure. 4. The values of optical band gaps E_{opt}^{asf} of the present glass samples calculated using ASF method were given in the Table 1.

The optical band (E_{opt}) values have decreased in each series of present glasses. The variation in E_{opt} values with the replacement of RO oxides in the glass matrix is small and therefore no significant structural changes might have occurred in the glass network. Urbach's energy refers to the width of the tails of localized states in the forbidden gap of a disordered material. According to Urbach's rule, optical absorption coefficient near the absorption edge is an exponential function of photon energy. The empirical rule proposed by Urbach has become universal and applicable to variety of disordered materials including insulators, semiconductors and glasses. Urbach energy is a measure of disorder in amorphous solids (Sanghi et al, 2004).

The observed increase in the Urbach energy in each glass series can be attributed to higher number of defects (Halimah et al., 2010). Hence increase in the Urbach energy with replacement of alkaline earth oxides in MO-B$_2$O$_3$ glass network reveals creation of more defects. The Urbach energies are attributed to phonon assisted indirect electronic transitions (Sanghi et al., 2004). The decrement in the values of E_{opt} means that more tails in the localized states and as a result Urbach energy has increased.
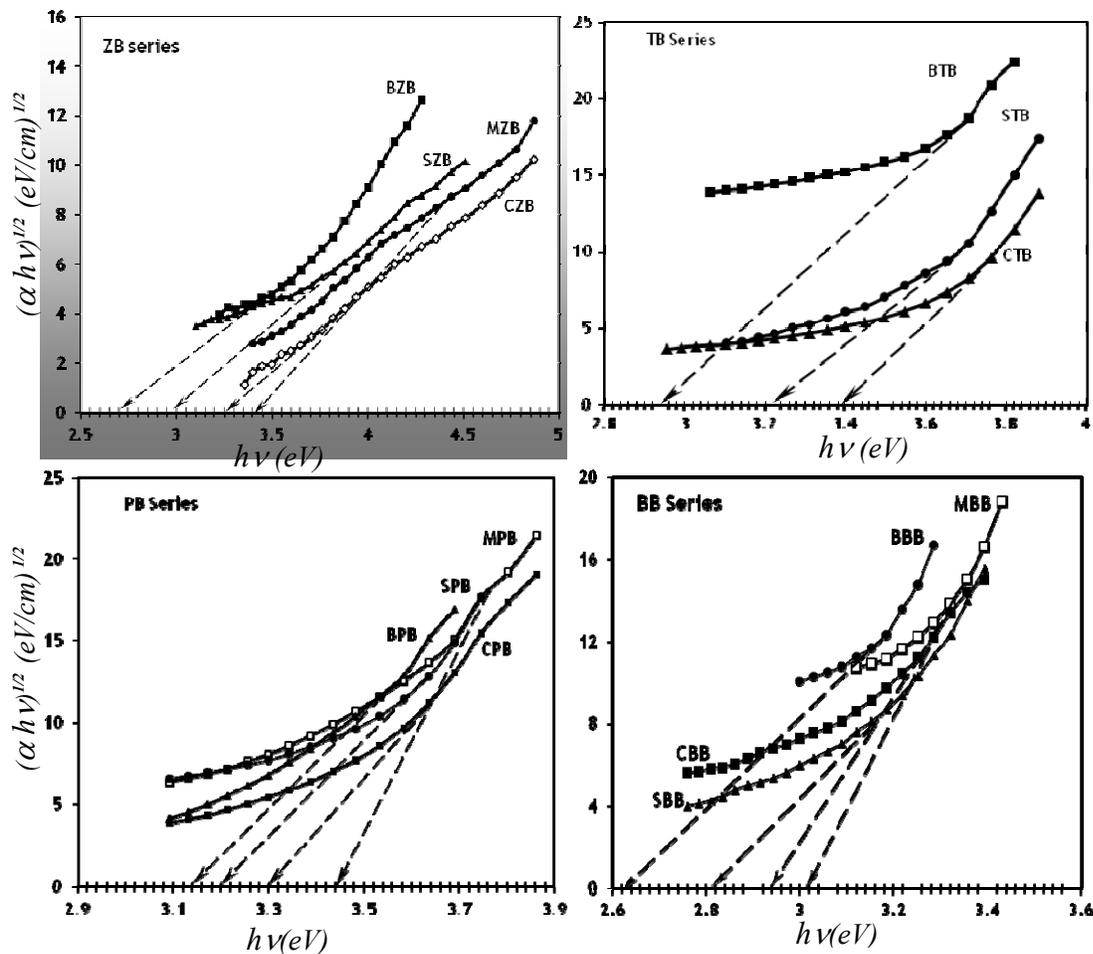

Figure 2. Tauc's plots of RO-MO-B$_2$O$_3$, where R= Mg, Ca, Sr, Ba and MO= ZnO, PbO, TeO$_2$, Bi$_2$O$_3$ glass samples

A red shift in the absorption edge towards higher wavelength was observed in the present glasses. The shift is probably due to increase of mass of the alkaline earth oxide as these oxides are replaced in the order MgO to BaO. The cut-off wavelengths ($\lambda_{cut-off}$) increased within each series and consequently the optical band gap (E_{opt}) values decreased with the substitution of alkaline earth oxides. The absorption edge is generally determined by the strength of oxygen bond in the glass network. The red shift in cut-off wavelengths and decrease in E_{opt} values with the substitution of alkaline earth oxides in the MO-B$_2$O$_3$ network is attributed to (i) formation/conversion of BO$_3$ triangular units into BO$_4$ tetrahedral units [FTIR spectra confirmed these facts- (Ramadevudu et al., 2011)] and (ii) increase in molecular mass of RO oxides. In addition to this, there could be formation of diborate, triborate and

tetra borate groups in the glass network which might have decreased the E_{opt} values. The optical band, cut-off wavelength and Urbach energy values of the present glass samples are consistent with the values reported for various glasses (Sanghi et al., 2004; Agarwal et al., 2003). The shift of $\lambda_{cut-off}$ to higher wavelengths and decrease in E_{opt} indicate the increase in non-bridging oxygen atoms (NBO) in MO-B_2O_3 glass network with gradual replacement of alkaline earth oxides. The substitution might have increased the breakage of glass network and might have increased the concentration of NBOs. The oxygen ions that act as bridges between the structural units in the glass structure are called bridging oxygens (BO). The addition of network modifiers such as alkaline earth oxides breaks these bridges and creates non-bridging oxygens (NBO). These oxygen ions carry a partial negative charge and are connected to structural unit only at one end in the glass network. As NBOs are more excited, the band gap is decreased (Rajasree and Krishna Rao, 2011). Thus decrease in E_{opt} values and increase in Urbach energies confirm an increase of disorder in the glass network and consequently there will be more extension of the localized states within the band gap as suggested by Mott and Davies (Mott and Davis, 1971).
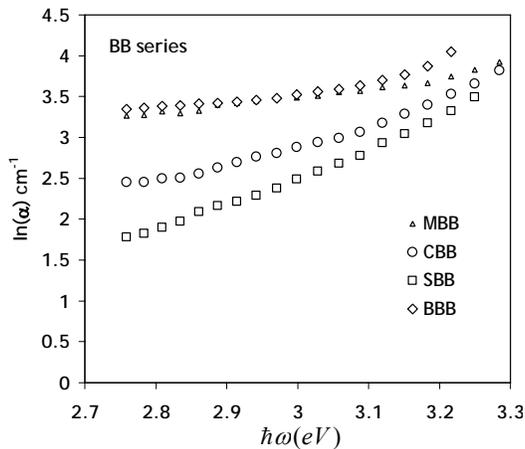

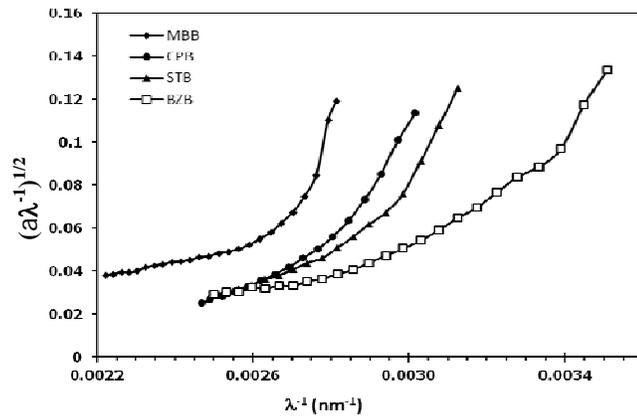Figure 3. *ln*α(ω) vs $\hbar\omega$ plots for BB series of glass samples

Figure 4. ASF plots of some glass samples

Table.1. Glass composition, cut-off wavelength ($\lambda_{cut-off}$), optical band gap values (E_{opt}), Urbach energy (ΔE) and refractive indices (*n*) values of the glass systems

Glass	Glass Series	$\lambda_{cut-off}$ (nm) ($\pm 5nm$)	E_{opt} (eV) (± 0.05)	E_{opt}^{asf} (eV)(± 0.02)	ΔE (eV) (± 0.005)	n_{opt} (± 0.02)	n_{LCR} (± 0.02	Reference
10MgO-40ZnO-50B$_2$O$_3$ (MZB)		245	3.42	4.02	0.588	2.290	2.185	Present
10CaO-40ZnO-50B$_2$O$_3$ (CZB)		247	3.26	3.71	0.651	2.330	2.288	Present
10SrO-40ZnO-50B$_2$O$_3$ (SZB)	ZB	250	2.98	3.53	0.738	2.400	2.382	Present
10BaO-40ZnO-50B$_2$O$_3$ (BZB)		276	2.70	3.22	0.874	2.480	2.487	Present
10CaO-40TeO$_2$-50B$_2$O$_3$ (CTB)		315	3.39	3.41	0.312	2.300	2.218	Present
10SrO-40TeO$_2$-50B$_2$O$_3$ (STB)	TB	320	3.22	3.28	0.399	2.350	2.340	Present
10BaO-40TeO$_2$-50B$_2$O$_3$ (BTB)		325	2.94	3.03	0.434	2.420	2.395	Present
10MgO-40PbO-50B$_2$O$_3$ (MPB)		321	3.45	3.39	0.277	2.290	2.155	Present
10CaO-40PbO-50B$_2$O$_3$ (CPB)		324	3.30	3.34	0.289	2.320	2.351	Present
10SrO-40PbO-50B$_2$O$_3$ (SPB)	PB	327	3.20	3.25	0.399	2.350	2.405	Present
10BaO-40PbO-50B$_2$O$_3$ (BPB)		336	3.14	3.19	0.420	2.360	2.575	Present
10MgO-40Bi$_2$O$_3$-50B$_2$O$_3$ (MBB)		350	3.19	3.23	0.256	2.350	2.353	Present
10CaO-40Bi$_2$O$_3$-50B$_2$O$_3$ (CBB)		353	2.99	3.12	0.268	2.400	2.420	Present
10SrO-40Bi$_2$O$_3$-50B$_2$O$_3$ (SPB)	BB	361	2.81	3.00	0.285	2.450	2.440	Present
10BaO-40Bi$_2$O$_3$-50B$_2$O$_3$ (BPB)		377	2.74	2.78	0.333	2.478	2.502	Present
20CaO-80B$_2$O$_3$		375	2.37		1.330			(Sanghi et al., 2004)
20CaO-30Bi$_2$O$_3$-50B$_2$O$_3$		395	2.14		0.970			(Sanghi et al., 2004)
10SrO-30ZnO-50B$_2$O$_3$-0.1CuO			4.136		0.341			(Sumalatha et al., 2011)

3.2. Refractive Index

The refractive indices (n) of the samples are evaluated from the optical band gap values (E_{opt}) using the relation proposed by Dimitrov and Sakka (Dimitrov and Sakka, 1996; Eraiah, 2006)

$$\frac{n^2-1}{n^2+2} = 1 - \sqrt{\frac{E_{opt}}{20}}$$

(8)

The refractive index values calculated from the equation (8) are given in table.1. The refractive index values quoted corresponds to the respective λ_g values of the present glass samples. However there are chances of creeping small errors in the estimation of E_{opt} *as well as in 'n'* owing to extrapolation $(\alpha h\nu)^{1/2}$ vs $(h\nu)$ plots.

Refractive index values increased almost linearly within each series as alkaline earth oxides are substituted progressively from MgO to BaO in glass matrix. The decrease in optical band gaps and increase in refractive index values are in agreement with the reported values (Honma et al., 2002; Dimitrov et al., 2002). The observed variation in refractive index (n) values is small indicating no significant changes in the basic MO-B_2O_3 glass network with the replacement of alkaline earth oxides. The slight increment of the refractive index values can be attributed to the replacement of alkaline earth oxides of increasing mass. The increment in the refractive index is assigned to increase in density and also increase in dielectric constant in each series.

3.3. Electronic Polarizability and Optical Basicity
3.3.1. Electronic Polarizability
The average molar refraction (R_m-expressed in cm^3/mol) for the glasses is given by the Lorentz- Lorentz equation (Yasser et al., 2010)

$$R_m = \left[\frac{n^2-1}{n^2+2}\right]\frac{M}{d} = \left[\frac{n^2-1}{n^2+2}\right] V_M$$

(9)

where the quantity $[(n^2-1)/(n^2+2)]$ is called the reflection loss, M is molecular weight, d is density and $M/d = V_m$ is the molar volume. According to the Clausius-Mosotti relation, molar polarizability of the materials (α_m x10^{-24}cm^3) is given by the relation

$$\alpha_m = \left[\frac{3}{4\pi \text{ N}}\right] R_m$$

(10)

where 'N' is the Avogadro's number. The electronic polarizability of oxide ions $\alpha_O^{2-}(E_{opt})$ has been calculated using the equation proposed by Dimitrov and Sakka (1996).

$$\alpha_{O^{2-}}(E_{opt}) = \left[\left(\frac{V_M}{2.52}\right)\left(1-\sqrt{\frac{E_{opt}}{20}}\right) - \sum\alpha_i\right](N_{O^{2-}})^{-1}$$

(11)

$$\alpha_{O^{2-}}(n) = \left[\frac{R_M}{2.52} - \sum\alpha_i\right](N_{O^{2-}})^{-1}$$

(12)

where $\sum\alpha_i$ in the above equation is molar cation polarizability and $N_{O^{2-}}$ is the number of oxide ions in the chemical formula. For the glass sample 10MgO-40ZnO-50B_2O_3, the value of $\sum\alpha_i$ is given by $[0.1\alpha_{Mg}+0.4\alpha_{Zn}+2(0.5)\alpha_B]$. The molar cation Polarizability (α) values of Mg^{2+}, Zn^{2+} and B^{3+} ions are respectively $\alpha_{Mg} = 0.094$Å^3, $\alpha_{Zn} = 0.283$Å^3 and $\alpha_B = 0.002$Å^3 (Dimitrov et al., 1996). Here $\alpha_O^{2-}(E_{opt})$ and $\alpha_O^{2-}(n)$ are electronic polarizability of oxide ions calculated from optical band gap and refractive index data.

The average oxide polarizability of ZnO, TeO_2, PbO, Bi_2O_3 is large and above 3Å^3 and their cation field strength is small. The cation field strength of alkaline earth oxides MgO, CaO, SrO and BaO is almost around the same order. The cation polarizability of Zn^{2+}, Pb^{2+}, Te^{4+}, Bi^{3+} is also high. So the present glass samples, as excepted have shown higher values of electronic polarizability α_O^{2-}. The cation polarizability values of glasses are taken as constant and equal to free ion values (Dimitrov et al., 2002). It is observed that α_O^{2-} values calculated from E_{opt} are larger than that of the values calculated from refractive index values and are in agreement with each other and consistent with the reported values (Yasser et al., 2008). The higher values of density and electronic polarizability observed in these glass systems can be attributed to the presence of Zn^{2+}, Pb^{2+}, Te^{4+}, Bi^{3+} ions (El-Kheshen and El-Batal, 2008).

The values of molar refraction (R_m), molar polarizability (α_m), electronic polarizability of oxide ions α_O^{2-} are given in table.2. An increase in the values of R_m, α_m, α_O^{2-} and oxygen packing density are observed with the substitution of alkaline earth oxides in the glass matrix. The molar refraction increased with the increase in refractive index which in turn increased oxide ion polarizability and electronic polarizability. The increase in molar refraction (R_m) and refractive index (n) accompany increase in polarizability. Hence refractive index of the present glasses not only depends on the density values but also on the polarizability values of the glasses. The density values of the present glasses samples are given elsewhere (Ramadevudu et al., 2011). The replacement of

alkaline earth oxides in MO-B_2O_3 glass network causes increase in R_m, α_m, and α_O^{2-} values which is assigned to increase in molar refraction (Yasser et al., 2008).

A condition for predicting metallic or insulating behavior in the condensed state matter is metallization criterion (Pradeesh et al., 2008), $M = 1 - \dfrac{R_m}{V_m}$. If $R_m/V_m > 1$, then the materials show metallic nature and if $R_m/V_m < 1$ they exhibit insulating behaviour. The so-called metallization parameter values of the present glasses are found to be less than one and are given in Table 2. Hence the present glasses systems with their metallization parameter values should exhibit insulating nature. These glass samples are poor electronic conductors and have shown ionic conductivity (from a.c. conductivity studies on these glass samples, whose results are not discussed in this paper).

Table 2. Molar refraction (R_m), metallization parameter ($1-R_m/V_m$), molar polarizability (α_m), oxide ion polarizability (α_O^{2-}) and oxygen packing density (OPD) values of the glass samples.

Glass	R_m (cm³/mol)	$1-R_m/V_M$	α_m $x10^{-24}$ cm^3	$\alpha_o^{2-}(E_{opt})$ Å³	$\alpha_o^{2-}(n)$ Å³	OPD g-atom litre⁻¹
MZB	19.140	0.414	7.595	2.137	2.134	61.218
CZB	19.388	0.404	7.693	2.152	2.152	61.501
SZB	19.402	0.387	7.699	2.158	2.153	63.231
BZB	19.425	0.368	7.708	2.161	2.154	65.062
CTB	22.550	0.412	8.949	1.835	1.836	62.630
STB	22.749	0.399	9.027	1.837	1.845	63.425
BTB	23.063	0.382	9.152	1.852	1.857	64.326
MPB	20.130	0.455	7.988	2.064	1.976	54.795
CPB	20.238	0.412	8.031	1.897	1.978	59.701
SPB	20.284	0.399	8.049	1.898	1.979	60.606
BPB	20.765	0.364	8.240	1.900	2.006	61.162
MBB	27.810	0.409	11.036	2.583	2.556	59.511
CBB	28.014	0.387	11.116	2.587	2.567	61.309
SBB	28.149	0.375	11.170	2.589	2.568	62.181
BBB	28.164	0.369	11.176	2.590	2.569	62.780

The oxides SrO, BaO, PbO, and Bi_2O_3 posses very high oxide ion polarizability, as they belong to very ionic or very basic oxides group. The valency of metal atoms in PbO, Bi_2O_3, TeO_2 increases as 2, 3 and 4 respectively. The three atoms carry lone pairs in their bonded states. The ion pairs are sources for electronic polarization. Therefore the values of R_m and α_O^{2-} within and across the series has increased in the order Zn< PB<TB<BB. BB series of glass systems have shown highest values of refractive index, R_m, α_m and α_O^{2-} when compared to other glass series. This is due to higher polarizability of Bi^{3+} ions. The increment in the values of electronic polarizability of oxide ions α_O^{2-} when alkaline earth oxides are successively replaced may also be due to increase in the total number oxygen atoms of the glass composition $ZnO(200)=PbO(200)<TeO_2(240)< Bi_2O_3(280)$.

3.3.2. Optical Basicity

The degree of acidity or basicity of glass is related to the electron donor power of oxygen atom. Oxides with low electron donating power having high chemical hardness are acids. Those having high electron density and weak chemical hardness are bases. The theoretical optical basicity (Λ_{th}) values of the present glass samples are calculated by the following relationship

$$\Lambda_{th} = X_{RO}\Lambda(RO) + X_{MO}\Lambda(MO) + X_{B_2O_3}\Lambda(B_2O_3) \tag{13}$$

where X_{MgO}, X_{PbO} and $X_{B_2O_3}$ are the proportions of oxide atoms that each oxide in the composition contribute to the stoichiometry of the glass. The optical basicity values of individual oxides are taken from the literature and are given by $\Lambda(B_2O_3) =0.425$, $\Lambda(MgO=0.78$ and $\Lambda(PbO)= 1.19$. For various oxide ions Duffy ((Duffy, 1989) proposed the following relationship between the oxide ion polarizability (α_O^{2-}) and optical basicity (Yasser et al 2010).

$$\Lambda = 1.67\left(1 - \frac{1}{\alpha_O^{2-}}\right) \tag{14}$$

The above relationship gives general trend of increase in the oxide ion polarizability with increasing optical basicity. The theoretical optical basicity values calculated using equation (13) and equation (14) with α_O^{2-} *(E_O) and* α_O^{2-} *(n)* values designated as $\Lambda(E_O)$ and $\Lambda(n)$ respectively are presented in table.3. There is a good matching between $\Lambda(E_O)$ and $\Lambda(n)$ values. However these values are higher compared to so called theoretical basicity $\Lambda_{th.}$

   It is clear from Table 3 that there is an increase in optical basicity values of present glass samples in each series. In the present glasses, BB series have shown higher values of optical basicity as it has higher polarizability and large ionic radius. Similar results have been reported in the literature (Yasser et al., 2008) earlier.

   In oxide glasses oxygen oxidation state is usually -2. However oxygen ion O^{2-} is unstable and ionic polarizability (α_O^{2-}) takes different values instead of a single value like stable halogen ions. The charge on oxygen ion varies according to bonding in the glass network. The composition of the glass determines the amount of negative charge on the oxide ion. The negative charge of oxygen in a given glass series may gradually increase or decrease and thereby optical basicity gives the extent of negative charge carried by the oxygen ion. The slight variation of optical basicity values of the present glass samples show that the charge on the oxygen ions in network is slightly modified.

3.3.3. Interaction Parameter (A_{th}) and Oxygen Packing Density

   The polarizability state of an average oxide ion can be described by the interaction parameters (A_{th}) proposed by Yamashita and Kurosawa (Yamashita et al., 1955; Dimitrov et al., 2000; Pauling, 1927). Dimitrov and Komatsu applied the interaction parameter *A* to describe the polarizability state of an average oxide ion in numerous simple oxides and its ability to form an ionic or covalent bond with the cation. The interaction parameter is a quantitative measure of the inter-ionic interaction of negative ions such as F^- and O^{2-} with the nearest neighbors. The interaction parameter *A* for a given cation-anion pair, represents the charge overlapping of the negative ion with its nearest positive neighbor. The theoretical interaction parameter A_{th} is calculated on the basis of the following equation (Dimitrov et al., 2000):

$$A_{th} = X_{MgO}\, A_{MgO} + X_{ZnO}\, A_{ZnO} + X_{B_2O_3} A_{B_2O_3} \tag{15}$$

where A_{MgO}, A_{ZnO} and $A_{B_2O_3}$ are the interaction parameters of the respective oxides. The values $A_{MgO}=0.156\mathring{A}^{-3}$, $A_{ZnO}=0.040\ \mathring{A}^{-3}$, $A_{B_2O_3}=0.244\mathring{A}^{-3}$ are taken from literature (Duffy, 1989). The refractive index based interaction parameter *A(n)* can be expressed sum of the contributions from each cation of the given oxide to the total interaction for an averaged cation-anion pair in the glass matrix (Honna et al 2002).

$$A(n) = X_{MgO}\left[\frac{\alpha_{f^-} - \alpha_{O^{2-}}}{(\alpha_{Mg^{2+}} + \alpha_{f^-})(\alpha_{Mg^{2+}} + \alpha_{O^{2-}})}\right] + X_{ZnO}\left[\frac{\alpha_{f^-} - \alpha_{O^{2-}}}{(\alpha_{Zn^{2+}} + \alpha_{f^-})(\alpha_{Zn^{2+}} + \alpha_{O^{2-}})}\right] + X_{B_2O_3}\left[\frac{\alpha_{f^-} - \alpha_{O^{2-}}}{2(\alpha_{B^{3+}} + \alpha_{f^-})(\alpha_{B^{3+}} + \alpha_{O^{2-}})}\right] \tag{16}$$

where $\alpha_{f,}$ the electronic polarizability of a free oxide ion is taken as $0.921\mathring{A}^3$ (Pauling, 1927). The interaction parameter $A(E_O)$ calculated from optical band gap can also be expressed in the similar manner. The values of interaction parameter A_{th}, $A(n)$ and $A(E_O)$ are calculated using the equations (15) and (16) and are presented in table.3.

Table.3 Theoretical basicity (Λ_{th}), basicity from E_{opt} and refractive index $\Lambda(E_o)$ and $\Lambda(n)$ and interaction parameter (A_{th} and A_n) values of the glass systems

Glass	Λ_{th}	$\Lambda(E_o)$	Λ_n	A_{th} $(\mathring{A}^{-3})$	A_n $(\mathring{A}^{-3})$
MZB	0.548	0.890	0.847	0.077	0.0759
CZB	0.558	0.895	0.879	0.072	0.0699
SZB	0.564	0.898	0.885	0.070	0.0682
BZB	0.566	0.903	0.886	0.069	0.0653
CTB	0.617	0.933	0.933	0.073	0.0754
STB	0.621	0.963	0.963	0.067	0.0681
BTB	0.623	0.963	0.963	0.067	0.0661
MPB	0.588	0.897	0.832	0.070	0.0491
CPB	0.599	0.900	0.842	0.065	0.0477
SPB	0.602	0.902	0.845	0.063	0.0456
BPB	0.606	0.904	0.861	0.062	0.0419
MBB	0.765	1.015	1.015	0.064	0.0229
CBB	0.773	1.019	1.016	0.063	0.0229
SBB	0.777	1.021	1.018	0.062	0.0224
BBB	0.778	1.033	1.023	0.062	0.0216

Yamashita-Kurosawa's interaction parameter *A* is a representative quantity of oxide ion polarizability or optical basicity which is the origin of chemical bond in simple oxides. Hence interaction parameter (*A*) might be a quantity useful to predict inter ionic interactions in multi component oxide glasses on the basis of their refractive index (Dimitrov et al, 2010). It was established that interaction parameter *A* decreases in the sequence MgO→CaO→ SrO→BaO. In the present glasses the interaction parameter decreased in each series with replacement of alkaline earth oxides (Zhao et al, 2007) in the order MgO→CaO→ SrO→BaO.

Based on the studies reported by Dimitrov and Komatsu (2010), the present glasses either belong to the group of glasses formed by glass-forming acidic and conditional glass-forming basic oxides or glasses formed by two basic oxides as they have shown high refractive index, high oxide ion polarizability, high optical basicity and low interaction parameter. The present glasses show the formation of strong covalent bonds between the oxygen and metal ions R-O and M-O-M bonds with increased ionicity. The oxygen packing density (OPD) of the samples is calculated from the density (ρ) data using the formula (Vasantharani and Vijayalakshmi, 2011).

$$\text{Oxygen Packing density} = \frac{\rho}{M} \text{x O}_n \tag{17}$$

where O_n is number of oxygen atoms per formula unit and *M* is the molecular weight of the glass expressed as the mole fractions of the oxides multiplied their molecular weights. The oxygen packing density within each series is increased as the number of oxygen atoms available in the glass composition is increased [ZnO(200)=PbO(200)<TeO$_2$(240)< Bi$_2$O$_3$(280)].

4. Conclusion

The values of optical band gaps and from the so-called metallization criteria, M=1–R$_m$/V$_m$ <1 it is concluded that the present glass samples behave as indirect band optical materials. The red shift in the $\lambda_{\text{cut-off}}$ values and decrease in optical band gaps with gradual replacement of alkaline earth oxides in the MO-B$_2$O$_3$ network is attributed to conversion of BO$_3$ triangular units into BO$_4$ tetrahedral units and increase in molecular mass of RO oxides. The decrease in E_{opt} confirms extension of more tails of localized states into the band gap and consequently the Urbach energy values increased. The observed variations in the values of optical band gaps and oxide ion polarizability are small and hence structural changes occurred in the glass network with the replacement of alkaline earth oxide are also small. It can be concluded that the alkaline earth oxides being in low concentration, occupied glass network modifier (GNM) position and thus acted as glass modifiers. The interaction parameter decreased in each series with substitution of alkaline earth oxides as predicted in the order MgO→CaO→ SrO→BaO. The increase in the values of R_m, α_m, α_O^{2-} and optical basicity with the replacement of alkaline earth oxides in MO-B$_2$O$_3$ glass network confirms increase in the number of NBOs in the glass which in turn caused increment in refractive index values.

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