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Optical and Electrical Properties of Borate Glasses in the System: $B_2O_3/Na_2O/TiO_2$

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Abstract: Dielectric constant, ϵ , loss $\tan \delta$ and, dc, conductivity of $B_2O_3/Na_2O/TiO_2$ glass system have been investigated with varying the concentrations of TiO_2 . The optical properties of this glass system were studied with respect to the density, refractive index, optical energy gap, Urbach energy and polarizability. The oxide ion polarizabilities were deduced from two different experimental quantities viz., refractive index and optical band-gap energy. Results obtained are discussed in terms of the glass structure.

Key words: Optical properties, dielectric constant, oxide ion polarizabilities

INTRODUCTION

Recently oxide glasses receive a considerable attention in view of their potential for use as laser hosts, in fiber and as nonlinear optical materials (Fuxi, 1992; Wang *et al.*, 1995; Vogel *et al.*, 1991). The studies on glasses of metal oxides are relatively meager due to difficulties in identifying and preparing such glasses although they show interesting electronic and nonlinear optical properties, (Sae *et al.*, 1993; Shelpy, 1988; Miyaji *et al.*, 1996). The present research pertains to optical and electrical properties glass systems. Dimitrov and Sakka (1996) have shown that for simple oxides, the average electronic oxide polarizability calculated on the basis of two different properties. Furthermore, they correlated between the linear refractive index and optical band-gap energy. In the present study we examine whether their observations can be extended to glasses formed from simple oxides. This is of a particular interest especially when the relevant quantities can be experimentally obtained for glass systems and polarizability values related to glasses are of value for developing glass systems with nonlinear optical properties. To our knowledge an attempt of this kind is being reported for the first time. We chose to $B_2O_3-Na_2O-TiO_2$ glass system for our study, as the oxide ion polarizability for TiO_2 is relatively high. In addition we report dielectric constant, the loss factor and the dc electrical conductivity of this suggested glass system.

MATERIALS AND METHODS

The glass samples were prepared using appropriate amounts of grade reagents boron oxide, sodium oxide and

titanium oxide, the weighted quantities of the starting materials for glass batch corresponding to the glass composition were mixed homogeneously. The mixture was placed in a ceramic crucible and heated slowly in an electric furnace to 1100°C. The temperature was raised gradually depending upon the glass composition. The crucible containing the melt was constantly agitated to ensure homogeneous mixing. Sufficient time was allowed for the melt to become visibly homogeneous and bubble free. The melt was rapidly quenched to room temperature between two stainless-steel plates. There was no noticeable reaction of the melt with crucible walls. The typical weight loss on melting under the experimental conditions can be neglected with respect to the values quoted for the components. The composition of the glass system was prepared in a series of 4 samples as shown in Table 1.

The samples were annealed at a temperature below glass transition temperature and subsequently polished with commercial media and water free lubricant. The glass samples were obtained with good transparency and uniform thickness of 4.0 mm. The dc electrical conductivity of prepared glasses, the polished glass samples were carbon painted on both sides and kept in a cell for good contacts. The value of applied voltage = 3.0 V and the voltage drop across the sample and across a standard resistor were measured. Space-charge effects were minimized by using a very low field, which was applied only briefly. The temperature of the glass sample was controlled and measured by a chromel-alumel thermocouple with an accuracy of $\pm 1\%$. It was observed that the conductivity behavior was always the same and the values of conductivity were within $\pm 2\%$ error in different runs. The densities of the samples were

Table 1: Compositions, densities, molar volumes, refractive indices, molar refraction, polarizability, Urbach energy and optical energy of the prepared glasses

System composition (mol%)	Density (g cm ⁻³)	Molar volume (cm ⁻³)	Refractive index (n)	Polarizability		Molar refraction R _m (mol ⁻¹ cm ³)	Optical basicity (Δ)	Activation energy E _a in (eV)	Optical energy E _{opt} eV
				α ₀ ² in 10 ⁻²⁴ cm ³	α ₀ ² (n)				
80B ₂ O ₃ 20Na ₂ O ---	2.28	31.5	1.7	2.3	1.6	46.5	0.5	1.28	3.3
79B ₂ O ₃ 20Na ₂ O 1.0TiO ₂	2.32	30	2	2.39	1.7	45.69	0.51	1.28	3.1
77.5B ₂ O ₃ 20Na ₂ O 2.5TiO ₂	2.35	28.5	2.1	2.4	1.9	45.1	0.53	1.28	3
75B ₂ O ₃ 20Na ₂ O 5.0TiO ₂	2.47	28	2.2	2.5	2	43	0.57	1.28	3

measured by Archimedes method using toluene as the immersion liquid. The refractive index was measured by using the prism spectrometer. The absorption spectra were measured using Shimadzu (3031) spectrophotometer.

Also an LCR bridge (Hioki model 3031, Japan) was used to carry out the dielectric measurements. The samples were coated with Carbon coatings for obtaining good contact. The accuracy in the measurements of dielectric constant ε' is ~±0.001 and that in dielectric loss tan δ is ~10⁻⁴.

THEORETICAL CONSIDERATIONS

The optical band-gap and Urbach energies of the glasses were obtained from the absorption spectra. the absorption coefficient α(ω) is given by Dayanand *et al.* (1994).

$$\alpha(\omega) = \frac{1}{d} \cdot \log(I_0/I) \tag{1}$$

Where d is the thickness of the glass sample in cm, T and A are the spectral transmittance and absorbance measured by the spectrophotometer as shown in fig. 1, for one sample of the glass series, as an example, α(ω) is related to E_p, the optical band-gap is given by;

$$\alpha(\omega) = \text{Const.} \left[\frac{\eta\omega - E_p}{\eta\omega} \right] \tag{2}$$

Thus (αhω)^{1/2} in cm^{-1/2}ev^{1/2} units is plotted against ηω. The Urbach energies ΔE were obtained from the slopes of the linear region of the plots of ln α(ω) against ηω.

Another optical parameter used as a measure of acidity of glass called the theoretical optical basicity of glass is given by Duffy and Ingram (1975)

$$\Lambda = 1 - \sum_i \left(\frac{Z_i r_i}{2} \right) \left(1 - \frac{1}{\gamma_i} \right) \tag{3}$$

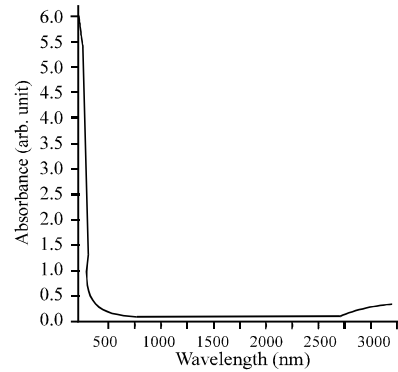


Fig. 1: The absorbance with different wavelength (nm) of the glass with composition 77.5B₂O₃- 20Na₂O- 2.5 TiO₂ the sample thickness (4 mm) as an example

Where z_i is the valence of ith, cation, r_i is the ratio of the number of ith cations to that of oxide ions, γ_i is the basicity moderating parameter given by;

$$\gamma_i = 1.36(\chi_i - 0.26) \tag{4}$$

Where χ_i is Pauling's electro negativity of the ith atom. The molar refraction is calculated using the following relationship (Fanderlik, 1983);

$$R_m = \frac{(n^2 - 1)}{(n^2 + 2)} V_m \tag{5}$$

Where n is the refractive index and V_m is the molar volume of the glass. The molar volume calculated from the density and the average molecular weight of the composition.

RESULTS AND DISCUSSION

The range of the glass formation in B₂O₃ - Na₂O - TiO₂ system extends up to (TiO₂ = 5 mol%) and all the glasses samples prepared are transparent. The compositions in mol %, density (ρ), average molecular weight (M), refractive index and molar refraction for the glasses under study were determined.

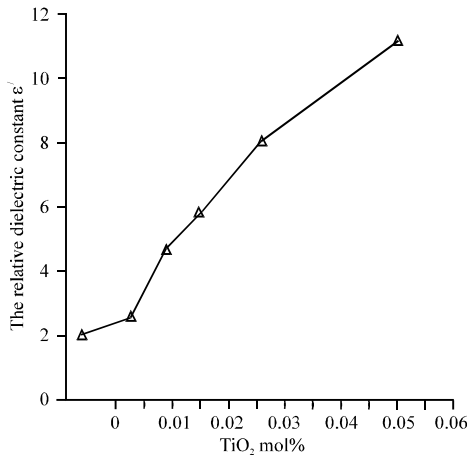


Fig. 2: The variation of the relative dielectric, ϵ' with TiO_2 mol%

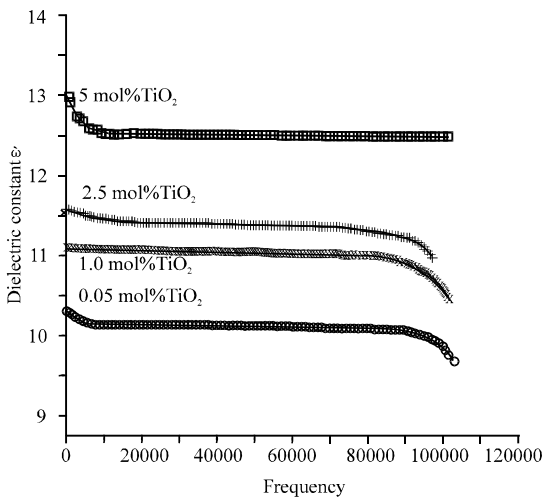


Fig. 3: The variation of dielectric constant versus the frequency for the prepared glasses

Table 1 reports the density (ρ), molar volume (V_m), average molecular weight (M), refractive index (n) and molar refractivity (R_m), optical basicity (Λ), oxide ion polarizability (α_o^2), optical band gap (E_{opt}) and Urbach energy (ΔE) for B_2O_3 - Na_2O - TiO_2 glasses.

The dielectric constant ϵ' , of glasses samples depends on electronic, ionic and dipole orientation contribution to the polarizability. The ionic polarizability arises from the displacement of ions of opposite sign from their regular lattice sites, resulting from the applied electric field, as well as from the deformation of the electronic shells, resulting from the relative of the ions. The behavior of ϵ' our system described in Fig. 2 may be attributed at low frequency to the polarizability arising

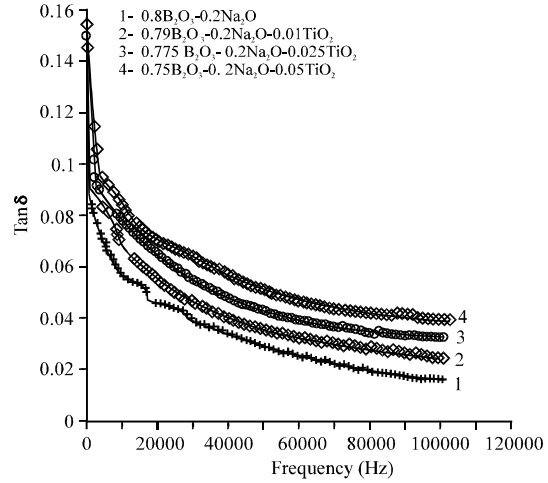


Fig. 4: The variation of $\tan \delta$ with frequency versus the temperature of prepared glasses

from the contribution of multi components in the glassy system. As the frequency increases the ionic and orientation sources of polarizability decreases and finally disappear due to the inertia of the molecules and ions. The electronic polarizability α_e is the only process which follows the alternative fields at the visible spectrum. The ionic polarizability α_i , contributes to the polarizability at high frequency. The space charge α_s and α_o contribute to the polarizability of the suggested glass system at low frequency (~ 1000 Hz), hence the dielectric constant ϵ' increases as α_s and α_o increases by increasing the ratio of TiO_2 in the glass system as shown in Fig. 2.

The relative dielectric constant ϵ_r' for our glass system lie between the two values 3.5 to 11 at $\sim 10^5$ Hz, as shown in Fig. 3.

The Fig. 4 shows the change of $\tan \delta$ with the applied frequency in Hz. The frequency variation of $\tan \delta$ often displays peaks whose positions depend on the glass composition. A typical spectrum of $\tan \delta$ values may be as little as 0.002 in the low loss region compared to as much as 0.03 in the high loss region. According to Jayaseelan *et al.*, (2004), loss split into four components; firstly, conduction loss due to the mobility of network modifiers. With the increase in applied field frequency, the ions are increasingly unable to respond to the field. Hence this component decreases with frequency as shown in Fig. 4.

Likewise, when the mobility increases with temperature, the conduction loss component increases with temperature too. Secondly the relaxation losses that occur because of the relaxation process. These losses can be observed in the low frequencies. Thirdly the resonance losses occur when the applied frequency is the same as

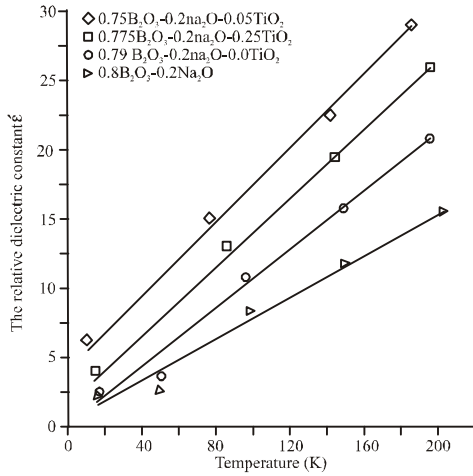


Fig. 5: The variation of the relative dielectric constant, ϵ' , of the prepared glasses versus the temperature

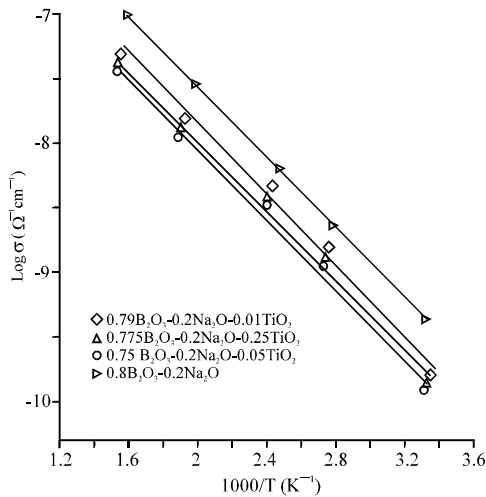


Fig. 6: The electrical conductivity, $\log \sigma$, versus $1000/T$ of prepared glasses

the characteristics vibration frequency of the atoms. And finally, the deformation losses occur when the atomic structure begins to vibrate. Accordingly, the dielectric loss at low and moderate frequency takes relatively high values due to the contribution of both ion jump and conduction loss in addition to the electronic polarizability. At high frequency the ion vibrations is the main source of dielectric loss, Jayaseelan *et al.*, (2004).

Also the relative dielectric constant ϵ'_r for our glass system increases with increasing temperature as shown in Fig. 5.

The ac conductivity σ is calculated at different temperatures using the following relationship;

$$\sigma = \omega \epsilon_0 \epsilon' \tan \delta \quad (6)$$

Where, ϵ_0 , is the vacuum dielectric constant for different frequencies.

Figure 6 shows the plot of $\log \sigma$ against $1/T$ for the prepared glasses system ($B_2O_3 - Na_2O - TiO_2$). From these plots the activation energy for conduction in the high temperature region was obtained over which a near linear dependence of $\log \sigma$ with $1/T$.

Also the dc conductivity can be determined from the measured values of R_p (real part) i.e., the parallel resistance (the equivalent circuit of the glass sample) as follows;

Since $Z^* = Z' - jZ''$ is the complex impedance of equivalent circuit for the sample of the glass system, so

the real part of conductivity is $\sigma = \frac{G_p \times d}{A}$, where $G_p = 1/R_p$ called the conductance, d is the thickness sample, A is the area of contact of the sample and the electrode holder, in or work ($A = 0.5 \text{ cm}^2$). The electrical conductivity of glasses may be related to temperature by the Arrhenius equation;

$$\sigma = \sigma_0 e^{-E_a/kT} \quad (7)$$

Where, σ is the electrical conductivity of the sample, σ_0 is the pre- exponential factor around $10^2 - 10^3$ for glass. E_a is the activation energy and K is the Boltzmann constant. The plots of $\log \sigma$ against reciprocal of temperature for different glass samples are reproduced in Fig. 6 and show a linear behavior in the temperature range under study. The activation energy E_a obtained from the slope are given in Table 1. Sodium borate oxide doped with titanium glass show a wide range of conductivity behavior were reported by Shelby (1988), furthermore the glasses such as fluoborates show relatively high conductivity attributed to ionic conduction of fluoride anions. The present glass shows also the latter behavior. For these glasses, the activation energies (E_a) are relatively higher and are of the order of 1.28 eV, as shown in Table 1. Temperature dependence of conductivity also shows a similar behavior. These results show that TiO_2 contributes to conductivity significantly in this ternary glass. An increase in content would result in an increase in covalent- linkages leading to a lowering of the band gap and hence increase in isothermal conductivity.

Assuming that molar refractivity (R_m) and polarizability α_m are additive quantities Dimitrov and Sakka obtained the relationship (1996).

$$R_p = pR_i + qR_{O^{2-}} = 2.52 \left[p\alpha_i + q\alpha_{O^{2-}} \right] \quad (8)$$

Where, R_i is ionic refraction of cation, $R_{O^{2-}}$ is the refraction of oxide ion, respectively. P and q denote the number of cation and oxide ion in the chemical formula A_pO_q . This relationship leads to;

$$\alpha_{O^{2-}}(n) = \left[\left(\frac{V_m}{2.52} \right) \frac{(n^2 - 1)}{(n^2 + 2)} - \sum_i p\alpha_i \right] q^{-1} \quad (9)$$

Duffy and Ingram (1995) put an experimental formula for obtaining the polarizability of oxide ion as a function of optical band gap as follows

$$\alpha_{O^{2-}}(n) = \left[\left(\frac{V_m}{2.52} \right) \left(1 - \frac{(E_{opt})^{1/2} - 1.14}{0.98} \right) - \sum_i p\alpha_i \right] q^{-1} \quad (10)$$

Using the Lorenz-Lorenz, Eq. (5) for simple oxides, Dimitrov and Sakka (1996) used the following linear relationship suggested by Duffy and Ingram (1975):

$$\sqrt{E_{opt}} = (4.472)[1 - (R_m / V_m)] \quad (11)$$

Substituting Eq. (11) in Eq. (8), these authors obtained the required relationship between $\alpha_{O^{2-}}(n)$ and E_{opt} . This formula was modified to the following relationship;

$$\sqrt{E_{opt}} = (1.23)[1 - (R_m / V_m)] + 0.98 \quad (12)$$

The values of $\alpha_{O^{2-}}$ for the glass system obtained from the experimentally measured refractive indices and optical bang-gap energies using the expressions (9) and (12), respectively are compared in Table 1. The result shows that there is close agreement in the polarizability values obtained from the two different experimental quantities. The agreement is particularly good in view of the possible errors in E_{opt} due to factors like thickness of the glass samples and the extrapolation method used for evaluating E_{opt} .

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samples and the extrapolation method used for evaluating E_{opt} . Our results further suggest that one should not come to conclusion on the polarizability of oxide ions in glasses simply from the values of the individual oxide components as other quantities such as R_m and V_m characteristics of the glass also influence the results. For instance, the oxide ion polarizability for the metal oxide such as the TiO_2 in order of $\sim 2.368 \times 10^{-24} \text{ cm}^3$. However, in glasses where this oxide is taken as the third component.

The widths (ΔE) of the tails of localized states within the optical band gap obtained in term of Urbach energy for the present glass system lie in the range reported earlier for other glasses. It is known that the broadening of the excitation levels at the absorption edge is dominated by the random internal electric fields due either to the lack of long-range order or presence of defects Elkholy, (2003). For the glass system under study, the least Urbach energy ($\Delta E = 0.79 \text{ eV}$) and sharp absorption edge is observed for 5 mol% TiO_2 . This suggests that defects in this glass are a minimum facilitating long range order resulting in the least Urbach energy

CONCLUSIONS

Present study reports some optical and electrical properties of B_2O_3 - Na_2O - TiO_2 glass system for different ratio of doping with TiO_2 content. We calculated the oxide ion polarizabilities ($\alpha_{O^{2-}}$) from two different quantities viz., refractive index and the optical band gap energy. The density, refractive index, polarizability, and optical basicity increase with increasing TiO_2 content in the prepared glasses. On the other hand, the molar volume, molar refraction and optical energy gap decrease with increasing TiO_2 content in the studied glasses. We concluded in the present study a large agreement between the summation of theoretical optical basicity of each component in the ternary prepared glass system and the optical basicity calculated as a function of the refractive index, n.

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