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The Estimation of Oxide Polarizability using the Electronegativity for $Li_2O:B_2O_3:SiO_2$ Glass System

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Abstract

Glass samples of the Lithium borosilicate $42.5Li_2O\cdot(57.5-x)\ B_2O_3$-$xSiO_2$, x=0-57.5 in the step of 5,7.5,10,20, were prepared by conventional melt-quench technique. The density and molar volume of some silicate glasses were determined in order to study their structure. Molar volume decreases linearly as mole % of B_2O_3 decreases. The refractive index and the energy gap, which have remarkable correlation. Molar refraction Molar polarizability, Average elecrtonegativity also decreases linearly as mole % of B_2O_3 decreases; except for B_2O_3 and SiO_2 they are smaller. In the present study, the electronic oxide polarizability of prepared ternary oxide glasses has been estimated on the basis of average optical electronegativity. The value of the oxide ion polarizability $\alpha_{O\text{-}2(Dimitrov)}$, $\alpha_{O\text{-}2(Reddy)}$, oxides ion polarizability as a function of refractive index $\alpha_{O\text{-}2(Dimitrov\ \&\ Sakka)}$, has a good correlation between them. The basicity, $\Lambda_{(Duffy\ \&\ Ingram)}$ and $\Lambda_{(Reddy)}$ determined by using the average electronegativity shows increasing behavior with increasing mol % of SiO_2; The values of basicity has a good correlation between them, except for B_2O_3 and SiO_2 they are larger in $\Lambda_{(Duffy\ \&\ Ingram)}$. The present research is another trend of the oxide ion polarizability and basicity determination for ternary glasses.

Keywords: *oxide ion polarizability, electronegativity, molar refraction, molar polarizability, basicity, density, molar volume, dielectric constant, band gap energy, ternary glasses.*

1. Introduction

One of the most important properties of materials, which are closely related to their applicability in the field of optics and electronics, is the electronic polarizability. An estimate of the state of polarization of ions is obtained using the so-called polarizability approach based on the Lorentz –Lorenz equation. Oxide glasses take a considerable attention in view of their potential for use as laser hosts, in fiber and as nonlinear optical materials (Varshneya, Chimalawong). [1;2] 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 (Vithal M.) [3]. (Dimitrov.v & Sakka) [4] have shown that for simple oxides, the average electronic oxide polarizability calculated on the basis of two different properties linear refractive index and optical band-gap energy shows remarkable correlation..

The present work on Lithium borosilicate ternary glass systems pertains to some new optical parameters. 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. A lithium borate glass system is chose for study, as the lithium borates glasses are promising materials have many applications in the electronics components.

2. Theoretical Considerations

2.1. Molar refraction and molar polarizability

The most familiar and widely used relationship in the polarizability approach is the Lorentz-Lorenz equation [5,6] . The Lorentz-Lorenz equation relates molar refraction R_m to refractive index n_m and molar volume V_m of the substance by,

$$R_m = [(n_m^2 - 1)/ (n_m^2 + 2)]\ V_m \qquad (1)$$

This equation gives the average molar refraction of isotropic substances, i.e., for liquids, glasses and cubic crystals. The Lorentz-Lorenz equation presents the polarizability, i.e., the magnitude of the response of the electrons to an electromagnetic field. The molar
refraction R_m has the dimension of a volume (cm^3/mol). When Avogadro's number A_v is introduced, the molar refraction R_m can be expressed as a function of molar polarizability α_m

$$R_m = 4\pi\alpha_m A_v/3 \qquad (2)$$

With α_m in ($Å^3$) this equation can be transformed to,

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

On the other hand, Duffy [7] has obtained an empirical formula that relates energy gap E_g to molar refraction R_m for a large number of simple oxides,

$$E_g = 20(1 - R_m/V_m)^2 \qquad (4)$$

This equation gives the explicit expression for R_m in respect to the band gap E_g.

2.2. Oxide ion polarizability and electronegativity

It is well known that the relative ability of an atom to draw electrons in a bond toward itself is called the electronegativity of the atom. Atoms with large electronegativities, such as F & O attract the electrons in a bond better than those that have small

electronegativities such as Na & Mg. The electronegativities of the main group elements are given by Asokamany and Manjula, [8] introduced the concept of average electronegativity and defined an average electronegativity parameter χ_{1av} in the following manner:

$$\chi_{lav} = \Sigma\, n_i\chi_i/N \qquad (5)$$

Σ over i takes values from 1to N

Where χ_i is the pauling electronegativity of element, n_i is the number of atoms of the i^{th} element and N is the number of elements present in the compound. In this connection Reddy [9] have derived the empirical relationship for the average electronic oxide ion polarizability as follows:

$$\alpha_{o-2} = 4.624\text{-}0.7569\ \chi_{lav} \qquad (6)$$

where χ_{lav} is the average electronegativity of the simple oxide. Reddy et al [6] have calculated α_{o2-} for many oxides and in general there is agreement with previously obtained data by Dimitrov. But it should be mentioned that polarizability of B_2O_3 ($2.426A^3$) and SiO_2 ($2.419A^3$) calculated by equation (6) seems to be too large.

Reddy et al [6] and Zhao et al [10] have applied the electronegativity approach to the same glasses already studied by Dimitrov and Komatsu [11] According to Reddy et al [6], the following empirical relations between oxide ion polarizability and average electronegativity is as follows:

$$\alpha_{o-2} = 4.519\text{-}0.3444\ \chi_{lav} \qquad (7)$$

Another formula for all binary oxide glass compositions except TeO_2 , GeO_2 and TiO_2 as a second oxide also was proposed as follows:

$$\alpha_{o-2} = (\chi_{lav} - 1.35)/(\chi_{lav} - 1.8) \qquad (8)$$

Where, χ_{1av} is the average electronegativity of binary oxide glass. On the other hand

Zhao.et al.[8] have introduced the optical electronegativity calculated from the refractive index to predict oxide ion polarizability of binary oxide glasses.

$$\alpha_{o-2} = 3.5\text{-}0.9\ \chi_{glass} \qquad (9)$$

It should be noted that the estimated values of by Reddy et al [6] and zhao et al [8] are in good agreement with the refractive index based oxide ion polarizability of the same glasses obtained by Dimitrov and Komatsu [12].

Assuming that molar refractivity (R_m) and molar polarizability (α_m) are additive quantities Dimitrov and Sakka [4] obtained the relationship:

$$R_p = pR_i + qR_{o2-} = 2.52lp\alpha_i + q\alpha_{o2-}l \qquad (10)$$

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 the following equation:

$$\alpha_{o2-}(n_m) = [(V_m/2.52(n^2\text{-}1)/(n^2\text{+}2)\text{-}p\alpha_i]q^{-1} \qquad (11)$$

where V_m is the molar volume of the glass sample.

2.3. Optical basicity and electronegativity

Another approach for prediction of the theoretical optical basicity of an oxide solid is based on the Pauling type electronegativity. Duffy and Ingram [13;14] have suggested that a good correlation exists between basicity Λ and electronegativity χ:

$$\Lambda = 0.75/(\chi\text{-}0.25) \qquad (12)$$

The optical basicity of main group elements holds well with the electronegativity rule but for other elements equation (12) must be used with caution, especially with transition metal and heavy metal oxides. Optical basicity values for K_2O, Na_2O, BaO, Li_2O, CaO, MgO, Al_2O_3, ZnO, SiO_2, B_2O_3, H_2O, P_2O_5, CO_2, SO_3, N_2O_5 and $C_{l2}O_7$ have been determined.

Reddy et al. [6] also derived the following empirical relationship for the optical basicity of simple oxides on the basic of average electronegativity:

$$\Lambda = 1.59 - 0.2279\chi_{1av} \qquad (13)$$

where χ_{1av} is the average electronegativity of the simple oxide. Reddy et al. [6] have calculated Λ for many oxides and in general there is agreement with previously obtained data by Duffy [10] and Dimitrov and Sakka [4]. But it should be mentioned that the optical basicities of B_2O_3 (0.928) and SiO_2 (0.926) calculated by equation (13) are not correct. Briefly, it seems that in the case of oxides the oxide ion polarizability is more sensitive quantity to the basicity of the oxides than the element electronegativity. The electronegativity does not take into account the real crystal structure of the oxide. It does not estimate the real distances of the chemical bonds in the structure under consideration. In contrast oxide ion polarizabilty is based on the experimentally obtained materials constant such as refractive index or energy gap which closely is related to the real electronic structure of the oxides.

3. Experimental Work

The glass samples were prepared using appropriate amounts of grade reagents boron oxide, lithium oxide and silicate oxide. The weighted quantities of the starting materials for glass system 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^{o}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 densities of the samples were measured using Archimede's method using toluene as immersion liquids with accuracy around ±1%. The samples were annealed at a temperature below glass transition temperature. Surfaces of glass samples are made perfectly plane and smoothened by 120 No. emery papers. The glass samples were obtained with a uniform thickness of 4.0- 5.0 mm. Thickness of the samples has been measured using digital vernier calipers with an accuracy of 0.0001mm.The prepared glasses were coated with silver painted on both sides and kept in a cell for good contacts. The temperature of the glass sample was measured by thermocouple with an accuracy of ± 1%. An LCR bridge was used to carry out the dielectric measurements. The accuracy in the measurements of dielectric constant is ~ ± 0.001. The composition of the glass system was prepared in a series of 10 samples as illustrated in Table (1) along with Density, Molar volume, Band energy gap, Refractive index and Dielectric constant.

Table1. Composition of glass samples with there names, Densities, Molar volumes, Band energy gaps Refractive index and Dielectric constants.

.

Name of samples	Composition in mol %			Density ρ (gm/cm^3)	Molar volume V_m (cm^3/mole)	E_g (eV)	Refractive index (n_m)	Dielectric constant (∈)
	Li_2O	B_2O_3	SiO_2					
LBS.1	42.5	57.5	0	2.249	23.447	1.15	3.24	10.500
LBS.2	42.5	52.5	5	2.25	23.224	0.55	3.999	15.993
LBS.3	42.5	47.5	10	2.25	23.012	0.95	3.426	11.736
LBS.4	42.5	37.5	20	2.249	22.599	0.93	3.447	11.882
LBS.5	42.5	30	27.5	2.25	22.165	1.11	3.275	10.723
LBS.6	42.5	27.5	30	2.251	20.99	1.01	3.369	11.350
LBS.7	42.5	20	37.5	2.25	21.211	1.08	3.296	10.862
LBS.8	42.5	10	47.5	2.25	21.423	1.11	3.271	10.700
LBS.9	42.5	5	52.5	2.251	21.837	1.04	3.336	11.131
LBS.10	42.5	0	57.5	2.25	22.271	1.18	3.212	10.320

4. Results and Discussions

Monotonically variation in density, molar volume, band energy gap, refractive index and dielectric constant is due to transformation of BO_3 triangle units to BO_4 tetrahedral units can be expected to increase the network linkage of the glass. The refractive index and the energy gap, shows remarkable correlation (Figure 1).

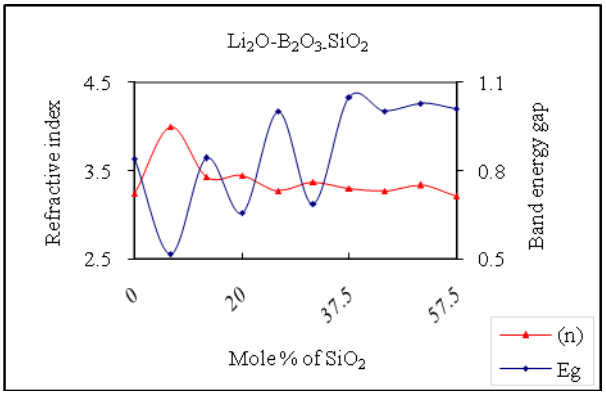

Figure1. Variation of band energy gap and refractive index with mol% of SiO_2

Variation of band energy gap and refractive index with increasing mol% of SiO_2, are exactly apposite to each other. This indicates that is due to break down of borate bonds to create non-bridging oxygen atoms.

The estimated values of the parameters molar refractivity (R_m), molar polarizability (α_m), average electronegativity (χ_{1av},), average electronic oxide ion polarizabilities $\alpha_{0\text{-}2(Dimitrov)}$, $\alpha_{0\text{-}2(Reddy)}$, oxides ion polarizability as a function of refractive index $\alpha_{o\text{-}2(Dimitrov\ \&\ Sakka)}$, and basicities ,$\Lambda_{(Duffy\ \&\ Ingram)}$ and $\Lambda_{(Reddy)}$ are reported as in Table(2).

From the values reported in Table (2) it is observed that the values of molar refractivity, molar polarizability, and average electronegativity are decreasing with increasing mol% of SiO_2 except in binary composition Li_2O-B_2O_3 (17.817 cm^3/mol, 7.063 10^{24} ions/cm^3, 0.352) and for Li_2O-SiO_2 (15.879 cm^3/mol, 6.296 10^{24} ions /cm^3, 0.384) their values are smaller this means that there are some correlation between molar refractivity, molar polarizability, and average electronegativity with refractive index and molar volume.

The average oxide ion polarizability $\alpha_{0\text{-}2(Dimitrov)}$, $\alpha_{0\text{-}2(Reddy)}$, and $\alpha_{o\text{-}2(Dimitrov\ \&\ Sakka)}$, is obtained according to the average electronegativity χ_{1av} by using equation (6), (7) and (11). Comparing these values of average oxide ion polarizability $\alpha_{o\text{-}2}$ it is obvious that there is a good agreement between them; this means that there is some correlation between the oxide ion polarizability and the electronegativity in the case of LBS ternary glass system.

The new addition in our work is the suggestion of an accurate formula for the calculations of the optical basicity, with minor change in equation (12) for our samples under test. Accordingly equation (12) can rewrite as the following:

$$\Lambda = 0.75 / (\chi lav - 0.25) \qquad (14)$$

This formula is more convenience for our system under study, so optical basicity $\Lambda_{(Duffy\ \&\ Ingram)}$ can be evaluated by using equation (14), i.e. in place of electronegetivity, average electronegativity is used. Optical basicity $\Lambda_{(Reddy)}$ can also be

evaluated by equation (13). Comparing these values of the optical basicities $\Lambda_{(Duffy\ \&\ Ingram)}$ and $\Lambda_{(Reddy)}$ it is obvious that there is some correlation between optical basicities and the electronegativity in the case of ternary glasses , except in binary composition Li_2O-B_2O_3 ($\Lambda_{(Duffy\ \&\ Ingram)}$ =7.332), and for Li_2O-SiO_2 ($\Lambda_{(Duffy\ \&\ Ingram)}$ =5.583) these values are larger, this also means that there are some correlation between optical basicity and average electronegativity in the case of LBS ternary glass system.

Table2. Molar refractivity, Molar polarizability, Average electronegativity χ_{1av}, Average electronic oxide ion polarizability and oxide ion polarizability as a function of refractive index Basicity.

Molar Refractivity R_m(cm^3/mol)	Molar polarizability α_m*(10^{24}ions /cm^3)	X_{lav}	$\alpha_{O-2}(\chi_{lav})$ (Dimitrov)	$\alpha_{O-2}(\chi_{lav})$ (Reddy)	$\alpha_{O-2}(\eta_m)$ (Dimitrov & Sakka	Basicity(Λ) (Duffy & Ingram)	Basicity(Λ) (Reddy)
17.814	7.063	0.352	4.398	4.357	4.479	7.332	1.509
19.348	7.672	0.741	4.265	4.062	4.624	1.524	1.420
17.985	7.131	0.738	4.266	4.065	4.266	1.536	1.421
17.708	7.021	0.731	4.268	4.071	4.199	1.559	1.423
17.019	6.748	0.725	4.271	4.074	4.018	1.577	1.424
17.18	6.812	0.723	4.271	4.076	4.063	1.583	1.425
16.746	6.64	0.718	4.273	4.080	3.950	1.601	1.426
16.36	6.487	0.711	4.275	4.085	3.854	1.625	1.427
16.364	6.488	0.707	4.276	4.088	3.857	1.637	1.428
15.879	6.296	0.384	4.387	4.333	3.944	5.583	1.502

The dielectric constant Є, of glasses samples depends on electronic polarizability, ionic polarizability, 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 Є our system described may be attributed at low frequency to the polarizability arising from the contribution of multi components in the glassy system. As frequency increases the ionic and orientation sources of polarizability decreases; and finally disappear due to the inertia of the molecules and ions (S. F. Khor et al,). [15]. The electronic polarizability 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 oxide polarizability (α_o) contribute to the polarizability of the suggested glass system at low frequency.

5. Conclusions

The oxide ion polarizability has been estimated with more accuracy (± 5%) for the prepared samples of LBS ternary glass system. It was found that there is a good correlation between the average electronegativity and the oxide ion polarizability. There is also a well correlation between average electronegativity and optical basicity as in the LBS system of glasses at the limit of oxide metal (5mol %). This is a new trial to make a correlation between the electronic polarizability of the oxide ion and the electronegativity as well as correlation between average electronegativity and optical basicity.

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