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The Estimation of the Oxide Ion polarizability using the Electronegativity for B_2O_3-Li_2O-Mo glass system

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Abstract

Recently Optical electronegativity of many binary oxide glasses has been evaluated on the basis of two different parameters, the linear refractive index and the energy gap, which have demonstrated remarkable correlation. In the present study, an improvement method to estimate the oxide ion polarizability through the average optical electronegativity for the lithium borate metal (Mo) glass system has been proposed. The electronic oxide polarizability of our prepared ternary oxide glasses have been estimated on the basis of the average optical electronegativity. In other side the value of the oxide ion polarizability has been determined using the equation of Dimitrov based on the measured linear refractive index.

The estimated values are in good agreement with the available experimental data. The present research is another trend of the oxide ion polarizability determination for ternary glasses.

Keywords: oxide ion polarizability , optical electronegativity ,ternary glasses**.**

1- Introduction:

One of the most important properties of materials , which is 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.

Recently oxide glasses take a considerable attention in view of their potential for use as laser hosts, in fiber and as nonlinear optical materials (Varshneya, A.K.,1993, P. Chimalawong et al, 2010).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.et al. 1997). The present work pertains to some new optical parameters in the case of some ternary glass systems. (Dimitrov.v and Sakka 1996) 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. In the present work we examine whether their observations can be extended to glasses formed from ternary oxides glasses. 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 lithium borate glass system for our study, as the lithium borates glasses are promising materials have many applications in the electronics components.

2- **Theoretical considerations:**

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 and O) attract the electrons in a bond better than those that have small electronegativities (such as Na and Mg). The electronegativities of the main group elements are given by (R. Asokamany and R. manjula,1989) introduced the concept of average electronegativity and defined an average electronegativity parameter χ_{1av} in the following manner:

$$\chi_{lav} = \sum_{i=1}^{N} \frac{n_i \chi_l}{N} \qquad (1)$$

Where χ_1 is the pauling electronegativity of element, n_i is the number of atoms of the ith element and N is the number of elements present in the compound. In this connection (R.R. Reddy et al. 2001) have derived the following empirical relationship for the average electronic oxide ion polarizability as follows:

$$\alpha_{O^{-2}} = 4.624 - 0.7569\chi_{lav} \qquad (2)$$

Where χ_{1av} is the average electronegativity of the simple oxide. Reddy et al have calculated α_o^{2-} 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 (2) seems to be too large.

(Reddy.R.R et al. 2001) and (Zhao.X.X et al. 2007) have applied the electronegativity approach to the same glasses already studied by(Dimitrov.V and Komatsu.T,1999) According to Reddy et al, the following empirical relations between oxide ion polarizability and average electronegativity is as follows:

$$\alpha_{O^{-2}} = 4.519 - 0.3422\chi_{lav} \qquad (3)$$

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:

$$\alpha_{O^{-2}} = (\chi_{lav} - 1.35)/(\chi_{lav} - 1.8) \qquad (4)$$

Where χ_{1av} is the average electronegativity of binary oxide glass. On the other hand (Zhao.X.X et al. 2007) have introduced the optical electronegativity calculated from the refractive index to predict oxide ion polarizability of binary oxide glasses.

$$\alpha_{O-2} = 3.5 - 0.9\chi_{glass} \quad (5)$$

It should be noted that the estimated values of by Reddy et al and zhao et al are in good agreement with the refractive index based oxide ion polarizability of the same glasses obtained by (Dimitrov.V and Komatsu.T 2010).

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

$$R_p = pR_i + qR_{O^{2-}} = 2.52\left[p\alpha_i + q\alpha_{O^{2-}}\right] \quad (6)$$

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:

$$\alpha_{o^{2-}}(\mathrm{n}) = [(\frac{V_m}{2.52})\frac{(n^2-1)}{(n^2+2)} - \sum_i p\alpha_i]q^{-1} \quad (7)$$

Where V_m is the molar volume of the glass sample.

3- Experimental work:

The glass samples were prepared using appropriate amounts of grade reagents boron oxide, lithium oxide and copper oxide, ferrite oxide zinc, Aluminum and Cadmium 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^{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 composition of the glass system was prepared in a series of 6 samples as illustrated in table (1).

The density of the samples were measured using Archimede's method using toylene as immersion liquids with accuracy around ±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 a uniform thickness of 4.0- 5.0 mm. The dc electrical conductivity of prepared glasses, the polished glass samples were silver 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 measured by a chromel- alumel (the measurements have been carried out at room temperature),thermocouple with an accuracy of ± 1%.

Also an LCR bridge (Hioki model 3031, Japan) was used to carry out the dielectric measurements. The samples were coated with silver coatings for obtaining good contact. The accuracy in the measurements of dielectric constant ε^{-} is ~ ± 0.001 .

4- Results:

The estimated values of the parameters (ρ , V_m , χ_{1av} , $\alpha_{o-2}(\chi_{1av})$, α_{o-2} (n_m) and n_m) are reported as in table (1).

Where α_{o-2} (n_m) is the calculated value as a function of the measured refractive index using equation (7), n_m is the experimental value according to the dielectric constant. The refractive index has been determined according to the electromagnetic relationship ($n=\varepsilon^{1/2}$) in the optical range. $\alpha_{o-2}(\chi_{1av})$ is the obtained value of oxide ion polarizability according to the average glass electronegativity χ_{1av} which estimated by equation (1).

5 **- Discussions:**

Considering the data in table (2), the concept of average electronegativity χ_{1av} can be used to determine and predict the electronic polarizability of the oxide ion for some ternary glasses. The new addition in our work is the suggestion of an accurate formula for the calculations of the oxide ion polarizability. Equation (5) is more suitable to obtain α_{o-2} through χ_{glass} with minor change in equation (5) for our samples under test. Accordingly equation (5) can rewritten as the following:

$$\alpha_{o-2} = 3.5 - 0.7\chi_{lav} \quad (9)$$

This formula is more convenience for our system under study, so α_{o-2} can be evaluated by equation (9).

The range of the glass formation in B_2O_3–Li_2O -Mo system extends up to 5 mol % of Mo and all the glass samples prepared are semi-transparent.

The dielectric constant $\varepsilon^{'}$, 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 $\varepsilon^{'}$ our system described may be attributed at low frequency to the polarizability arising 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 (S. F. Khor et al,2009). 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. Finally using the the refractive index n_m. and the molar volume Vm ,the estimated value of oxide ion polarizability α_{o-2} , has been evaluated according equation (7) with accurate method.

Comparing the two values of α_{o-2} in table (2), it is obvious that there is a good agreement between them, this means that there are some correlation between the oxide ion polarizability and the electronegativity in the case of ternary glasses as our samples.

6-Conclusions:

-The oxide ion polarizability has been estimated with more accuracy (± 5%) for the prepared samples of ternary glasses. It was found that there are a good correlation between the average electronegativity and the oxide ion polarizability as in the binary systems of glasses at this 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 for some ternary glasses as our samples.

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Table (1) : The prepared samples in mole percent.

Ratio in mole%	**80**	**15**	**5**
N_0	**B_2O_3**	**Li_2O (20%)**	-
No.1	**B_2O_3**	**Li_2O**	CuO
No. 2	**B_2O_3**	**Li_2O**	Fe_2O_3
No. 3	**B_2O_3**	**Li_2O**	Al_2O_3
No. 4	**B_2O_3**	**Li_2O**	ZnO
No. 5	**B_2O_3**	**Li_2O**	CdO

Table (2) illustrates the calculated values of the density , the molar volume,the average electronegativity, oxide ion polarizability $\alpha_{o-2}(\chi_{1av})$ and the oxide ion polarizability as a function of the refractive index of the prepared glasses.

Type of glass	ρ g/cm^3	**V_m** cm^3/mol	χ_{1av}	$\alpha_{O-2}(\chi_{1av})$	n_m	$\alpha_{O-2}(n_m)$
$B_2O_3 - Li_2O$	**2.12**	**29**	**3.14**	**1.304**	**1.53**	**1.373**
$B_2O_3 - Li_2O$ -CuO	**2.20**	**28.5**	**3**	**1.451**	**1.54**	**1.365**
$B_2O_3 - Li_2O$ -Fe_2O_3	**2.10**	**29**	**2.90**	**1.480**	**1.51**	**1.350**
$B_2O_3 - Li_2O$-Al_2O_3	**2.15**	**29.5**	**2.80**	**1.535**	**1.52**	**1.355**
$B_2O_3 - Li_2O$-ZnO	**2.16**	**30**	**2.76**	**1.550**	**1.50**	**1.351**
$B_2O_3 - Li_2O$-CdO	**2.14**	**30**	**2.70**	**1.600**	**1.54**	**1.352**