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The Estimation of Oxide Polarizability and Basicity using Electronegativity for B_2O_3:M_2O Glass System (M=Li, Na, K, Rb)

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ABSTRACT: Glass samples of binary glass system [100-(x+10)] B_2O_3: (x+10) M_2O; x take values in the step of 10, were prepared by conventional melt-quench technique. The concept of average oxide ion polarizability (α_0^{2-}), and optical basicity (Λ) are estimated by using electronegativity; for some binary oxide glasses. The value of the oxide ion polarizability, α_0^{2-} (Reddy) has a good correlation with basicity, Λ(Duffy). The average electronegativity (χ_{1av}) values are smaller than, oxide ion polarizability (α_0^{2-}), and basicity, Λ(Duffy) determined with increasing mol % of glass modifiers. It has a good correlation between α_0^{2-} (Reddy), and Λ (Duffy). The present research is another trend of the oxide ion polarizability and basicity determined for binary glasses by using different glass modifier.

KEYWORDS: Average electronegativity, average electronic oxide ion polarizability, optical basicity, binary glasses.

I. 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 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 fibre 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. In the present work examine whether their observations can be extended to glasses formed from ternary oxides glasses. This is of a particular interest especially for glass systems and polarizability; basicity 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 binary B_2O_3:M_2O glass systems were (M= Li, Na, K, Rb).

II. 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[5] introduced the concept of average electronegativity and defined an average electronegativity parameter χ_{1av} in the following manner:

$$\chi_{lav} = \Sigma\, n_i\chi_i/N \qquad (1)$$

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Σ over i takes values from 1 to N Where χ_i is the pauling electronegativity of element, ni 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[6] have derived the empirical relationship for the average electronic oxide ion polarizability as follows:

$$\alpha_o^{2-} = 4.624\text{-}0.7569\ \chi_{lav} \qquad (2)$$

where χ_{lav} is the average electronegativity of the simple oxide

Reddy et al[6] 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 average electronic oxide ion polarizability for binaries calculated by equation (2) seems to be too large. Reddy et al[6] and Zhao et al[7] have applied the electronegativity approach to the same glasses already studied by Dimitrov and Komatsu [8] According to Reddy et al[6], the following empirical relations between average oxide ion polarizability and average electronegativity is as follows:

$$\alpha_o^{2-} = 4.519\text{-}0.3444\ \chi lav \qquad (3)$$

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.

III. OPTICAL BASICITY & ELECTRONEGATIVITY

Another approach for prediction of the theoretical optical basicity of an oxide solid is based on the Pauling type electronegativity. Duffy and Ingram[9;10] have suggested that a good correlation exists between basicity Λ & electronegativity χ

$$\Lambda = 0.75/(\chi\text{-}0.25) \qquad (5)$$

The optical basicity of main group elements holds well with the electronegativity rule but for other elements equation (5) must be used with caution, especially with transition metal and heavy metal oxides. Optical basicity values for Li_2O, Na_2O, K_2O, and Rb_2O, with B_2O_3, 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:

$$\Lambda = 1.59 – 0.2279\chi 1av \qquad (6)$$

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 [11] and Dimitrov and Sakka [4]. But it should be mentioned that the optical basicities for binaries calculated by equation (6) are not correct. But their exists a very good correlation between basicity (Λ) and average oxide ion polarizability (α_0^{2-}) suggested by formula given by (Duffy)[10] as

$$\Lambda = 1.67*(1\text{-}1/\alpha_0^{2-}) \qquad (7)$$

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.

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IV. RESULTS & DISCUSSION

For explanation of results we can used the standered values of glass modifiers in terms of theire Ionic radius Density and Atomic volume are display in Table (1).

Table (1) : Glass modifier element with their Ionic rarius, Density , and Atomic volume.

Element	Ionic radius A^O	Density (gm/cm^3)	Atomic volume (cm^3)
Li	0.6	0.53	12.97
Na	0.96	0.97	23.68
K	1.33	0.86	45.36
Rb	1.48	1.53	55.8

Table (1) shows the standard values of glass modifiers with their values of Ionic rarius (A^O) , Density (gm/cm^3), and Atomic volume (cm^3).
The values of average electronegativity, of B_2O_3:M_2O where (M= Li, Na, K, Rb), are reported in Table (2).

Table 2. Mol % of glass modifiers with respect to glass former B_2O_3 and average electronegativity.

Mol% of modifier	Li_2O	Na_2O	K_2O	Rb_2O
	(χ_{lav})	(χ_{lav})	(χ_{lav})	(χ_{lav})
20	0.8711	1.0708	1.1447	1.2407
30	0.7883	1.0581	1.1771	1.3366
40	0.7199	1.0456	1.2114	1.4486
50	0.6624	1.0335	1.2477	1.5811
60	0.6134	1.0216	1.2863	1.7402
70	0.5711	1.0100	1.3274	1.9350
80	0.5343	0.9987	1.3711	2.1789

Table 2. shows the values of average electronegativity with variation of mol % of glass modifiers with respect to glass former B_2O_3 calculated by using equation (1).

The variation of average electrnegativity with mol% of glass modifiers are shown in Figure (1)

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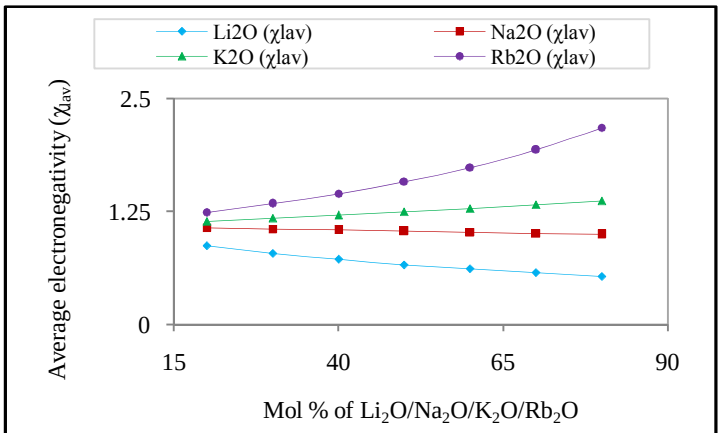

Figure 1: Variation of average electronegativity, against the mol% of Li_2O, Na_2O, K_2O and Rb_2O, with repect to glass former B_2O_3.

From Figure (1) it is observed that the average electronegativity values are decreasing by increasing the mol % of glass modifier Li_2O and Na_2O which is due to, the smaller values of Ionic radius, density and atomic volume. Average electronegativity values gradually increasing when mol% of K_2O and Rb_2O increasing. This behaviour is due to, the larger values of Ionic radius, density and atomic volume as comparing to Li_2O and Na_2O.

Table 3. Mol % of glass modifiers with respect to glass former B_2O_3 and average oxide ion polarizibility.

Mol% of modifier	Li_2O	Na_2O	K_2O	Rb_2O
	(α_0^{2-})	(α_0^{2-})	(α_0^{2-})	(α_0^{2-})
20	4.221	4.153	4.127	4.094
30	4.249	4.157	4.116	4.062
40	4.273	4.161	4.104	4.023
50	4.292	4.165	4.092	3.978
60	4.309	4.169	4.079	3.923
70	4.324	4.173	4.065	3.857
80	4.336	4.177	4.05	3.773

Table (3) shows the variation of average oxide ion polarizabilities, of B_2O_3:M_2O where (M= Li, Na, K, Rb), calculated by using equation (2).

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Where as, in case of average oxide ion polarizabilities, with variation of mol % of glass modifiers with respect to glass former B_2O_3 are shown in Figure (2).

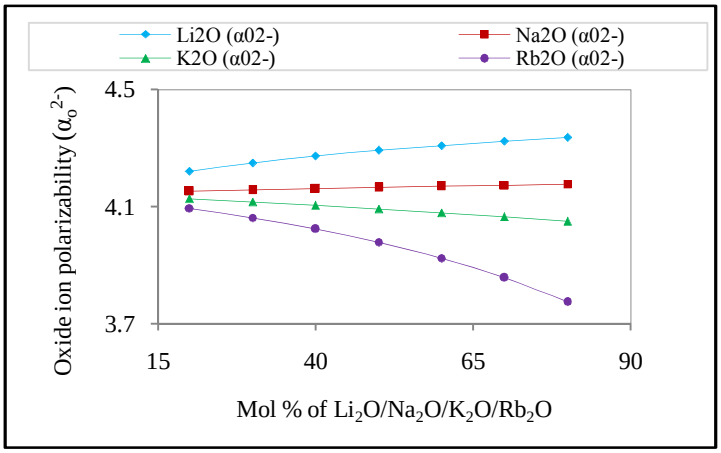

Figure 2: Variation of average oxide ion polarizability, against the mol% of Li_2O, Na_2O, K_2O and Rb_2O, with repect to glass former B_2O_3.

Figure (2) shows that the oxide ion polarizability values are increasing by increasing the mol % of glass modifier Li_2O and Na_2O which is due to, the smaller values of Ionic radius, density and atomic volume. Where as the oxide ion polarizability values gradually decreasing for K_2O and Rb_2O on increasing their mol %, this behaviour is due to, the larger values of Ionic radius, density and atomic volume as comparing to Li_2O and Na_2O. From Figure (1 & 2) it is observed that the variation of average electronegativity and average values of oxide ion polarizabilities shows exaclly opposite behaviour .
The values of optical basicity of B_2O_3:M_2O where (M= Li, Na, K, Rb), are reported in Table (4).

Table 4. Mol % of glass modifiers with respect to glass former B_2O_3, and optical basicity with variation of glass modifier

Mol% of modifier	Li_2O	Na_2O	K_2O	Rb_2O
	(Λ)	(Λ)	(Λ)	(Λ)
20	1.391	1.346	1.329	1.307
30	1.41	1.349	1.322	1.285
40	1.426	1.352	1.314	1.26
50	1.439	1.354	1.306	1.23
60	1.45	1.357	1.297	1.193
70	1.46	1.36	1.287	1.149
80	1.468	1.362	1.278	1.093

Table (4) shows the variation of optical basicity, of B_2O_3:M_2O where (M= Li, Na, K, Rb), calculated by using equation (6).

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Where as, in case of optical basicity, with variation of mol % of glass modifiers with respect to glass former B_2O_3 are shown in Figure (3).

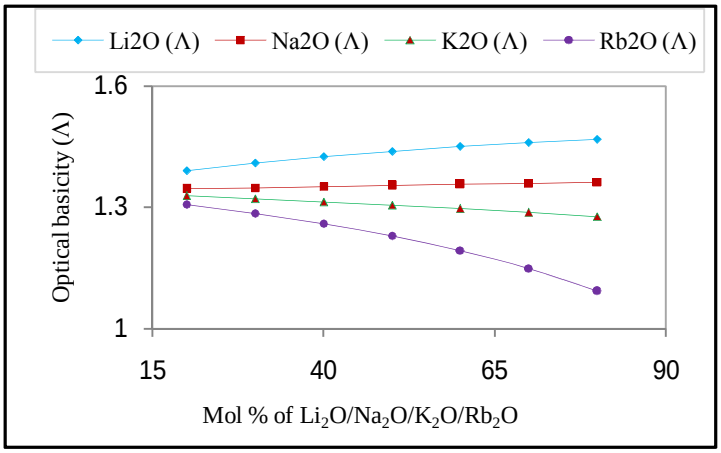

Figure 3: Average electronegativity, for Li_2O, Na_2O, K_2O and Rb_2O, with variation of glass modifier

Result of Figure 3 gives that the optical basicity values are increasing by increasing the mol % of glass modifier Li_2O and Na_2O which is due to, the smaller values of Ionic radius, density and atomic volume. Where as the optical basicity values gradually decreasing for K_2O and Rb_2O on increasing their mol %, this behaviour is due to, the larger values of Ionic radius, density and atomic volume as comparing to Li_2O and Na_2O.
Figure (1-3) shows, straight lines with R^2 values = 0.980, 0.999, 0.997 and 0.973 for Li_2O, Na_2O, K_2O and Rb_2O.
Average oxide ion polarizabilities and Optical basicity shows exaclly parallel behaviour (Figure 2, 3) which is clearly observed from equations (7) suggested by (Duffy).[10] for average oxide ion polarizabilities, and optical basicity.

V. CONCLUSIONS

The average oxide ion polarizability has been estimated with more accuracy for the prepared samples for B_2O_3:M_2O of binary glass System (M=Li, Na, K, Rb). It was found that there is a good correlation between the average electronegativity, average oxide ion polarizability. There is also a well correlation between average electronegativity, average oxide ion polarizability and optical basicity as in this system of glasses at the limit of oxide metal. The variation of average electronegativity and average oxide ion polarizability shows exaclly opposite behaviour whereas, average oxide ion polarizabilities and Optical basicity shows exaclly parallel behaviour. This is a new trial to make a correlation between average oxide ion polarizability average electronegativity, and optical basicity. It gives well behaviour to their standard values.

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