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The Estimation of Oxide Polarizability, Basicity using Electronegativity for B_2O_3:M_2O:V_2O_5 Glass System (M=Li, Na, K, Rb)

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Abstract

Glass samples of the ternary glass system [100-(2x+20] B_2O_3 :(x+20) M_2O:xV_2O_5, x=0-25 in the step of 5, by keeping mol % of B_2O_3 constant, were prepared by conventional melt-quench technique. In the present work, the concept of the optical electronegativity & basicity is used to predict basic properties of some ternary oxide glasses. Now Optical electronegativity & basicity of many ternary oxide glasses has been evaluated on the basis of different parameters. 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 by using the average electronegativity with increasing mol % of glass modifiers. It has a good correlation between them, except for B_2O_3 & V_2O_5, they are larger of α_0^{2-} (Reddy), and Λ (Duffy). The present research is another trend of the oxide ion polarizability and basicity determined for ternary glasses by using different glass modifier.

Keywords: Average electronegativity, average electronic oxide ion polarizability, optical basicity, 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. 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 first time, in case of ternary B_2O_3:M_2O:V_2O_5 glass systems were (M = Li, Na, K, Rb).

Fajan Rule of Polarization states that, the polarization will be increased by; (1) Cations have high charge and small size i.e. covalent character increases with decreasing cation size or increasing cation charge. The high charge density of small and/or highly charged cations is able to exert a powerful polarizing effect which distorts the electron cloud around the anion. (2) High charge and large size of the anion. i.e. Covalent character increases with an increase in anion charge or anion size. (3) The polarizability of an anion is related to the deformability of its electron cloud (i.e. its "softness") the electrons of larger, more negatively charged anions are more loosely held because they are more shielded from the nuclear charge. Thus, these anions are more easily polarized by cations. (4) An incomplete valence shell electron configuration. Noble gas configuration of the cation produces better shielding and less polarizing power

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

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

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 [6] have derived the empirical relationship for the average electronic oxide ion polarizability as follows:

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

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 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:

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

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:

$$\alpha_o^{2-}=(\chi lav-1.35)/((\chi lav-1.8) \quad (4)$$

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

3. 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, 10,11] have suggested that a good correlation exists between electronegativity χ & basicity Λ

$$\Lambda=0.75/(\chi-0.25) \quad (5)$$

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, Rb_2O B_2O_3, V_2O_5, 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

$$\Lambda=1.59-0.2279\chi 1av \quad (6)$$

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 and average oxide ion polarizability suggested by formula given by (Duffy) [10] as

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

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.

4. Result & Discussion

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

Table 1 : Modifier element with their Ionic rarius, Density, and Atomic volume.

Glass modifiers	Ionic radius (A^O)	Density (gm/cm^3)	Atomic volume (cm^3)
Li	0.60	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 radius (A^o), Density (gm/cm^3), and Atomic volume (cm^3).

The values of average electronegativity, of B_2O_3:M_2O:V_2O_5 where (M= Li, Na, K, Rb), are reported in Table (2).

Table 2: Average electronegativities with mol % of modifiers Li_2O, Na_2O, K_2O, and Rb_2O.

Mol % of modifier	Average electronegativities B_2O_3:Li_2O:V_2O_5	Average electronegativities B_2O_3:Na_2O:V_2O_5	Average electronegativities B_2O_3:K_2O:V_2O_5	Average electronegativities B_2O_3:Rb_2O:V_2O_5
20	1.36647	1.68285	1.80635	1.95783
25	3.73799	4.84993	5.32714	5.92834
30	3.63838	4.97274	5.59911	6.42031
35	3.54395	5.10194	5.90034	7.00131
40	3.45429	5.23803	6.23582	7.69794
45	3.36906	5.38157	6.61176	8.54851
50	3.28793	5.53321	7.03593	9.61039
55	3.21062	5.6936	7.51826	10.9735
60	1.39416	3.90910	3.58737	5.68320

Average electronegativities, for ternary glass system B_2O_3-M_2O-V_2O_5 where (M=Li, Na, K, Rb), with mol % of modifiers is shown in Table 2.

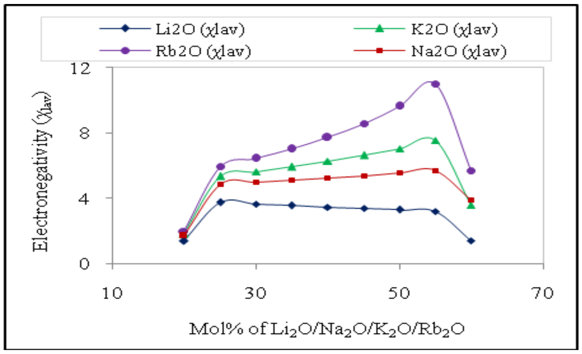

Figure 1: Average electronegativities (χ_{lav}) values against the mol% of modifiers Li_2O, Na_2O, K_2O and Rb_2O.

Figure 1shows the variation of average electronegativity with respective mol % of glass modifiers.

It is observed that for Li_2O, Na_2O, K_2O and Rb_2O the average electronegativity values are increasing in between the 20 mol% to 25 mol% of glass modifiers and decreasing in between the 55 mol% to 60 mol% of glass modifiers. At the mid portion i.e. from 25 mol% to 55 mol% average electronegativity gradually decreasing in case of Li_2O and average electronegativity increasing for Na_2O, K_2O, Rb_2O. Gradually decreasing average electronegativity is due to, smaller values of ionic radius, density and atomic volume of Li_2O than that of Na_2O, K_2O, Rb_2O and vice-versa; as shown in Table 1.

Table 3: Oxide ion polarizabilities ($\boldsymbol{\alpha_0}^{2-}$), with mol % of modifiers Li_2O, Na_2O, K_2O, and Rb_2O.

Mol % of modifier	Average oxide ion polarizabilities (B_2O_3:Li_2O:V_2O_5)	Average oxide ion polarizabilities B_2O_3:Na_2O:V_2O_5	Average oxide ion polarizabilities (B_2O_3:K_2O:V_2O_5)	Average oxide ion polarizabilities B_2O_3:Rb_2O:V_2O_5
20	4.05139	3.94312	3.90086	3.84902
25	3.23985	2.85935	2.69605	2.49031
30	3.27394	2.81732	2.60298	2.32196
35	3.30625	2.77311	2.49990	2.12314
40	3.33694	2.72654	2.38509	1.88476
45	3.36610	2.67742	2.25645	1.59369
50	3.39386	2.62553	2.11130	1.23032
55	3.42032	2.57063	1.94625	0.76386
60	4.04191	3.62720	3.29140	2.57420

The values of average oxide ion polarizabilities, for ternary glass system B_2O_3-M_2O-V_2O_5 where (M=Li, Na, K, Rb), with mol % of modifiers is shown in Table 3.

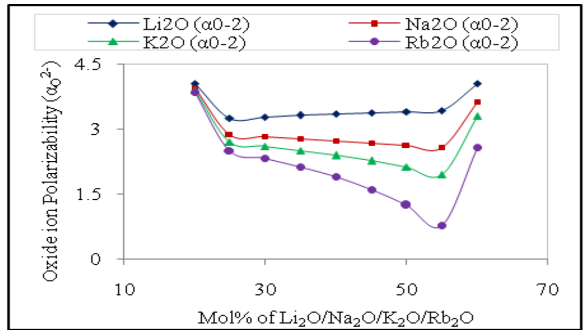

Figure 2: Average Oxide ion polarizability ($\boldsymbol{\alpha_0}^{2-}$) values against the mol% of modifiers Li_2O, Na_2O, K_2O and Rb_2O.

Figure 2 shows the variation of oxide ion polarizability with respective mol % of glass modifiers.

It is observed that for Li_2O, Na_2O, K_2O and Rb_2O the oxide ion polarizability values are decreasing in between the 20 mol% to 25 mol% of glass modifiers and increasing in between the 55 mol% to 60 mol% of glass modifiers. At the mid portion i.e. from 25 mol% to 55 mol% oxide ion polarizability gradually increasing in case of Li_2O and oxide ion polarizability *is* decreasing for Na_2O, K_2O, Rb_2O. Gradually increasing oxide ion polarizability is due to, smaller values of ionic radius, density and atomic volume of Li_2O than that of Na_2O, K_2O, Rb_2O and vice-versa; as shown in Table 1.

Table 4: Optical basicity (Λ), with mol % of modifiers Li_2O, Na_2O, K_2O, and Rb_2O.

Mol % of modifier	Optical basicity B_2O_3:Li_2O:V_2O_5	Optical basicity B_2O_3:Na_2O:V_2O_5	Optical basicity B_2O_3:K_2O:V_2O_5	Optical basicity B_2O_3:Rb_2O:V_2O_5
20	1.25779	1.24647	1.24188	1.23612
25	1.15454	1.08595	1.05057	0.99940
30	1.15991	1.07723	1.02842	0.95078
35	1.16489	1.06778	1.00197	0.88343
40	1.16954	1.05750	0.96981	0.7839
45	1.17387	1.04626	0.92990	0.64212
50	1.17793	1.03393	0.87901	0.51263
55	1.18174	1.02035	0.81193	0.46554
60	1.25682	1.14505	1.16261	1.02125

The values of optical basicity, for ternary glass system B_2O_3-M_2O-V_2O_5 where (M=Li, Na, K, Rb), with mol % of modifiers is shown in Table 4.

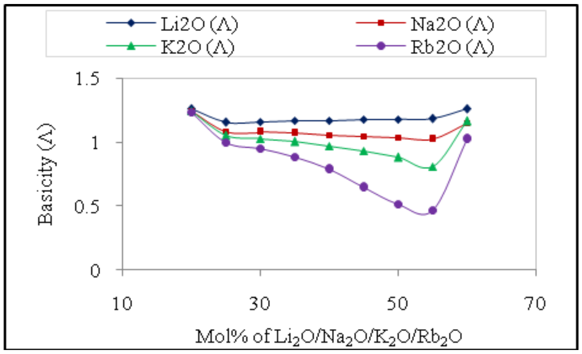

Figure 3:Shows the variation of basicity with respective mol % of glass modifiers Li_2O, Na_2O, K_2O and Rb_2O.

Figure 3 shows the variation of optical basicity with respective mol % of glass modifiers. It is observed that for Li_2O, Na_2O, K_2O and Rb_2O the optical basicity values are decreasing in between the 20 mol% to 25 mol% of glass modifiers and increasing in between the 55 mol% to 60 mol% of glass modifiers. At the mid portion i.e. from 25 mol% to 55 mol% optical basicity gradually increasing in case of Li_2O and optical basicity *is* decreasing for Na_2O, K_2O, Rb_2O. Gradually increasing in optical basicity is due to, smaller values of ionic radius, density and atomic volume of Li_2O than that of Na_2O, K_2O, Rb_2O and vice-versa; as shown in Table 1.

Hence it is concluded that the average electronegativities shows opposite nature than that of oxide ion polarizability and optical basicity (Figure 1, Figure 2 and Figure 3). Oxide ion polarizability and optical basicity shows alike nature(Figure 2 and Figure 3). which is clearly observed for oxide ion polarizabilities, and optical basicity from equations 6 and 7.

From Table 2, 3 and 4 it is also observed that the valves of average electronegativity, oxide ion polarizabilities, optical basicity for B_2O-Li_2O (1.3664, 4.0513, 1.2577); B_2O-Na_2O (1.6829, 3.9431, 1.2465); B_2O-K_2O (1.8064, 3.9009, 1.2419) and for B_2O-Rb_2O (1.9578, 3.849, 1.2361); Where as for V_2O_5-Li_2O (1.3941, 4.0419, 1.2568; V_2O_5-Na_2O (3.9091, 3.6272, 1.1451 V_2O_5-K_2O (3.5874, 3.2914, 1.1626) and V_2O_5-Rb_2O (5.6832, 2.5742, 1.0213). It is notable that for B_2O_3:Li_2O:V_2O_5 (80:20:0) and for B_2O_3:Li_2O:V_2O_5 (0:60:40) the average electronegativity, oxide ion polarizability and optical basicity are approximately same, which is due to the absence of any one off the glass former i.e. for binary system; similarly for other modifiers [12].

5. Conclusions

The average oxide ion polarizability has been estimated with more accuracy (± 5%) for the prepared samples for B_2O_3:M_2O:V_2O_5 Glass System (M=Li, Na, K, Rb) ternary glass system .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 (5mol %); i.e. the average electronegativities shows opposite nature than that of oxide ion polarizability and optical basicity where as Oxide ion polarizability and optical basicity shows alike nature. This is a new trial to make a correlation between average oxide ion polarizability average electronegativity, and optical basicity. It gives well behavior to their standard values.

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