International Journal of Scientific Research in Engineering and Management (IJSREM)
Volume: 07 Issue: 12 | December - 2023 SJIF Rating: 8.176 ISSN: 2582-3930

Oxide ion polarizability, Optical basicity, Bond strength, Nonlinear susceptibility of glass systems (Review)

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Abstract – A review of an interpretation of optical properties of oxides and oxide glasses in terms of the electronic ion polarizability and average single bond strength, given by V. Dimitrov and T. Komatsu.
Here a review is taken in glass systems in terms of refractive index, optical band gap, oxide ion polarizabilities, optical basicities, average single bond strength and Third-order nonlinear optical susceptibilities.

***Key Words*:** Refractive index, optical bang gap, oxide ion, polarizability, optical basicity, average single bond strength, third-order nonlinear optical susceptibility

1. INTRODUCTION

The estimation of free ion electronic polarizability of ions is a subject of so-called polarizability approach in material science, which is well known especially in the field of glass science as done by Pauling [1], Born and Heisenberg [2], Fajans and Joos [3], J. Mayer and M. Mayer [4], Kordes [5] and
Estimation of polarizability would be useful especially with respect to oxide crystals and glasses, which are of technological importance as optical and electronic materials. The most familiar and widely used relationship in this approach is Lorentz-Lorenz equation.
Duffy and Ingram[6,7] proposed Optical basicity properties of the oxides and glasses related to the polarization of oxide ions in the material matrix and represents their ability to transfer electron density to surrounding cations.
Dimitrov and Komatsu[8,9] have shown a good agreement between theoretical optical basicity (Λ_{th}) and refractive index based optical basicity $\Lambda(n)$ for large number of binary oxide glasses, including phosphate, borate, silicate, germanate, tellurate and titanate. The optical basicity can be experimentally determined but the applicability of the method is rather limited. Hence it is desirable to derive the values for many oxides on the basis of the similarity in the physical nature of the polarizability and the optical basicity.
Honma et al. [10-11] studied the refractive index based optical band gap, oxide ion polarizabilities and optical basicities.
Terashima [12-13] study on average single bond strength and Third-order nonlinear optical susceptibility in binary glasses and more recently Dimitro and Komatsu [14] have established the correlation existing between third order nonlinear susceptibility $\chi^{(3)}$, average single bond strength B_{M-O} , optical basicity and oxide ion polarizability with high refractive index basic alkali and alkaline earth glasses.

2. THEORY

Dimitrov and Sakka [15 have determined the optical basicity for numerous single oxides on the basis of their refractive index $\Lambda(n_o)$ and Energy gap $\Lambda(E_g)$ by using equations,

$$\alpha_{o2-}(n_o) = [(V_m/2.52)(n_o^2-1)/(n_o^2+2) - p\alpha_i](q)^{-1} \quad (1)$$

$$\alpha_{o2-}(E_g) = [(V_m/2.52)(1-(E_g/20)^{1/2}) - p\alpha_i](q)^{-1} \quad (2)$$

In above equations V_m is molar volume, n_o is refractive index, p & q are cations and oxide ions in the chemical formula of oxide A_pO_q, α_i is cation polarizability, E_g is energy gap, and α_{o2-} polarizability of the oxide ion.

$$\Lambda = 1.67[1-(1/\alpha_{o2-})] \quad (3)$$

Honma et.al.[10,11] have applied above equations (2) to calculate the electronic oxide ion polarizability $\alpha_{o2-}(E_o)$ and refractive index based $\alpha_{o2-}(n_o)$ for Sb_2O_3-B_2O_3 and Bi_2O_3-B_2O_3 glasses using experimental data for optical band gap E_o. Similarly by using equation (3) the optical basicity of Sb_2O_3-B_2O_3 and Bi_2O_3-B_2O_3 glasses are calculate using the experimental data for optical band gap E_o are listed in Tale 1.
It was observed that there is general tendency of increase oxide ion polarizability with increasing refractive index and decreasing energy gap.
The average single bond strength of oxide glasses have been determined by Terashima et, al.[12,13] using following equations,

For Bi_2O-B_2O_3 glasses

$$B_{M-O} = x\,B_{Bi-O}^{(6)}+(1-x)[N_3B_{B-O}^{(3)}+N_4B_{B-O}^{(4)}] \quad (4)$$

For Sbi_2O-B_2O_3 glasses

$$B_{M-O} = x\,B_{Sb-O}^{(3)}+(1-x)[N_3B_{B-O}^{(3)}+N_4B_{B-O}^{(4)}] \quad (5)$$

where N_3 and N_4 are mol fraction of BO_3 and BO_4groups in one molecule of glass and $B_{B-O}^{(3)}$ and $B_{B-O}^{(4)}$ are the single bond strength of B-O bonds in the BO_3 and BO_4 groups , respectively. $B_{Bi-O}^{(6)}$ and $B_{Sb-O}^{(3)}$ are the single bond strength of Bi-O and Sb-O bonds in BiO_6 and SbO_3 groups , respectively.
Third-order nonlinear optical susceptibility is calculated by using equations,

$$\chi^{(3)} = (1.4*10^{-11})/[(E_{opt}-1.96)(E_{opt}-1.31)(E_{opt}-0.65)] \quad (6)$$

$$\chi^{(3)} = \{[(n_o^2-1)/4\pi]^4 * 10^{-10} \text{ esu.} \quad (7)$$

Where n_o = linear refractive index.
The purpose of the article is to consider the status of oxide ion polarizability and optical basicity approach in the glass systems and to emphasize the role of the optical band gap, which helpful to the new researchers.

3. RESULT AND DISCUSSION

3.1 Refractive index and optical band gap: In this review the refractive index and optical band gap in Sb_2O_3-B_2O_3 systems and Bi_2O_3-B_2O_3 systems studied by Honma et.al, are taken,

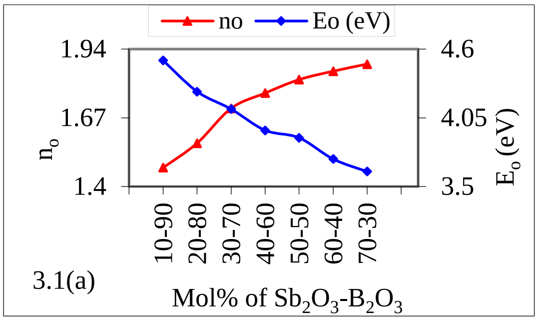

Fig. 3.1.(a) Variation of n_o & E_o(eV) of Sb_2O_3-B_2O_3 system.

Figure 3.1.(a) shows that the refractive index (n_o) increasing form 1.474–1.881 optical energy gap E_o(eV) decreases from 4.51–3.62 (eV). It was observed that there is general tendency of increasing refractive index with decreasing energy gap.

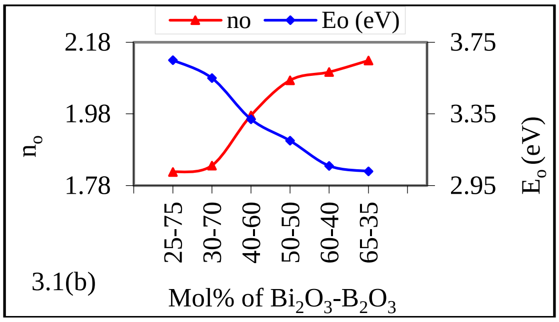

Fig. 3.1.(b) Variation of n_o & E_o(eV) of Bi_2O_3-B_2O_3 systems.

Figure 3.1.(b) shows that the refractive index increasing form1.818–2.129, optical energy gap decreases from3.65–3.03 E_o(eV). It was observed that there is general tendency of increasing refractive index with decreasing energy gap.

3.2 Oxide ion polarizability and Optical basicity: In this review the refractive index based electronic oxide ion polarizability $\alpha_{o2-}(n_o)$, $\alpha_{o2-}(E_o)$ and optical basicity $\Lambda(n_o)$, $\Lambda(E_o)$ in Sb_2O_3-B_2O_3 and Bi_2O_3-B_2O_3 glasses studied by Honma et.al, are taken on four axis graph,

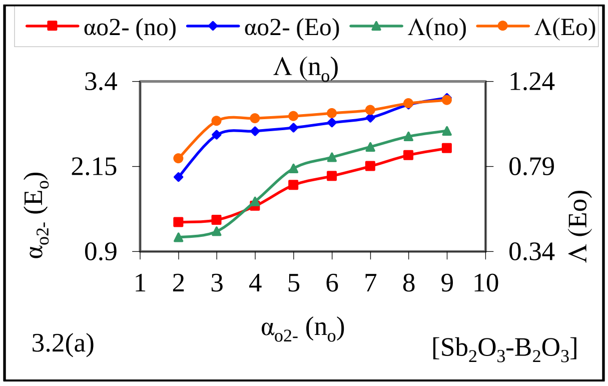

Fig. 3.2(a) plot of αo2-(n_o), αo2-(E_o); Λ(n_o), Λ(E_o) of Sb_2O_3-B_2O_3 systems

Figure 3.2 (a) shows that the refractive index based oxide ion polarizability in Sb_2O_3-B_2O_3 systems $\alpha_{o2-}(n_o)$ increasing form1.331–2.417 and $\alpha_{o2-}(E_o)$ also increases from 1.995-3.159; Optical basicity $\Lambda(n_o)$ increases from 0.415-0.979 and $\Lambda(E_o)$ increases from 0.833-1.141. It is general tendency of increasing oxide ion polarizability and optical basicity.

Table 1:

System	Mol % of first oxide	n_o	E_o (eV)	α_{o2-} (n_o)	α_{o2-} (E_o)	$\Lambda(n_o)$	$\Lambda(E_o)$
Sb_2O_3-B_2O_3	0	1.446	7.20	1.331	1.995	0.415	0.833
	10	1.474	4.51	1.365	2.614	0.447	1.031
	20	1.570	4.26	1.570	2.670	0.606	1.045
	30	1.707	4.12	1.877	2.720	0.78	1.056
	40	1.767	3.95	2.010	2.794	0.839	1.072
	50	1.820	3.89	2.153	2.867	0.894	1.088
	60	1.853	3.72	2.317	3.059	0.949	1.124
	70	1.881	3.62	2.417	3.159	0.979	1.141
Bi_2O_3-B_2O_3	25	1.818	3.65	1.48	2.03	0.542	0.847
	30	1.836	3.55	1.626	2.224	0.643	0.919
	40	1.976	3.32	1.97	2.452	0.822	0.989
	50	2.074	3.2	2.171	2.557	0.901	1.017
	60	2.097	3.06	2.284	2.704	0.939	1.052
	65	2.129	3.03	2.37	2.759	0.965	1.065

Table 1 Refractive index n_o, optical band gap E_o, oxide ion polarizabilities $\alpha_{o2-}(n_o)$, $\alpha_{o2-}(E_o)$, optical basicity $\Lambda(n_o)$ and $\Lambda(E_o)$ of Sb_2O_3-B_2O_3 and Bi_2O_3-B_2O_3 glasses.

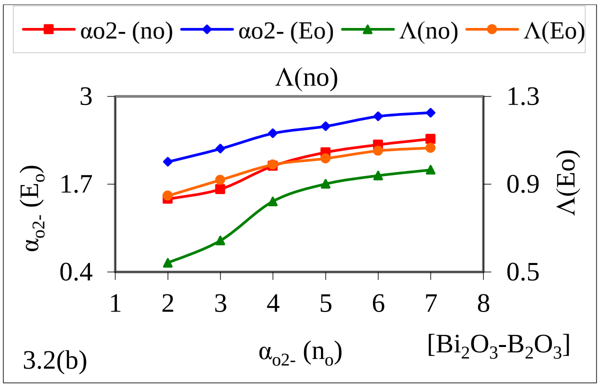

Fig. 3.2.(b) plot of αo2-(n_o), αo2-(E_o); Λ(n_o), Λ(E_o) of Bi_2O_3-B_2O_3 systems

Figure 3.2 (b) It shows that the refractive index based oxide ion polarizability in Bi_2O_3-B_2O_3 systems $\alpha_{o2-}(n_o)$ increasing form1.48–2.37 and $\alpha_{o2-}(E_o)$ also increases from 2.03-3.2.759; Optical basicity $\Lambda(n_o)$ increases from 0.542-0.965 and $\Lambda(E_o)$ increases from 0.847-1.065. It is general tendency of increasing oxide ion polarizability and optical basicity.

3.3 Bond strength and third order nonlinear optical - susceptibility:

Single bond strength B_{M-O} introduced by Sun in fact represents the single bond energy of an averaged M-O chemical bond in the oxide expressed by its dissociation energy; later on equations for calculation of average single bond strength B_{M-O}

in glasses have been derived taking into account the contribution of different structural units.

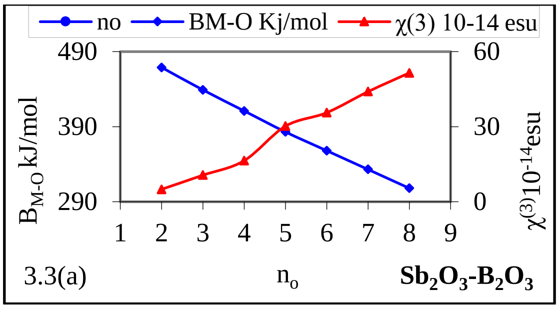

Fig. 3.3.(a) R.I.(n_o), B_{M-O} kJ/mol, $\chi^{(3)}$ 10^{-14} eus.of Sb_2O_3-B_2O_3 systems

Figure 3.3 (a), shows that the refractive index based values of average single bond strength B_{M-O} decreases from 469-308 kJ/mol, and third order nonlinear susceptibility $\chi^{(3)}$ increases from 4.96-51.5x10^{-14}esu., in Sb_2O_3-B_2O_3 systems It is general tendency of increasing third order nonlinear susceptibility and decreasing of average single bond strength.

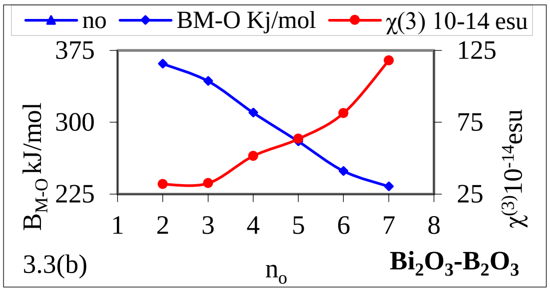

Fig. 3.3.(b) R.I.(n_o), B_{M-O} kJ/mol, $\chi^{(3)}$ 10^{-14} esu., of Bi_2O_3-B_2O_3 systems

Figure 3.3 (b) It shows that the refractive index based values of average single bond strength B_{M-O} decreases from 361-233 kJ/mol, and third order nonlinear susceptibility $\chi^{(3)}$ increases from 31.9-118x10^{-14}esu., in Bi_2O_3-B_2O_3 systems It is general tendency of increasing third order nonlinear susceptibility $\chi^{(3)}$, and decreasing average single bond strength B_{M-O}.

3.4 Bond strength and third order nonlinear optical - susceptibility in alkali and alkaline earth glasses:

Dimitro and Komatsu [12] have established the correlation existing between third order nonlinear susceptibility $\chi^{(3)}$, average single bond strength B_{M-O} , optical basicity and oxide ion polarizability with high refractive index basic alkali and alkaline earth glasses.

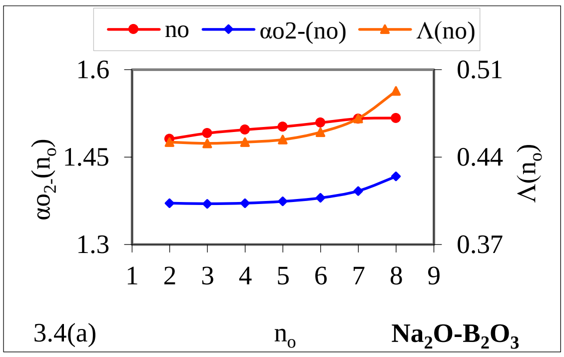

Fig. 3.4.(a) R.I.(n_o), αo2-(no), Λ(no) of Na_2O_3-B_2O_3 systems

Figure 3.4(a) shows that the refractive index increases from 1.481-1.517, oxide ion polarizability $\alpha_{o2-}(n_o)$ increases from 1.31-1.417 and optical basicity $\Lambda(n_o)$ also increases from 0.452-0.493 in Na_2O-B_2O_3 systems. It is general tendency of increasing oxide ion polarizability and optical basicity.

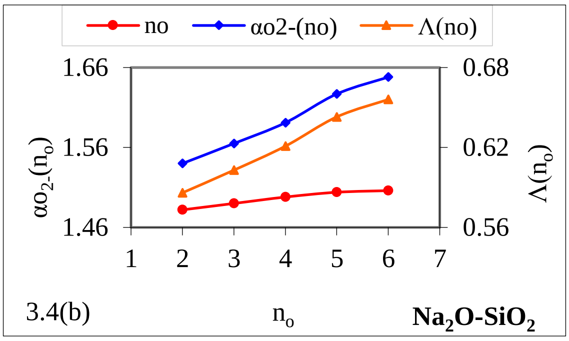

Fig. 3.4.(b) R.I.(n_o), αo2-(no), Λ(no) of Na_2O_3-SiO_2 systems.

Figure 3.4(b) shows that the refractive index increases from 1.482-1.506, oxide ion polarizability $\alpha_{o2-}(n_o)$ increases from 1.54-1.648 and optical basicity $\Lambda(n_o)$ also increases from 0.586-0.656 in Na_2O-SiO_2 systems. It is general tendency of increasing oxide ion polarizability and optical basicity.

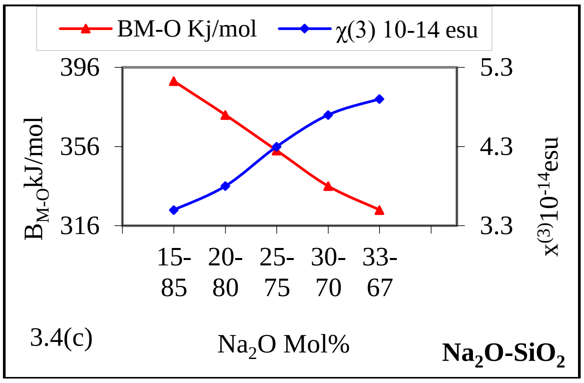

Fig. 3.4.(c) R.I.(n_o), B_{M-O} kJ/mol, $\chi^{(3)}$ 10^{-14} esu., of Na_2O-SiO_2 systems.

Figure 3.4 (c) It shows that the refractive index based values of average single bond strength B_{M-O} decreases from 389-324 kJ/mol, and third order nonlinear susceptibility $\chi^{(3)}$ increases from 3.5-4.9x10^{-14}esu., in Na_2O-SiO_2 systems It is general tendency of increasing oxide ion polarizability and optical basicity.

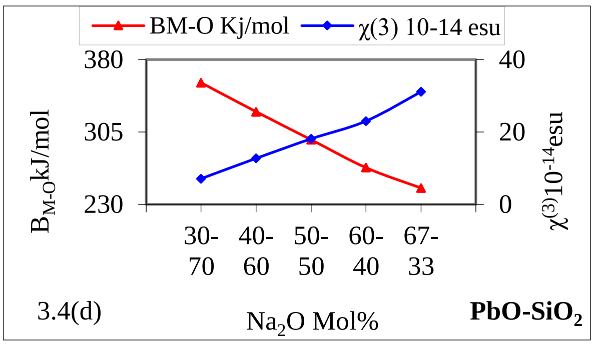

Fig. 3.4.(d) R.I.(n_o), B_{M-O} kJ/mol, $\chi^{(3)}$ 10^{-14} esu., of PbO-SiO_2 systems.

Figure 3.4 (d) It shows that the refractive index based values of average single bond strength B_{M-O} decreases from 356-247 kJ/mol, and third order nonlinear susceptibility $\chi^{(3)}$ increases from 7.1-31.1x10^{-14}esu., in PbO-SiO_2 systems It is general tendency of increasing third order nonlinear susceptibility $\chi^{(3)}$ decreasing average single bond strength B_{M-O}.

Table 2:

System	Mol % of first oxide	n_o	$\alpha_{o2-}(n_o)$	$\Lambda(n_o)$	B_{M-O} kJ/mol	$\chi^{(3)}$ 10^{-14} esu
Na_2O-B_2O_3	5.12	1.481	1.371	0.452	477	
	10.33	1.491	1.37	0.451	455	
	15.2	1.497	1.371	0.452	435	
	20.23	1.502	1.374	0.454	414	
	25.13	1.509	1.38	0.46	394	
	29.85	1.516	1.392	0.471	374	
	34.2	1.517	1.417	0.493	356	
Na_2O-SiO_2	15	1.482	1.54	0.586	389	3.5
	20	1.49	1.565	0.603	372	3.8
	25	1.498	1.591	0.621	354	4.3
	30	1.504	1.627	0.643	336	4.7
	33	1.506	1.648	0.656	324	4.9
PbO-SiO_2	30	1.749	1.442	0.513	356	7.1
	40	1.811	1.516	0.568	326	12.7
	50	1.859	1.608	0.631	297	18.1
	60	1.942	1.65	0.658	268	23
	67	1.996	1.74	0.71	247	31.1

Table 2 Refractive index n_o, oxide ion polarizabilities $\alpha_{o2-}(n_o)$, optical basicity $\Lambda(n_o)$ B_{M-O} kJ/mol and $\chi^{(3)}$ 10^{-14} esu of Na_2O-B_2O_3 and Na_2O-SiO_2, PbO-SiO_2 glass systems.

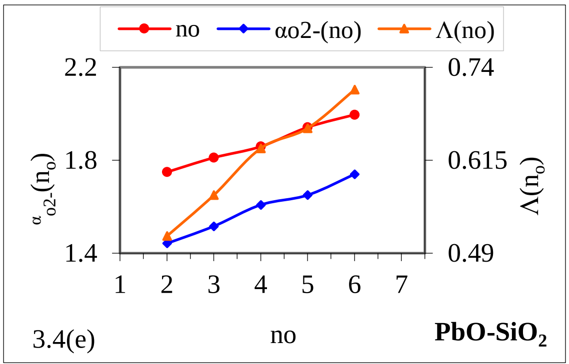

Fig. 3.4.(e) R.I.(n_o), αo2-(no), Λ(no) of PbO-SiO_2 systems

Figure 3.4(e) shows that the refractive index increases from 1.749-1.996, oxide ion polarizability $\alpha_{o2-}(n_o)$ increases from 1.442-1.740 and optical basicity $\Lambda(n_o)$ also increases from 0.513-0.710 in PbO-SiO_2 systems. It is general tendency of increasing oxide ion polarizability and optical basicity.

CONCLUSION

The polarizability increases with increasing Sb_2O_3 and Bi_2O_3 content, but the values of oxide ion polarizabilities $\alpha_{o2-}(E_o)$ and the values of optical basicity $\Lambda(E_o)$ are larger than those obtained for oxide ion polarizabilities $\alpha_{o2-}(n_o)$ and optical basicity $\Lambda(n_o)$.Consequently it seems to be more informative to use oxide ion polarizabilities $\alpha_{o2-}(n_o)$ and optical basicity $\Lambda(n_o)$ for the analysis of the electronic polarizability of these glass. It has been concluded that high refractive index basic glasses with increased tendency in oxide ion polarizabilities $\alpha_{o2-}(n_o)$, $\alpha_{o2-}(E_o)$ and in optical basicity $\Lambda(n_o)$, $\Lambda(E_o)$; and decreasing average single bond strength B_{M-O} with increasing the third order nonlinear optical susceptibility $\chi^{(3)}$.

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