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

Correlation between Optical Basicity and Oxide ion Polarizability In Glass formers and Glass modifiers (Review)

D.B.Thombre

Ex. Associate Professor, Department of Physics, Jagdamba Mahavidyalaya, Achalpur City, India

---

Abstract - The oxide ion polarizability and Optical Basicity approach in the glasses has been studied detail by V. Dimitrov and T. Komatsu, V. Dimitro and S. Sakka Duffy. Here a review is taken on the basics of their literature values. The average values of ion polarizability and average values of optical basicity given on the basics of refractive index and energy gap is correlated in glass formers, conditional glass formers, alkaline and alkaline earth oxides glass modifiers.

Key Words: Ionic polarizability, Basicity, Glass formers, Conditional glass formers, alkaline and alkaline earth oxides glass modifiers.

1. INTRODUCTION

Glass forming oxides are classically described as a network composed by building entities such as SiO_2, B_2O_3, P_2O_5, GeO_2, As_2O_3, and Sb_2O_3. There are also other glass former oxides called as conditional glass former oxides. Here I have studied it in to two groups. From group of periodic table III (A,B) & IV (A,B); Y_2O_3, HfO_2, ZrO_2, Sc_2O_3, TiO_2, Al_2O_3, In_2O_3, Ga_2O_3, SnO_2 are considered as conditional glass former oxides (I).and from group V(A,B) & VI(A,B); Ta_2O_5, Nb_2O_5, V_2O_5, Cr_2O_3, Bi_2O_3, TeO_2, MoO_3, As_2O_3, WO_3, Se_2O_3 are considered as conditional as glass forming oxides (II). Li_2O, Na_2O, K_2O, Rb_2O, Cs_2O CaO, MgO, and SrO, BeO, MnO, CoO, ZnO, CuO, NiO, CdO, PbO, BaO [1, 2]; are Glass modifier alkali oxides and alkaline earth modifier oxides respectively.

All conditional glass former oxides (I) and (II) are according to Pauling's packing rule, Goldschmidt radius ratio rule, Zachariasen's random network theory, and Sun's single bond strength theory. For Glass formers r_c/r_a = 0.142-0.314 [except P_2O_5 (0.642)].For conditional glass formers (I) radius ratio r_c/r_a = 0.250-0.492. For Conditional glass formers (II) radius ratio r_c/r_a = 0.528-0.875, and single bond strength greater than 90 Kcal/mol. According to Sun's, high bond strength oxides are not good glass formers because they themselves do not forms glass; but when they forms small ring in the melt of these materials which result in easy crystallization.

The polarizability approach has shown renewed interest because of the need to design optical functional materials and to search for novel glasses with higher optical performances such as oxide glasses. Dimitrov and Sakka[1] calculated the electronic oxide ion polarizability (α_{o2-}) of larger number of single component oxides on the basis of linear refractive index (n_o) and energy gap (E_g). It was established that there is general tendency of increase oxide ion polarizability with increasing refractive index and decreasing energy gap. Dimitrov and Komatsu [2] extended this approach for numerous binary oxide glasses and have found similar trend. Optical basicity as proposed by Duffy and Ingram [3, 4] is used with transition metal and heavy metal oxides. Reddy et al.[5] calculates the basicity on the basics of average electronegativity for simple oxides, binary oxides, alkaline and alkaline earth oxide glasses. Zhao et al.[6] on the basics of optical electronegativity for binary oxides glasses.

The purpose of the article is to consider the status of the oxide ion polarizability approach in the glass science and to emphasize the role of the optical basicity helpful to the new researchers.

2. THEORETICAL CONSIDERATIONS

Dimitrov and Sakka [1] have determined the optical basicity for numerous single oxides on the basis of their refractive index $\Lambda(n_o)$ and Energy gap $\Lambda(E_g)$.

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

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

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.

Duffy [7] has established an relation exists between electronic polarizability of the oxide ions α_{o2-} and optical basicity of the oxide medium Λ, as given by equation

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

By using equation (3) Dimitrov and Sakka [1] also calculates optical basicity, on the basis of their refractive index $\Lambda(n_o)$ and Energy gap $\Lambda(E_g)$.

Duffy and Ingram [3,4] calculates the basicity on the basics of Pauling electronegativity by using equation for metal oxides as well as for alkaline earth oxides.

$$\Lambda = 0.75/(\chi-0.25) \quad (4)$$

where χ is Pauling electronegativity.

Sun [8] has given a general treatment to all kinds of glasses, particularly oxide glasses. His observations reveal that the bond strengths of is greater than 80 kcal/mol foe all the glass formers.

3. RESULT AND DISCUSSION

In the review of this article $\alpha_{o2-}{}^{av}$ $(A^o)^3$ is the average values of oxide ion polarizability calculated from refractive index ($\alpha_{o2-}(n_o)$) and energy gap ($\alpha_{o2-}(E_g)$). Similarly Λ^{av} is the average values of optical basicity calculated from refractive index $\Lambda(n_o)$ and energy gap $\Lambda(E_g)$ by Dimitrov and Sakka[1]. The average values of basicity given by Duffy[7] are considered. Classifying oxides and arranging basicity values in ascending order, the result and discussion is as follow;

3.1 Glass formers:

For Glass formers SiO_2, B_2O_3, P_2O_5, GeO_2, r_c/r_a = 0.142-0.314 [except P_2O_5 (0.642)].

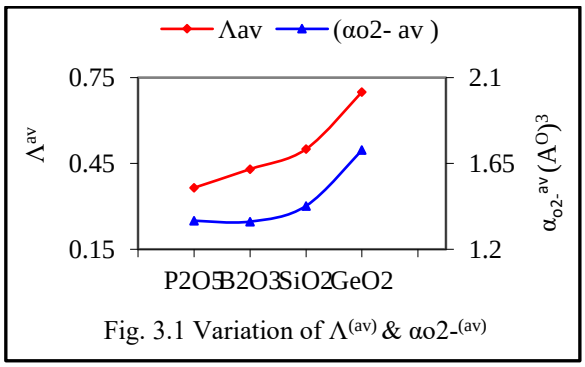

Fig. 3.1 Variation of $\Lambda^{(av)}$ & $\alpha o2^{-(av)}$

Figure 3.1 shows that oxide ion polarizability increases from 1.345 to 1.72 $(A^o)^3$ and optical basicity also increases from 0.365-0.7 i.e. oxide ion polarizability increases on increasing the optical basicity with glass formers.

Table 3.1:

Glass formers	Λ^{av}	$(\alpha o2-^{av})$
P_2O_5	0.365	1.350
B_2O_3	0.430	1.345
SiO_2	0.500	1.427
GeO_2	0.700	1.720

Table 3.1 Glass formers, optical basicity (Λ^{av}) and oxide ion polarizability (α_{o2-}^{av}) of simple oxides.

3.2 Conditional glass formers (I):

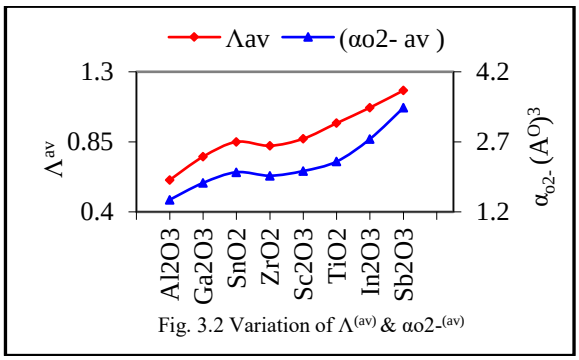

Fig. 3.2 Variation of $\Lambda^{(av)}$ & $\alpha o2^{-(av)}$

Figure 3.2 shows that oxide ion polarizability increases from 1.46 to 3.492 $(A^o)^3$ and optical basicity also increases from 0.605 to 1.18 i.e. in conditional glass formers (I) oxide ion polarizability also increases on increasing the optical basicity.

Table 3.2:

Cond.glass formers (I)	Λ^{av}	$(\alpha o2-^{av})$
Al_2O_3	0.605	1.460
Ga_2O_3	0.755	1.822
SnO_2	0.850	2.050
ZrO_2	0.825	1.975
Sc_2O_3	0.870	2.075
TiO_2	0.970	2.278
In_2O_3	1.070	2.762
Sb_2O_3	1.180	3.429

Table 3.2 Cond. glass formers (I), optical basicity (Λ^{av}), and oxide ion polarizability (α_{o2-}^{av}) of simple oxides.

3.3 Conditional glass formers (II):

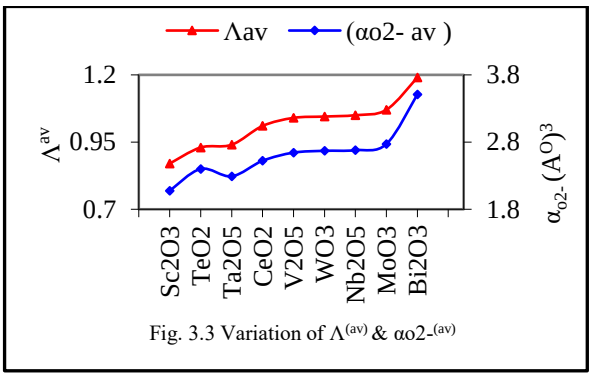

Fig. 3.3 Variation of $\Lambda^{(av)}$ & $\alpha o2^{-(av)}$

Figure 3.3 shows that oxide ion polarizability increases from 2.075-3.507 $(A^o)^3$, basicity increases from 0.87-1.19 i.e. in conditional glass formers (II) oxide ion polarizability also increases on increasing the optical basicity.

Table 3.3:

Cond. glass formers (II)	Λ^{av}	$(\alpha o2-^{av})$
Sc_2O_3	0.87	2.075
TeO_2	0.93	2.401
Ta_2O_5	0.94	2.291
CeO_2	1.01	2.522
V_2O_5	1.04	2.643
WO_3	1.045	2.670
Nb_2O_5	1.05	2.679
MoO_3	1.07	2.769
Bi_2O_3	1.19	3.507

Table 3.3 Cond. glass formers (II), optical basicity (Λ^{av}) , oxide ion polarizability (α_{o2-}^{av}) of simple oxides.

3.4 Alkaline and Alkaline earth glass oxide modifiers: Alkaline and alkaline earth oxide glass modifiers are mostly used in glasses to modify the network to study the so many properties.

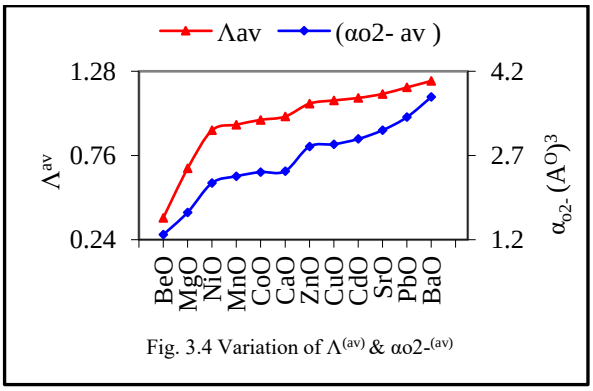

Fig. 3.4 Variation of $\Lambda^{(av)}$ & $\alpha o2^{-(av)}$

Figure 3.4 shows that oxide ion polarizability increases from 2.075-3.507 $(A^o)^3$, basicity increases from 0.87-1.19 i.e. in conditional glass formers (II) oxide ion polarizability also increases on increasing the optical basicity.

Table 3.4:

Alkaline & Alkaline earth oxides	Λ^{av}	($\alpha o2-^{av}$)
BeO	0.375	1.290
MgO	0.680	1.687
NiO	0.915	2.210
MnO	0.950	2.330
CoO	0.980	2.405
CaO	1.000	2.420
ZnO	1.080	2.859
CuO	1.100	2.900
CdO	1.115	2.993
SrO	1.140	3.150
PbO	1.180	3.381
BaO	1.220	3.741

Table 3.4 Alkaline & Alkaline earth oxides, optical basicity (Λ^{av}) , and oxide ion polarizability (α_{o2-}^{av}) of simple oxides.

3.5 Mix glass formers: The relation between refractive index and energy gap for mix glass formers gives,

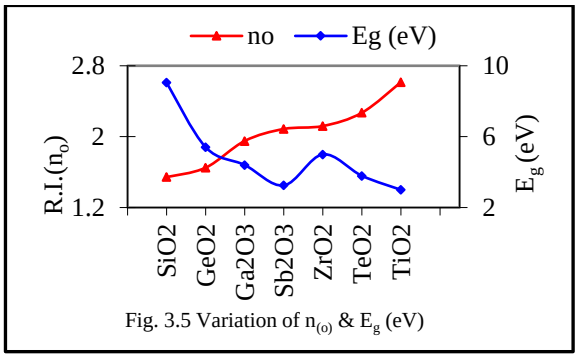

Fig. 3.5 Variation of $n_{(o)}$ & E_g (eV)

Figure 3.5 shows that the refractive index (n_o) increases from 1.544-2.616 where as energy gap (E_g) decreases from 9.05-3 (eV) i.e. in mix glass formers refractive index and energy gap are inversely varying.

Table 3.5:

Mix glass formers	R.I.(n_o)	E_g(eV)
SiO_2	1.544	9.05
GeO_2	1.650	5.40
Ga_2O_3	1.952	4.40
Sb_2O_3	2.087	3.25
ZrO_2	2.120	5.00
TeO_2	2.270	3.79
TiO_2	2.616	3.00

Table 3.5 Mix glass formers, Refractive index (n_o), Energy gap E_g (eV) of simple oxides

3.6 Alkaline and Alkaline earth glass oxide modifiers: The relation between refractive index and energy gap for alkaline and alkaline earth oxide glass modifiers gives,

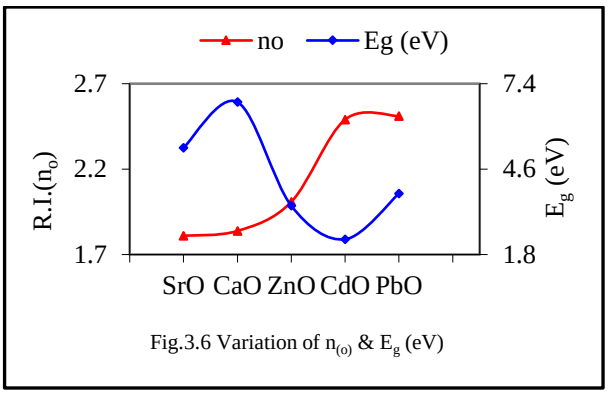

Fig.3.6 Variation of $n_{(o)}$ & E_g (eV)

Figure 3.6 shows that the refractive index (n_o) increases from 1.81-2.51 where as energy gap (E_g) decreases from 3.8-6.8 (eV) i.e. in alkaline and alkaline earth oxides refractive index and energy gap are also inversely varying.

Table 3.6:

Alkaline & Alkaline earth oxides	R.I. (n_o)	E_g(eV)
SrO	1.81	5.3
CaO	1.838	6.8
ZnO	2.008	3.4
CdO	2.49	2.3
PbO	2.51	3.8

Table 3.6 Alkaline & Alkaline earth oxides, Refractive index (n_o), Energy gap E_g (eV) of simple oxides.

CONCLUSION

It is all ready concluded by Dimitrov & Sakka, and Duffy that is, increase of refractive index increases optical basicity and oxide ion polarizability. In case of mix glass formers and alkaline & alkaline earth oxide modifiers energy gap is decreasing on increasing refractive index.

REFERENCES

[1] V.Dimitrov and S. Sakka, J. Appl.Phys. 79(1996) 1736
[2] V.Dimitrov and T. Komatsu, Journal of the University of Chemical Technology and Metallurgy. 45, 3, (2010), 219-250.
[3] J.A. Duffy and M.D. Ingram, optical properties of glasses, Eds. D. Uhlman, N. Kreidl, Am. Ceram. Soc, Westervill, (1991).
[4] J.A. Duffy and M.D. Ingram, in Electrochemistry of Glasses and Glass Melts, Including Glass electrodes, Eds. H. Bach, F. Baucke, D. Krause, Springer, (2000).
[5] R.R. Reddy, Y. Nazeer Ahammed, P. Abdul Azeem, K. Rama Gopal, T.V.R.Rao, J. Non-Cryst. Solids, 286, (2001), 169.
[6] X. Zhao. X. Wang, H. Lin, Z. Wang, Physica B, 403, (2008), 2450.
[7] J.A. Duffy, Phys.Chem.Glasses, 30(1989) 1
[8] K. H. Sun. J. Am. Ceram. Soc.,30, (1947), 277.
[9] Goldschmidt V M Naturwiss 21 (1926), 477
[10] W. Zachariasen. J. Am. Chem. Soc., 54, (1932), 3841.