

Study of Conditional Glass Formers (II) on Basics of Optical Electronegativity

D.B.Thombre

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

Abstract - Concept of Electronegativity is used by so many researchers to calculate Refractive index Band energy, Dielectric constant, Metallization criterion, Basicity, Oxide ion polarizability, Bond ionicity, Third order non-linear optical susceptibility to study the so many glass systems. Here the concept of optical electronegativity is used to study these parameters for conditional glass formers refer as (II) of group V(A,B) and VI(A,B). They are Ta₂O₅, Nb₂O₅, V₂O₅, Cr₂O₃, Bi₂O₃, TeO₂, MoO₃, As₂O₃, WO₃, Se₂O₃. It is observed that on decreasing the values of optical electronegativity, optical band energy, metallization criterion, and bond ionicity decreases; and optical dielectric constant, optical basicity, oxide ion polarizability refractive index, third order non linear optical susceptibility increases. All conditional glass forming oxides (II) are according to Pauling's packing rule, Goldschmidt radius ratio rule, Zachariasen's random network theory and rules for formation of glass and Sun's single bond strength theory. For Conditional glass formers (II) radius ratio $r_o/r_a = 0.250-0.492$, [except Bi₂O₃ (0.75) & TeO₂ (0.87)] 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 would result in easy crystallization.

Key Words: Refractive index Band energy, Dielectric constant, Metallization criterion, Basicity, Oxide ion polarizability, Bond ionicity, Third order non-linear optical susceptibility.

1. INTRODUCTION

Glass forming oxides are SiO₂, B₂O₃, P₂O₅, GeO₂, As₂O₃, and Sb₂O₃. Conditional glass forming oxides are Y₂O₃, HfO₂, ZrO₂, Sc₂O₃, TiO₂, Al₂O₃, In₂O₃, Ga₂O₃, and Ta₂O₅, Nb₂O₅, V₂O₅, Cr₂O₃, Bi₂O₃, TeO₂, MoO₃, As₂O₃, WO₃, Se₂O₃. Glass modifier alkali oxides are Li₂O, Na₂O, K₂O, Rb₂O, Cs₂O. Glass modifier alkaline earth oxides are CaO, MgO, SrO, BeO, MnO, CoO, ZnO, CuO, NiO, CdO, PbO, and BaO [1, 2]. In such glasses the oxygen from the metal oxide becomes part of the covalent glass network, creating new structural units. The cations of the modifier oxide are generally present in the neighborhood of the non-bridging oxygen (NBO) in the glass structure. The extent of the network modification obviously depends on the concentration of the modifier oxide present in the glass. A glass network affects various physical properties such as density, molar volume, glass transition temperature & polarization, etc. 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.

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 [3]. Dimitrov.V and 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. The present work contains optical parameters in the case of conditional glass formers on the basics of optical electronegativity.

2. THEORETICAL CONSIDERATIONS

2.1 Definition of glass: There are number of different definitions of glass; according to the A.S.T.M. definition "glass is an inorganic product of fusion, which has cooled to a rigid condition without crystallization". This is a clear cut and practical definition of glass, but it does not say much about its structure. It does, however, express very clearly that glass is a solid. According to the thermodynamic definition "glass is a solid system obtained from a liquid without a first order phase transition". The second order phase transition that is responsible for the glass formation is highly temperature dependent it usually takes place comparatively slowly, due to the absence of short time fluidity. Finally, according to the crystallographic definition "glass is a solid system, the structure of which, if considered over more than a few atomic distances, does not show either periodicity or symmetry". In other words, glass is a solid system, characterized by the absence of long range order. Broadly, glass may be defined as "super cooled liquid".

Basically electronegativity is calculated by stander equation,

$$\Delta\chi = \chi_{\text{anion}} - \chi_{\text{cation}} \quad (1)$$

where $\Delta\chi$ = electronegativity difference, χ_{anion} and χ_{cation} are Pauling electronegativity of anion and cation.

Similarly

Optical electronegativity is calculated by stander equation,

$$\Delta\chi^* = \chi^*_{\text{anion}} - \chi^*_{\text{cation}} \quad (2)$$

Where $\Delta\chi^*$ = optical electronegativity difference, χ^*_{anion} and χ^*_{cation} are based on the Pauling electronegativity of anion and cation.

The optical electronegativity ($\Delta\chi^*$) is a key parameter to understand the nature of chemical bonding and other important parameters.

2.2 Refractive Index (n): The optical refractive index is one of the fundamental properties of materials because it is closely related to the electronic polarizability of ions and local field inside the material, which plays an important role in determining the electrical properties of such materials.

Therefore, the evaluation of refractive index has been a matter of considerable importance and several investigations have been carried out for this purpose. [5,6] The optical refractive indexes are calculated by empirical relationship related optical

electronegativity given by Reddy et al. [7] which is given as follows:

$$n = -\ln(0.102 \cdot \Delta\chi^*) \quad (3)$$

where $\Delta\chi^*$ = optical electronegativity difference, χ^*_{anion} and χ^*_{cation} are based on the Pauling electronegativity of anion and cation.

Moss [12] and Ravindra's relation [8] related to optical electronegativity which is given as follows,

$$n = (25.54/\Delta\chi^*)^{1/4} \quad (4)$$

Where $\Delta\chi^*$ = optical electronegativity difference, χ^*_{anion} and χ^*_{cation} are based on the Pauling electronegativity of anion and cation.

In case of result and discussion, average value of RI is taken calculated from eq. (3 & 4).

2.3 Band Gap Energy (E_g): One of the properties of semiconductors which are extremely significant for device functions is the band gap. Some simplistic theoretical methods were recognized that can calculate band gap, refractive index and optical electronegativity of binary and complex structured solids from selected atomic properties of their constituent elements. The optical electronegativity is a key parameter to understand the nature of chemical bonding and other important parameters Duffy [9,10,11] has correlated the energy gap and optical electronegativity difference for various systems as

$$E_g = 3.72 (\Delta\chi^*) \quad (5)$$

where $\Delta\chi^*$ = optical electronegativity difference, χ^*_{anion} and χ^*_{cation} are based on the Pauling electronegativity of anion and cation.

2.4 Optical oxide ion polarizability (α_{o2}): The electronic polarizability of oxide ions calculated by Dimitrov and Sakka using the equation depending on molar refraction and molar volume. The oxide ions polarizability calculated by Duffy using the equation depending on relationship between the oxide ion polarizability and optical basicity. Oxide ion polarizability calculated by using the equation which gives relationship between the oxide ion polarizability and electronegativity [Zhao et.al.] [12]

$$\alpha_{o2} = (-0.9 \cdot \Delta\chi^*) + 3.5 \quad (6)$$

where $\Delta\chi^*$ = optical electronegativity difference, χ^*_{anion} and χ^*_{cation} are based on the Pauling electronegativity of anion and cation.

2.5 Optical basicity (Λ): The degree of basicity of glass is related to the electron donor power of oxygen atom. Optical basicity calculated by using the equation which gives relationship between the basicity and optical electronegativity Zhao et.al. [12]

$$\Lambda = (-0.5 \cdot \Delta\chi^*) + 1.7 \quad (7)$$

where $\Delta\chi^*$ = optical electronegativity difference, χ^*_{anion} and χ^*_{cation} are based on the Pauling electronegativity of anion and cation.

2.6 Bond Ionicity (I_b): Lambson (et.al.) [13] calculated the bond ionicity by using electronegativity as,

$$I_b = 1 - \exp[-0.25(\Delta\chi^*)^2] \quad (8)$$

Where $\Delta\chi^*$ = optical electronegativity difference, χ^*_{anion} and χ^*_{cation} are based on the Pauling electronegativity of anion and cation.

2.7 Optical Dielectric constant ($p(dt/dp)$): Schroeder [14] calculated the optical dielectric constant by using refractive index as,

$$P(dt/dp) = n^2 - 1 \quad (9)$$

Where n = refractive index

2.8 Polarizability per unit volume (R_m/V_m): Lorentz-Lorenz [15,16] calculated the polarizability per unit volume by using refractive index as,

$$R_m/V_m = (n^2 - 1/n^2 + 2)$$

where n = refractive index

2.9 Metallization criterion (M): Lorentz-Lorenz [15,16] calculated the metallization criterion by using polarizability per unit volume as,

$$M = 1 - (R_m/V_m) \quad (10)$$

Where (R_m/V_m) = polarizability per unit volume

2.10 Third-order nonlinear optical susceptibility ($\chi^{(3)}$): Kim-Yoko et.al. [17-20] calculated the third-order nonlinear optical susceptibility by using refractive index as.

$$\chi^{(3)} = [(n^2 - 1)/4\pi]^4 \cdot 10^{-10} \text{ esu} \quad (11)$$

where n = refractive index

All these parameters are inter-related with each other, study of some of these parameters; arranging on decreasing order of optical electronegativity is discussed here; their results and discussions are as follows;

Table -1:

Conditional glass formers (II)	Optical electronegativity ($\Delta\chi^*$)	Optical band energy E_g (eV)	Optical refractive Index (n)	Optical dielectric constant $p(dt/dp)$
Ta ₂ O ₅	0.7428	2.7635	2.5007	5.2535
Nb ₂ O ₅	0.652	2.4255	2.606	5.7917
V ₂ O ₅	0.6273	2.3337	2.6375	5.9564
Cr ₂ O ₃	0.6037	2.2458	2.6688	6.1228
Bi ₂ O ₃	0.3831	1.4251	2.8467	8.3013
TeO ₂	0.3458	1.2864	3.0498	8.8476
MoO ₃	0.3198	1.1900	3.2058	9.2775
As ₂ O ₃	0.3116	1.1592	3.2288	9.4252
WO ₃	0.2442	0.9084	3.4452	10.869
Se ₂ O ₃	0.1845	0.6865	3.7012	12.699

Table1: shows values of Optical electronegativity ($\Delta\chi^*$), Optical band energy E_g (eV), Optical refractive Index (n), Optical dielectric constant $p(dt/dp)$.

Table -2:

Conditional glass formers (II)	Λ	$\alpha_{o2} - (A^\circ)^3$	I_b	$\chi^{(3)} \cdot 10^{-14} \text{ esu}$
Ta ₂ O ₅	1.3285	2.8313	0.1288	0.3061
Nb ₂ O ₅	1.3739	2.9131	0.1008	0.4521
V ₂ O ₅	1.3863	2.9353	0.0937	0.5058
Cr ₂ O ₃	1.3981	2.9566	0.0871	0.5647
Bi ₂ O ₃	1.5084	3.1551	0.0361	1.9082
TeO ₂	1.5270	3.1887	0.0294	2.4623
MoO ₃	1.5401	3.2120	0.0252	2.9771
As ₂ O ₃	1.5441	3.2195	0.0239	3.1711
WO ₃	1.5778	3.2802	0.0147	5.6091
Se ₂ O ₃	1.6077	3.3339	0.0084	10.4512

Table2: Shows values of Optical basicity (Λ), Optical oxide ion polarizability ($\alpha_{o2} - (A^\circ)^3$), Optical bond ionicity (I_b), and Third order nonlinear optical susceptibility ($\chi^{(3)} \cdot 10^{-14} \text{ esu}$).

3. RESULT AND DISCUSSION

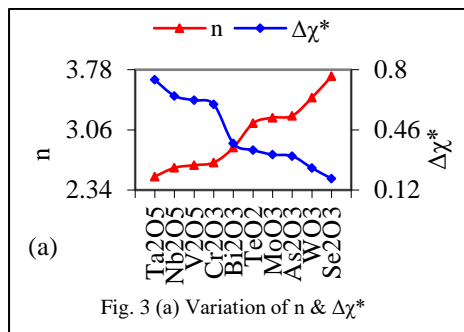


Fig. 3 (a) Variation of n & $\Delta\chi^*$

Figure 3(a) shows the variation of which refractive index increases from 2.5007-3.7012 and optical electronegativity decreases from 0.7428-0.1845 with respective to conditional glass formers (II).

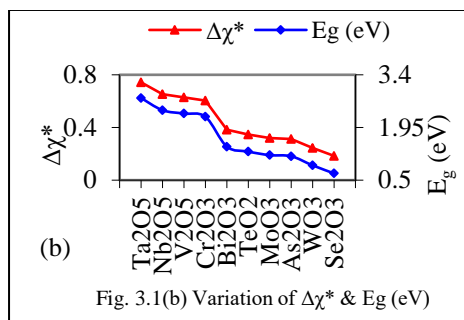


Fig. 3.1(b) Variation of $\Delta\chi^*$ & E_g (eV)

Figure 3 (b) shows variation of optical electronegativity and optical band energy decreases from 0.7428-0.1845 and from 2.7635-0.6865 respectively, with respective to conditional glass formers.

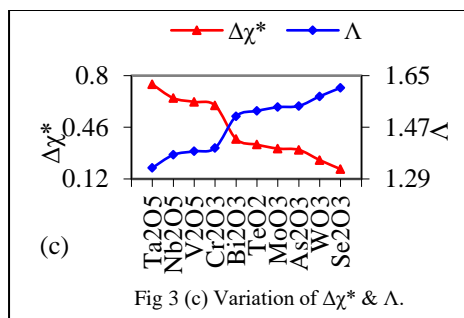


Fig 3 (c) Variation of $\Delta\chi^*$ & Λ .

Figure 3 (c) shows the variation of optical electronegativity which decreases from 0.7428-0.1845; and optical basicity increases from 1.3285-1.6077 with respective to conditional glass formers (II).

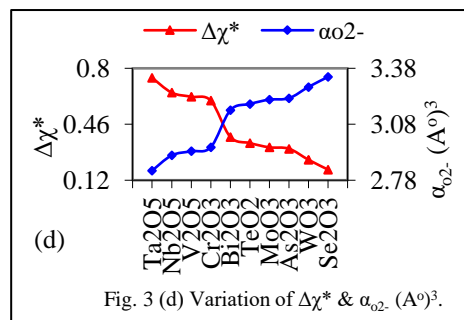


Fig. 3 (d) Variation of $\Delta\chi^*$ & α_{o2-} (A°)³.

Figure 3(d) shows the optical electronegativity decreases from 0.7428-0.1845 and oxide ion polarizability increases from 2.8313-3.3339 (A°)³ with respective to conditional glass formers(II).

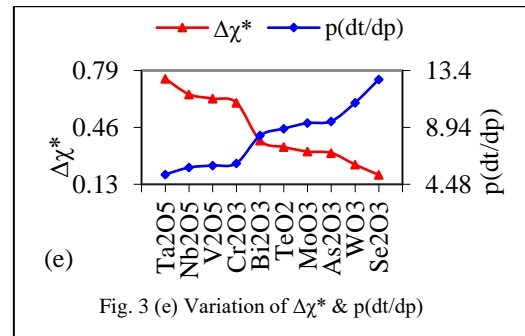


Fig. 3 (e) Variation of $\Delta\chi^*$ & $p(dt/dp)$

Figure 3.1(e) shows the optical electronegativity decreases from 0.7428-0.1845 and optical dielectric constant increases from 5.2535-12.6993 with respective to conditional glass formers (II).

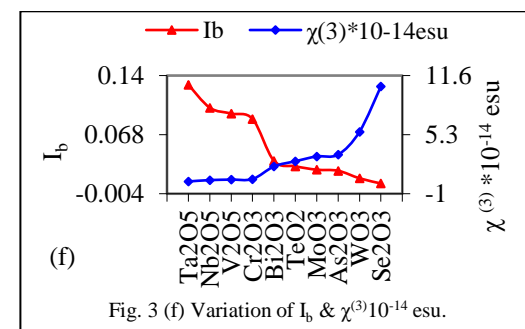


Fig. 3 (f) Variation of I_b & $\chi^{(3)}10^{-14}$ esu.

Figure 3 (f) shows the optical bond ionicity decreases from 0.1288-0.0084 and third order non-linear optical susceptibility increases from (0.3061-10.4512)* 10^{-14} esu with respective to conditional glass formers (II).

Graphs of any two parameters are always gives positive or negative straight line as below;

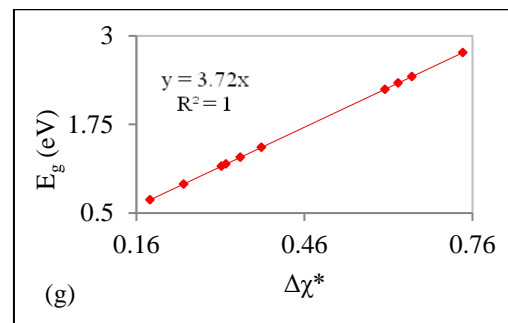


Fig. 3 (g) Variation of $\Delta\chi^*$ & E_g (eV)

Figure 3 (g) shows the variation of optical electronegativity which increases from 0.1845-0.7428; and optical band energy also increases from 0.6865-2.7635 (eV) gives positive straight line equation with slop = 3.72 and $R^2=1$.

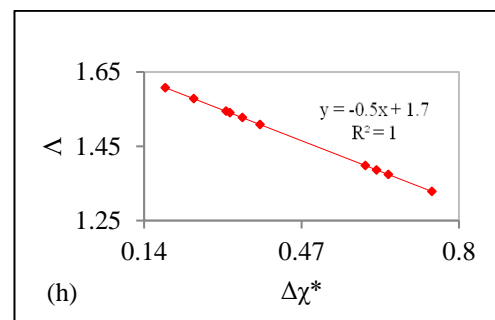


Fig. 3 (h) Variation of $\Delta\chi^*$ & Λ

Figure 3 (h) shows the variation of optical electronegativity which increases from 0.1845-0.7428; and optical basicity decreases from 1.6077 - 1.3265 gives negative straight line equation with $\text{slop} = -0.5$, $\text{constant} = 1.7$ and $R^2=1$. Values of R^2 for other parameters are lie between 0.556 - 0.985.

CONCLUSION

From the above result and discussion, it was found that, for conditional glass formers (II) [group V(A,B) and VI(A,B)] the optical electronegativity decreases; The optical basicity of the glass materials increase by increasing number of oxide ion polarizability. The value of optical basicity shows that the glass materials are more basic. It is suggested that the ability of oxide ion to donate electrons to surrounding cations increases. Also, it was found that the values of third order nonlinear susceptibility increase with decreasing the optical energy gap and increasing the refractive index the optical dielectric constant increases with decreasing metallization criterion. Finally above values are good bases.

REFERENCES

- [1] C. H. Lee, K. H. Joo, J. H. Kim, S. G. Woo, H. J. Sohn, T. Kang, Y. Park and J. Y. Oh.Characterizations of a new lithium ion conducting $\text{Li}_2\text{O}-\text{SeO}_2-\text{B}_2\text{O}_3$ glass electrolyte. *Solid State Ionics*, Vol. 149, (2002), pp. 59-65.
- [2] F. Muñoz, L. Montagne, L. Delevoye, A. Durán, L. Pascual, S. Cristol and J-F Paul. Phosphate speciation in sodium borosilicate glasses studied by, nuclear magnetic resonance. *J. Non-Cryst. Solids*, Vol. 352, (2006), pp. 2958-2968.
- [3] M. Vithal, P. Nachimuthu, T. Banu and R. Jagannathan,. (Optical and Electrical properties of $\text{PbO}-\text{TiO}_2$, $\text{PbO}-\text{TeO}_2$ glass system), (1997), *J. Appl. Phys.*, 81: 7923.
- [4] V. Dimitrov, S. Sakka. (Electronic oxide ion polarizability and optical basicity of simple oxides I, (1996), *J. Appl. Phys.* 79, 1736.
- [5] T.S. Moss, *Photoconductivity in the Elements*, Butterworth, London 1952.
- [6] R.R. Reddy, K. Rama Gopal, K. Narasimhulu, L. Siva Sankara Reddy, K. Raghavedra Kumar, C.V. Krishna Reddy, S.N. Ahmed, *Opt. Mater.* 31, 209 (2008).
- [7] R.R. Reddy, Y.N. Ahammed, K.R. Gopal, D.V. Raghuram, *Optical Materials* 10, 95 (1998).
- [8] N.M. Ravindra, S. Auluck, V.K. Srivastava, *Phys. Status Solidi B* 93, K155 (1979).
- [9] J.A. Du_y, *J. Phys. C, Solid. State Phys.* 13, 2979 (1980).
- [10] J.A. Du_y, *Bonding Energy Levels and Bonds in Inorganic Solids*, Longman Sci. Technol, England (1990).
- [11] J.A. Duffy, *Bonding, Energy Level and Bonds in Inorganic Solids*, Longman, England, (1990); *Phys. Chem Glass*, 42, 151 (2001).
- [12] Zhao , X., Wang,X., Lin , Z. Wang , Anew approach to estimate refractive index, electronic polarizabilty and optical basicity of binary oxide glasses, *Physica*, B,403,2450 (2008)
- [13] E. Lambson, G. Saunders, B. Bridge, R. A. El-allawany, "The elastic behaviour of TeO_2 glass under uniaxial and hydrostatic pressure," *J. Non-Cryst. Solids* 69 (1984) 117-133.
- [14] Schroeder, J. *Brillouin Scattering and Pockels Coefficients in Silicate Glasses*. *Journal of Non-Crystalline Solids*, 40, (1980) 549-566.
[http://dx.doi.org/10.1016/0022-3093\(80\)90129-5](http://dx.doi.org/10.1016/0022-3093(80)90129-5)
- [15] H.A. Lorentz, *Ann. Phys.*, 9, (1880), 641.
- [16] L. Lorenz, *Wiedem. Ann.*, 11,1881,70
- [17] T. Hashimoto, T. Yoko, Third-order nonlinear optical properties of sol-gel-derived V_2O_5 , Nb_2O_5 and Ta_2O_5 thin films, *Appl. Opt.*, 34, (1995), 2941-2948.
- [18] S.H. Kim, T. Yoko, S. Sakka, Linear and nonlinear optical properties of TeO_2 glasses, *J. Am. Ceram. Soc.*, 76, 10, (1993), 2486-2490.
- [19] H. Kim, T. Yoko, Nonlinear optical properties of TeO_2 -based glasses: $\text{MOx}-\text{TeO}_2$ (M=Sc, Ti, V, Nb, Mo, Ta, and W) binary glasses, *J. Am. Ceram. Soc.*, 1995, 78, 1061-1065.
- [20] H Kim, T. Yoko, S. Sakka, Nonlinear optical properties of TeO_2 -based glasses: $\text{RO}-\text{TeO}_2$ (R=Mg, Sr and Ba) binary glasses, *Bull. Inst. Chem. Res., Kyoto Univ.*, 72, 2, (1994), 178-186.