STUDY OF GLASS FORMERS ON BASICS OF OPTICAL ELECTRONEGATIVITY

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Abstract - Concept of electronegativity is used by so many researchers to study Refractive index, Band energy, Dielectric constant, Metallization criterion, Basicity, Oxide ion polarizability, Bond ionicity, Third order non-linear optical susceptibility to study so many glass systems. Here the concept of optical electronegativity is used to study these parameters in glass formers. It is observed that on decreasing the values of optical electronegativity; optical band energy, metallization criterion, and bond ionicity decreases; where as optical dielectric constant, optical basicity, oxide ion polarizability refractive index and third order non linear optical susceptibility increases. All glass forming oxides 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 glass formers radius ratio r_c/r_a = 0.14-0.40, [except P_2O_5] and single bond strength greater than 90 Kcal/mol.

Key Words: Band energy, Basicity, Optical dielectric constant, Oxide ion polarizability, Refractive index.

1. INTRODUCTION

Glass forming oxides are SiO_2, B_2O_3, P_2O_5, GeO_2, As_2O_3, Sb_2O_3. Conditional glass forming oxides are TiO_2, Cr_2O_3, V_2O_5, WO_3, Ga_2O_3, Bi_2O_3 Glass modifier alkali oxides are Li_2O, Na_2O, K_2O, Rb_2O and Cs2O. Glass modifier alkaline earth oxides are CaO, MgO, SrO, BeO, MnO, CoO, ZnO, CuO, NiO, CdO, PbO and BaO. [1, 2] In glass forming oxides; 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 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 study contains optical parameters in the case of glass formers on the basics of optical electronegativity because the optical electronegativity ($\Delta\chi^*$) is a key parameter to understand the nature of chemical bonding and other important parameters.

2. THEORETICAL CONSIDERATIONS

2.1 Definition of Glass:

There are number of different definitions of glass; according to the A.S.T.M. "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. However it expresses 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 is considered by 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 using stander equation,

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

where $\Delta\chi$ = electronegativity difference; χanion and χcation are Pauling electronegativity of anion and cation. Similarly Optical electronegativity is calculated by using stander equation,

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

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

2.2 Optical 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] using equation,

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

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

Moss [5] and Ravindra's relation [8] related to optical electronegativity which is given by equation,

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

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

In present case value of refractive index is used as, average of refractive index calculated from equ.3 and 4.

2.3 Optical band Gap Energy (Eg): 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. Duffy [9, 10, 11] has correlated the energy gap and optical electronegativity difference for various systems as

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

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]

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

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]

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

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

2.6 Optical bond Ionicity (Ib): According to Lambson (et.al.) [13] Optical bond ionicity is calculated by using equation as,

$$I_b = 1\text{-}\exp\ [-0.25(\Delta\chi^*)^2] \qquad (8)$$

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] optical dielectric constant is calculated by using refractive index as,

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

where n= optical refractive index

2.8 Polarizability per unit volume (Rm/Vm): Lorentz-Lorenz [8, 9] calculate the polarizability per unit volume by using refractive index as,

$$R_m/V_m = (n^2-1/n^2+2) \qquad (10)$$

where n= optical refractive index

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

$$M = 1-(R_m/V_m) \qquad (11)$$

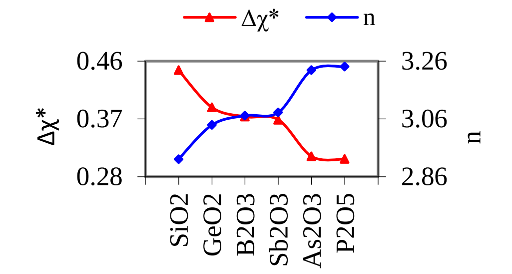
2.10 Third-order nonlinear optical susceptibility (χ)^3: Kim-Yoko et.al. [17-20] calculate the third-order nonlinear optical susceptibility by using refractive index as.

$$\chi^{(3)} = [(n^2-1)/4\pi]4*10^{-10}\ esu \qquad (12)$$

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;

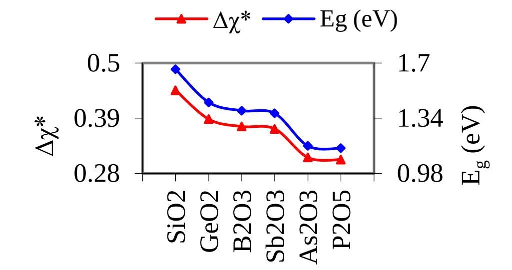
3. RESULT AND DISCUSSION

Glass formers: In glass forming oxides SiO_2, B_2O_3, P_2O_5, GeO_2, As_2O_3, and Sb_2O_3. Refractive index, Band energy, Dielectric constant, Metallization criterion, Basicity, Oxide ion polarizability, Bond ionicity, Third order non-liner optical susceptibility parameters are correlated hence from the theoretical aspects major interrelated optical properties studied here are as follows;



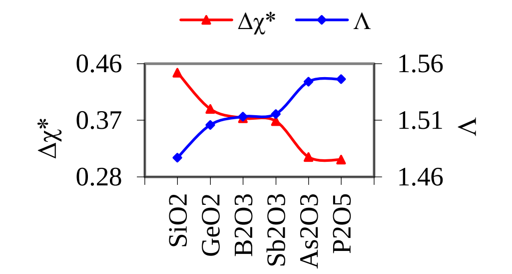
(a) Fig. 3.1(a) Variation of $\Delta\chi^*$ & R.I.

Figure 3.1(a) shows the variation of optical electronegativity which decreases from 0.4458-0.3075 and refractive index oppositely increases from 2.9207-3.2403 with respective to glass formers.



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

Figure 3.1(b) shows the variation of optical electronegativity which decreases from 0.4458-0.3075 and optical band energy decreases parallelly from 1.6587-1.4405 with respective to glass formers.



(c) Fig 3.1(c) Variation of $\Delta\chi^*$ & Λ

Figure 3.1(c) shows the variation of optical electronegativity which decreases from 0.4458-0.3075 and optical basicity oppositely increases from 1.4770-1.5462 (equ. 7) with respective to glass formers.

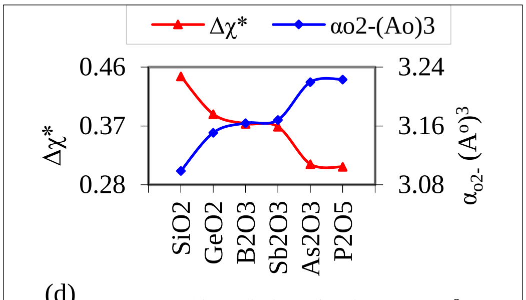


Fig 3.1(d) Variation of Δχ* & $\alpha_{o2-}(A^o)^3$

Figure 3.1(d) shows the optical electronegativity decreases from 0.4458-0.3075 and oxide ion polarizability oppositely increases from 3.0986-3.2232 $(A^o)^3$ with respective to glass formers.

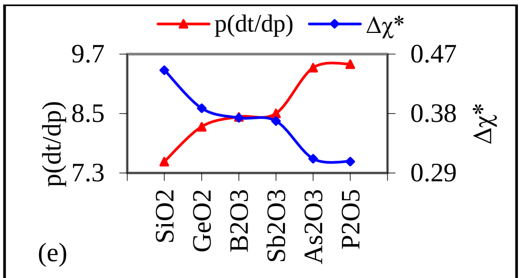


Fig 3.1(e) Variation of Δχ* & p(dt/dp)

Figure 3.1(e) shows the optical electronegativity decreases from 0.4458-0.3075 and optical dielectric constant increases from 7.5308-9.4998 with respective to glass formers.

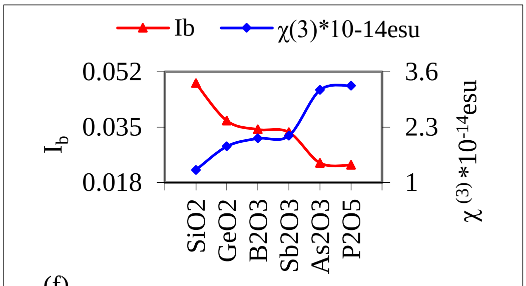


Fig 3.1(f) Variation of I_b & $\chi^{(3)}*(10^{-14})$esu.

Figure 3.1(f) shows the optical bond ionicity decreases from 0.0484-0.02336 and third order non-liner optical susceptibility increases oppositely from $(1.292-3.272)*10^{-14}$ esu with respective to glass formers.

Values of the parameters , Optical electronegativity (Δχ*), Optical band energy E_g (eV), Optical refractive Index (n), Optical dielectric constant p(dt/dp) are gigen in Table(1).

Table 1:

Glass formers	Optical electro negativity Δχ*	Optical energy gap Eg (eV)	Optical refractive index (n)	Optical dielectric constant p(dt/dp)
SiO_2	0.4458	1.6587	2.9207	7.5308
GeO_2	0.388	1.4434	3.0389	8.235
B_2O_3	0.3734	1.3893	3.0716	8.4352
Sb_2O_3	0.3687	1.3716	3.0826	8.5028
As_2O_3	0.3116	1.1592	3.2288	9.4252
P_2O_5	0.3075	1.144	3.2403	9.4998

Table (1): Glass formers, Optical electronegativity (Δχ*), Optical band energy Eg (eV), Optical refractive Index (n), Optical dielectric constant p(dt/dp).

Values of the parameters , Optical basicity (Λ), Optical oxide ion polarizability $(\alpha_{o2-}(A^o)^3)$, Optical bond iconicity (Ib), and Third order non linear optical susceptibility $(\chi^{(3)}\ 10^{-14}$ esu) are given in Table 2.

Table 2:

Glass formers	Optical basicity Λ	Oxide ion polarizability $\alpha_{o2-}(A^o)^3$	Optical bond iconicity (I_b)	$\chi(3)*10^{-14}$ esu
SiO2	1.4771	3.0986	0.0484	1.292
GeO2	1.5059	3.1507	0.0369	1.848
B2O3	1.5132	3.1638	0.0342	2.034
Sb2O3	1.5156	3.1681	0.0334	2.1
As2O3	1.5441	3.2195	0.0239	3.171
P2O5	1.5462	3.2232	0.0233	3.272

Table 2 Optical basicity (Λ), Optical oxide ion polarizability $(\alpha_{o2-}(A^o)^3)$, Optical bond iconicity (I_b), and Third order non linear optical susceptibility $(\chi^{(3)}\ 10^{-14}$ esu).

Plot of any two parameter give positive or negative straight line depending upon they lie parallel or reverse, are as shown below;

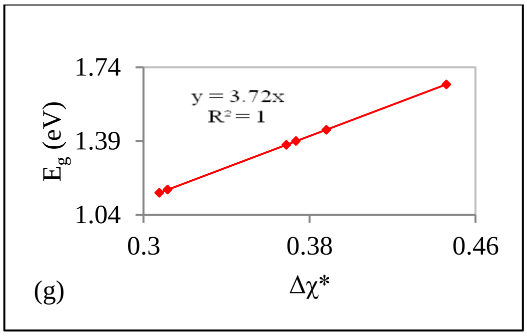


Fig. 3.1(g) Variation of Δχ* & Eg(eV)

Figure 3.1(g) shows the variation of optical electronegativity increases from 0.307-0.445and optical band energy also increases from 1.1440-1.6587gives positive straight line equation with slop = 3.72 and $R^2 = 1$.

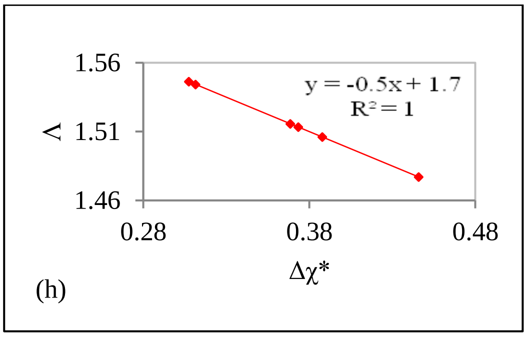


Fig. 3.1(h) Variation of Δχ* & Λ

Figure 3.1(h) shows the variation of optical electronegativity increases from 0.307-0.445 and optical bisicity which decreases from 1.5462-1.4770 gives negative straight line equation with slop = -0.5 and $R^2 = 1$.Values of R^2 for other any two parameters are lying between 0.921-1.

CONCLUSION

From all the above discussion, it was found that, for glass formers 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. It was also found that the values of third order nonlinear susceptibility increase with increasing the refractive index and decreasing the optical energy gap for all the glass formers. The optical dielectric constant increases with decreasing metallization criterion. Finally above values are good bases.

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