# Study of Conditional Glass Formers (I) on Basics of Optical Electronegativity

**D.B.Thombre**

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

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**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 referred as (1) taken from group III (A,B) and IV (A,B); they are $Y_2O_3$, $HfO_2$, $ZrO_2$, $Sc_2O_3$, $TiO_2$, $Al_2O_3$, $In_2O_3$, $Ga_2O_3$, and $SnO_2$. It is observed that optical band energy, metallization criterion, and bond iconicity decreases; and optical dielectric constant, optical basicity, oxide ion polarizability refractive index and third order non linear optical susceptibility increases. All conditional glass formers (I) oxides are according to Pauling's packing rule, Goldschmidt radius ratio rule, Zachariasen's random network theory, rules for formation of glass and Sun's single bond strength theory. For conditional glass formers (I) radius ratio $r_c/r_a$ = 0.40-0.75 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.

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

## 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 $Sb_2O_3$. $TiO_2$, $Cr_2O_3$, $V_2O_5$, $WO_3$, $Ga_2O_3$, $Bi_2O_3$, $Ta_2O_5$, $Nb_2O_5$, $MoO_3$ $Se_2O_3$and $Al_2O_3$are conditional glass forming oxides. Here the concept of optical electronegativity is used to study these parameters for conditional glass formers referred as (1) these are from group III (A,B) and IV (A,B); they are $Y_2O_3$, $HfO_2$, $ZrO_2$, $Sc_2O_3$, $TiO_2$, $Al_2O_3$, $In_2O_3$, $Ga_2O_3$, and $SnO_2$. Glass modifier alkali oxides are $Li_2O$, $Na_2O$, $K_2O$, $Rb_2O$ and $Cs_2O$. Glass modifier alkaline earth oxides CaO, MgO, SrO [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 from lanthanide series 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,

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

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

Similarly

Optical electronegativity is calculated by stander equation,

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

Where $\Delta\chi^*$ = optical electronegativity difference, $\chi^*_{anion}$ and $\chi^*_{cation}$ 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.

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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:

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

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

**2.4 Optical oxide ion polarizability ($\alpha_{o2-}$):** 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]

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

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

**2.5 Optical basicity ($\Lambda$):** 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]

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

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

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

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

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

**2.7Optical 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.

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

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 (1) | Optical electro-negativity ($\Delta\chi^*$) | Optical band energy Eg (eV) | Optical refractive Index (n) | Optical dielectric constant p(dt/dp) | Optical magnetization criterion (M) |
|---|---|---|---|---|---|
| $Y_2O_3$ | 1.0980 | 4.0848 | 2.1926 | 3.8077 | 0.4406 |
| $HfO_2$ | 0.9771 | 3.6347 | 2.2835 | 4.2145 | 0.4158 |
| $ZrO_2$ | 0.9363 | 3.4833 | 2.3169 | 4.3680 | 0.4071 |
| $Sc_2O_3$ | 0.8978 | 3.3401 | 2.3499 | 4.5222 | 0.3988 |
| $TiO_2$ | 0.7048 | 2.6220 | 2.5430 | 5.4669 | 0.3543 |
| $Al_2O_3$ | 0.6436 | 2.3944 | 2.6165 | 5.8464 | 0.3391 |
| $In_2O_3$ | 0.5185 | 1.9291 | 2.7942 | 6.8080 | 0.3058 |
| $Ga_2O_3$ | 0.4993 | 1.8575 | 2.8257 | 6.9848 | 0.3004 |
| $SnO_2$ | 0.4133 | 1.5378 | 2.9848 | 7.9094 | 0.2749 |

Table1: Lanthanide glass formers, Optical electronegativity ($\Delta\chi^*$), Optical band energy Eg (eV), Optical refractive Index (n), Optical dielectric constant p(dt/dp), Optical magnetization criterion (M).

**Table -2:**

| Conditional glass formers (1) | Optical basicity (Λ) | Optical oxide ion polarizability $\alpha_{o2-}(A^o)^3$ | Optical bond ionicity ($I_b$) | Third order non linear optical susceptibility $\chi^{(3)}$ $10^{-16}$ esu |
|---|---|---|---|---|
| $Y_2O_3$ | 1.1509 | 2.5117 | 0.2602 | 0.8447 |
| $HfO_2$ | 1.2114 | 2.6206 | 0.2123 | 1.2678 |
| $ZrO_2$ | 1.2318 | 2.6572 | 0.1968 | 1.4629 |
| $Sc_2O_3$ | 1.2510 | 2.6919 | 0.1825 | 1.6806 |
| $TiO_2$ | 1.3475 | 2.8656 | 0.1167 | 3.5894 |
| $Al_2O_3$ | 1.3781 | 2.9206 | 0.0983 | 4.6947 |
| $In_2O_3$ | 1.4407 | 3.0332 | 0.0650 | 8.6323 |
| $Ga_2O_3$ | 1.4503 | 3.0505 | 0.0604 | 9.5646 |
| $SnO_2$ | 1.4933 | 3.1279 | 0.0418 | 15.726 |

**Table2:** Optical basicity (Λ), Optical oxide ion polarizability ($\alpha_{o2-}(A^o)^3$), Optical bond iconicity ($I_b$), and Third order non linear optical susceptibility ($\chi^{(3)}$ $10^{-16}$ esu).

## 3. RESULT AND DISCUSSION

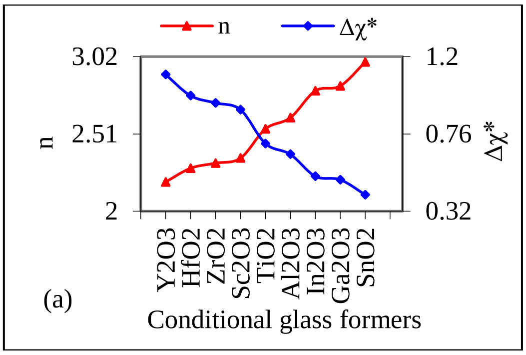


Figure 3 (a) Variation of n & Δχ* with conditional glass formers.

Figure 3(a) shows the variation of which refractive index increases from 2.1926-2.9848 and optical electronegativity decreases from 1.0981-0.4133 with respective to conditional glass formers (1).

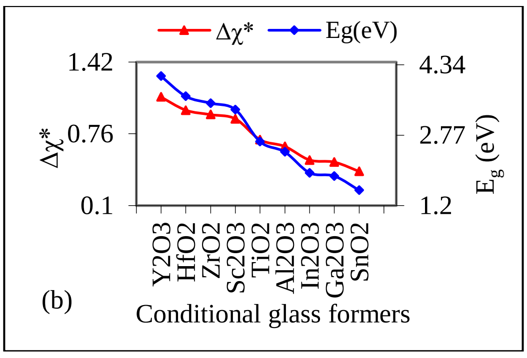


Figure 3 (b) Variation of Δχ* & Eg (eV) with conditional glass formers.

Figure 3(b) shows variation of optical electronegativity which decreases from 1.0981-0.4133 and optical band energy also decreases from 4.0848-1.5378 eV with respective to conditional glass formers (1).

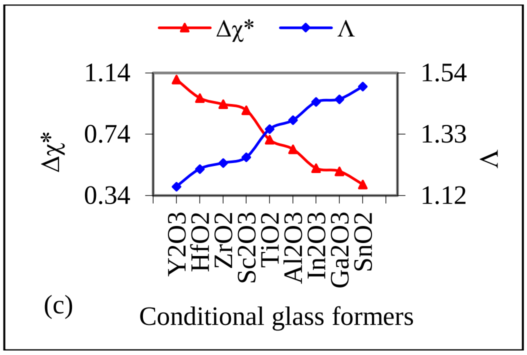


Figure 3 (c) shows variation of Δχ* & Λ with conditional glass formers.

Figure 3(c) shows the variation of optical electronegativity which decreases from 1.0981-0.4133 and optical basicity increases from 1.1509-1.4933 with respective to conditional glass formers (1).

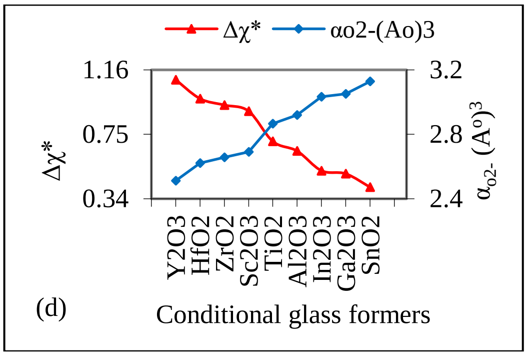


Figure 3(d) Variation of Δχ* & $\alpha_{o2-}$ $(A^o)^3$ with conditional glass formers.

Figure 3(d) shows the optical electronegativity decreases from 1.0981-0.4133 and oxide ion polarizability increases from 2.5117-3.1279 $(A^o)^3$ with respective to conditional glass formers (1).

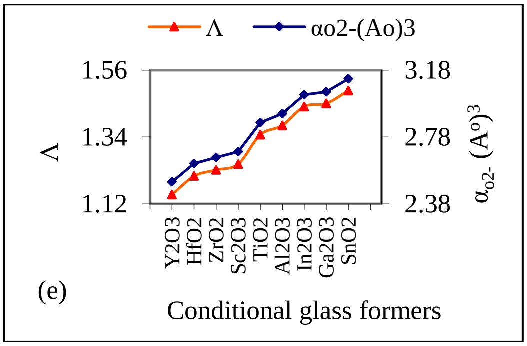


Figure 3 (e) Variation of Λ & $\alpha_{o2-}$ $(A^o)^3$ with conditional glass formers.

Figure 3(e) shows the variation of oxide ion polarizability and optical basicity increases from 2.5117-3.1279 $(A^o)^3$ and 1.1509-1.4933 respectively with respective to conditional glass formers (1).

Figure 3(f) shows the optical bond ionicity decreases from 0.2602-0.0418 and third order non-liner optical susceptibility increases from $(0.844\text{-}15.73)*10^{-15}$ esu with respective to conditional glass formers (1).

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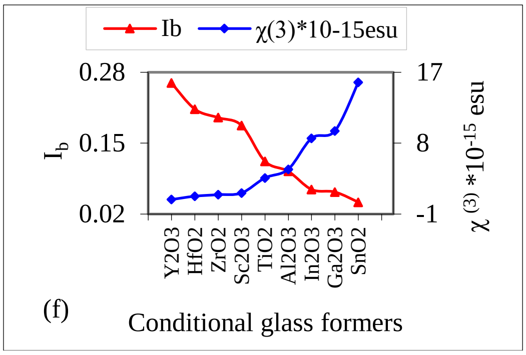


Figure 3 (f) Variation of $I_b$ , $\chi^{(3)}10^{-15}$ esu with conditional glass formers.

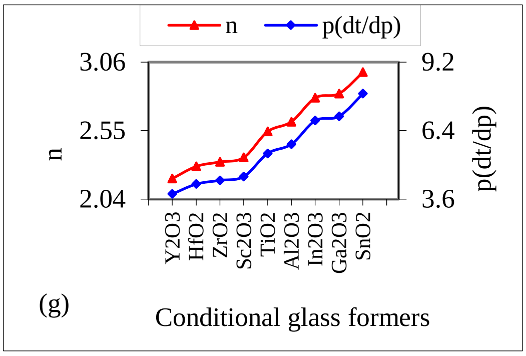


Figure 3 (g) Variation of n & p(dt/dp) with conditional glass formers.

Figure 3(g) shows the variation of refractive index which increases from 2.1926-2.9848 and optical dielectric constant increases from 3.8077-7.9094 with respective to conditional glass formers of lanthanide series.

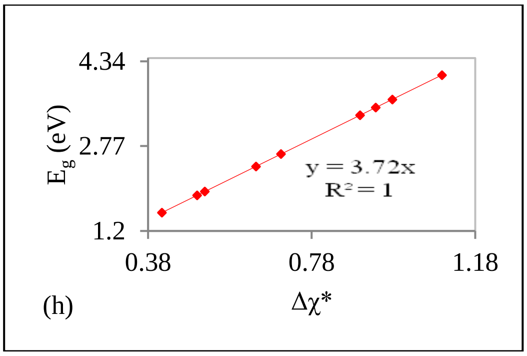


Figure 3 (g) shows Variation of Δχ* & $E_g$ (eV)

Figure 3 (h) shows the variation of optical electronegativity which increases from 0.4133-1.0980 and optical band energy which increases from 1.5378-4.0848(eV) gives positive straight line with slop = 3.72 and value of $R^2 = 1$.

Where as Figure 3 (i) shows the variation of optical bisicity which decreases from 1.1509-1.4933 and optical electronegativity increases from 0.4133-1.0980 with negative straight line with slop = -0.5, constant= 1.7 and $R^2 = 1$.

Values of $R^2$ for other parameters are varying in the range 0.985 – 1.

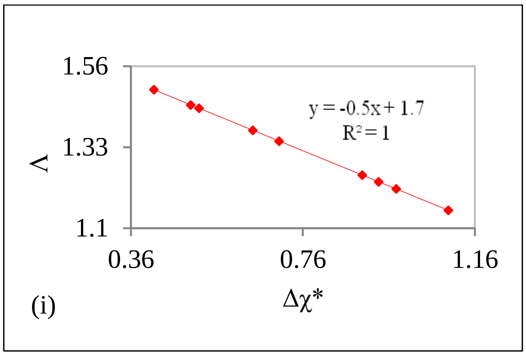


Figure 3 (i) Variation of Δχ* & Λ

## 4. CONCLUSIONS

From the above discussion, it was found that, for conditional glass formers (1) 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 decreasing the optical energy gap and increasing the refractive index for all conditional glass formers (I) [group III (A, B) and IV(A, B)]. The optical dielectric constant increases with decreasing metallization criterion. Above values are good bases.

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