

Study of Conditional Glass Formers from Lanthanide Series on basics of Optical Electronegativity

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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 the Refractive index Band energy, Dielectric constant, Metallization criterion, Basicity, Oxide ion polarizability, Bond ionicity, Third order non-linear optical susceptibility for Lanthanide series. 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. Lanthanide series are according to Paul, Goldschmidt-Zachariasen radius ratio rule and Sun's single bond strength theory for conditional glass forming oxides. Radius ratio lie between 0.71-0.81 therefore it called as conditional glass formers, single bond strength greater than 90Kcal/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 classically described as a network composed by building entities such as SiO₂, B₂O₃, P₂O₅, GeO₂, As₂O₃, and Sb₂O₃. TiO₂, Cr₂O₃, V₂O₅, WO₃, Ga₂O₃, Bi₂O₃, Ta₂O₅, Nb₂O₅, MoO₃, Se₂O₃ and Al₂O₃ are conditional glass forming oxides. Where as Yb₂O₃, CeO₂, Pr₂O₃, Pm₂O₃, Nd₂O₃, Sm₂O₃, Eu₂O₃, Gd₂O₃, Dy₂O₃, Ho₂O₃, Er₂O₃, Tm₂O₃, Lu₂O₃ are lanthanide series oxides theoretically, forms glass. Glass modifier alkali oxides are Li₂O, Na₂O, K₂O, Rb₂O and Cs₂O. 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,

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

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:

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

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]

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

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]

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

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.

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

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 Lanthanides	Optical electronegativity ($\Delta\chi^*$)	Optical band energy E_g (eV)	Optical refractive Index (n)	Optical dielectric constant $p(dt/dp)$	Optical magnetization criterion $n(M)$
Yb ₂ O ₃	2.5023	4.9207	2.0496	3.2009	0.4837
CeO ₂	2.5441	4.7652	2.0741	3.3020	0.4760
Pr ₂ O ₃	2.5643	4.6901	2.0862	3.3525	0.4722
Pm ₂ O ₃	2.5643	4.6901	2.0862	3.3525	0.4722
Nd ₂ O ₃	2.5840	4.6167	2.0983	3.4030	0.4685
Sm ₂ O ₃	2.6406	4.4063	2.1341	3.5546	0.4576
Eu ₂ O ₃	2.6936	4.2093	2.1694	3.7064	0.4473
Gd ₂ O ₃	2.6936	4.2093	2.1694	3.7064	0.4473
Dy ₂ O ₃	2.7270	4.0848	2.1926	3.8077	0.4406
Ho ₂ O ₃	2.7432	4.0245	2.2041	3.8584	0.4374
Er ₂ O ₃	2.7591	3.9654	2.2156	3.9091	0.4342
Tm ₂ O ₃	2.7747	3.9075	2.2270	3.9599	0.4310
Lu ₂ O ₃	2.8049	3.7951	2.2498	4.0616	0.4248

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

Table -2:

Conditional glass formers Lanthanides	Optical basicity (Λ)	Optical oxide ion polarizability $\alpha_{o2} (A^{\circ})^3$	Optical bond ionicity (I_b)	Third order non linear optical susceptibility $\chi^{(3)} 10^{-16}$ esu
Yb ₂ O ₃	1.0386	2.3095	0.3543	4.2186
CeO ₂	1.0595	2.3471	0.3364	4.7771
Pr ₂ O ₃	1.0696	2.3652	0.3279	5.0762
Pm ₂ O ₃	1.0696	2.3652	0.3279	5.0762
Nd ₂ O ₃	1.0794	2.3830	0.3195	5.3892
Sm ₂ O ₃	1.1077	2.4339	0.2958	6.4156
Eu ₂ O ₃	1.1342	2.4816	0.2739	7.5833
Gd ₂ O ₃	1.1342	2.4816	0.2739	7.5833
Dy ₂ O ₃	1.1509	2.5117	0.2602	8.4469
Ho ₂ O ₃	1.1590	2.5263	0.2536	8.9059
Er ₂ O ₃	1.1670	2.5406	0.2472	9.3836
Tm ₂ O ₃	1.1747	2.5546	0.2410	9.8807
Lu ₂ O ₃	1.1898	2.5818	0.2291	10.935

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

3. RESULT AND DISCUSSION

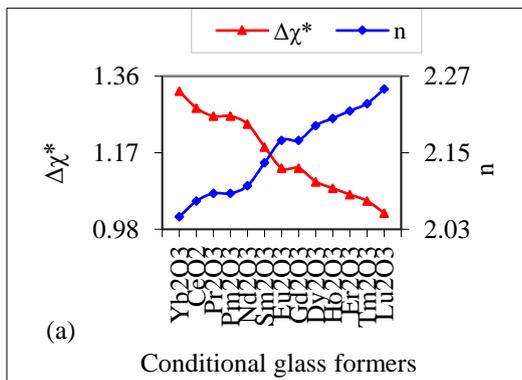


Figure 3 (a) Variation of R.I. & $\Delta\chi^*$ with conditional glass formers.

Figure 3(a) shows the variation of optical electronegativity which decreases from 1.3227-1.0202 and refractive index increases from 2.0496-2.2498 with respective to conditional glass formers of lanthanide series.

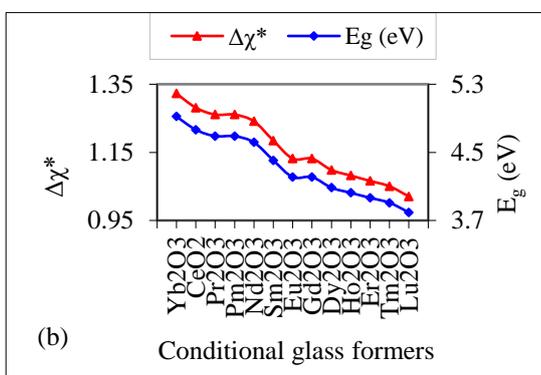


Figure 3 (b) Variation of $\Delta\chi^*$ & E_g (eV) with conditional glass formers.

Figure 3(b) shows variation of optical electronegativity which decreases from 1.3227-1.0202 and optical band energy also decreases from 4.9207-3.7951(eV) with respective to conditional glass formers of lanthanide series.

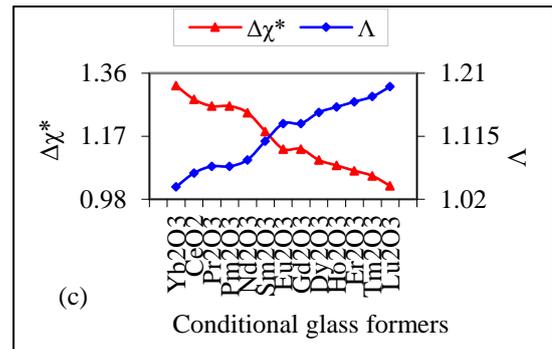


Figure 3 (c) shows variation of $\Delta\chi^*$ & Λ with conditional glass formers.

Figure 3(c) shows the variation of optical electronegativity which decreases from 1.3227-1.0202; and optical basicity increases from 1.0386-1.1898 with respective to conditional glass formers of lanthanide series.

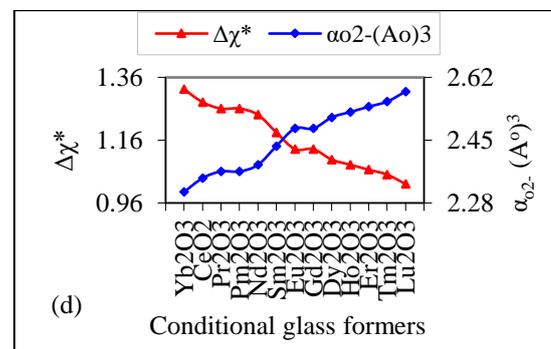


Figure 3(d) Variation of $\Delta\chi^*$ & $\alpha_{o2} (A^{\circ})^3$ with conditional glass formers.

Figure 3(d) shows the optical electronegativity decreases from 1.3227-1.0202 and oxide ion polarizability increases from 2.3095-2.5818 ($A^{\circ})^3$ with respective to conditional glass formers of lanthanide series.

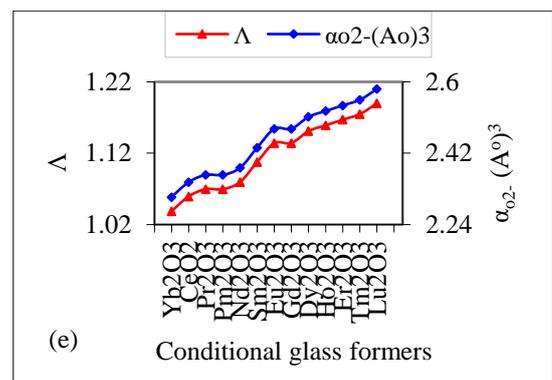


Figure 3 (e) Variation of Λ & $\alpha_{o2} (A^{\circ})^3$ with conditional glass formers.

Figure 3(e) shows the variation of oxide ion polarizability and optical basicity increases from 2.3095-2.5818 ($A^{\circ})^3$ and 1.0386-1.1898 respectively with respective to conditional glass formers of lanthanide series.

Figure 3(f) shows the optical bond ionicity decreases from 0.3543-0.2291 and third order non-linear optical susceptibility increases from (4.2186-10.935)* 10^{-16} esu with respective to conditional glass formers of lanthanide series.

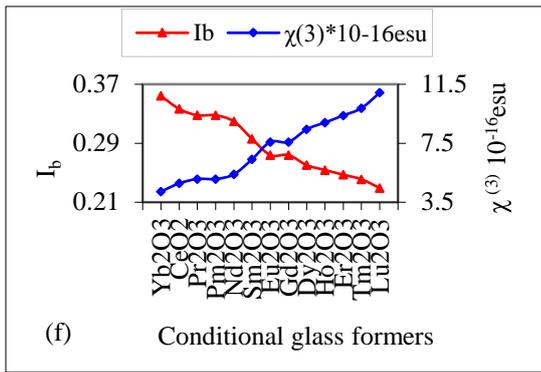


Figure 3 (f) Variation of I_b , $\chi^{(3)}10^{-14}$ esu with conditional glass formers.

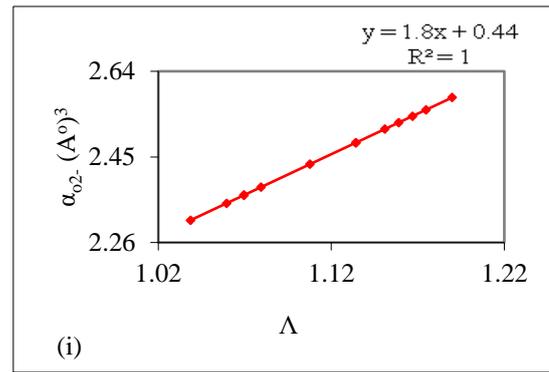


Figure 3 (i) Variation of $\Delta\chi^*$ & E_g (eV).

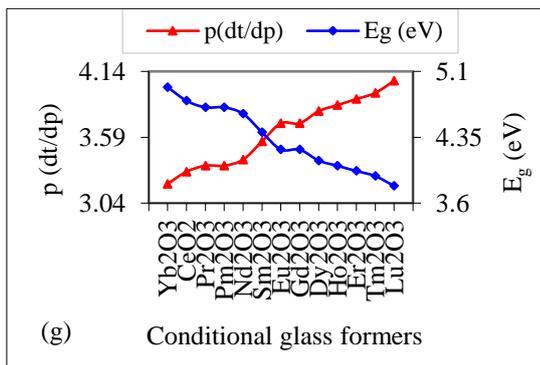


Figure 3 (g) Variation of E_g (eV) & $p(dt/dp)$ with conditional glass formers.

Figure 3(g) shows the variation of optical band energy decreases from 4.9207-3.7951(eV) and optical dielectric constant increases from 3.2009-4.0616 with respective to conditional glass formers of lanthanide series.

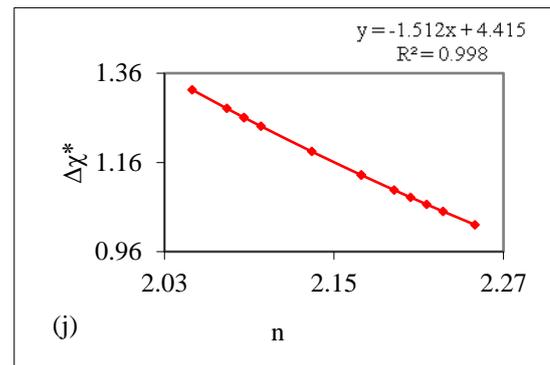


Figure 3 (j) Variation of $\Delta\chi^*$ & n

Figure 3(j) shows the variation of refractive index which increases from 2.0496-2.2498 and optical electronegativity 2.5023- 2.8049 gives negative straight line equation with slop value = -1.512 & $R^2 = 0.998$.

Values of R^2 for other parameters are lies from 1 to 0.982.

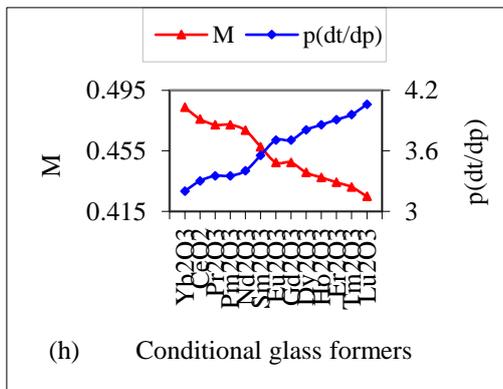


Figure 3 (h) Variation of $p(dt/dp)$ & M with conditional glass formers.

Figure 3 (h) shows the metallization criterion value decreases from 0.4837-0.4248 and optical dielectric constant increases from 3.2009-4.0616 with respective to conditional glass formers of lanthanide series.

Figure 3 (i) shows the variation of optical basicity and oxide ion polarizability which increases from 1.0386-1.1898 and 2.3095-2.5818 gives positive straight line equation with slop = 1.8 & $R^2 = 1$.

4. CONCLUSIONS

From all the above result and discussion on the basics of optical electronegativity it was found that, 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. The values of third order nonlinear susceptibility increase with decreasing the optical energy gap and increasing the refractive index for all the glass formers. The optical dielectric constant increases with decreasing metallization criterion. Hence in conditional glass formers of Lanthanide series have; high refractive index, high dielectric constant, high band energy gap and higher third order nonlinear susceptibility. Finally above values are good bases.

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