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CODEN: IAASCA **ORIGINAL ARTICLE**

Polarizability and Optical basicity of Pr^{3+} ions doped Zinc Lithium Bismuth Borate Glasses

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ABSTRACT
Glass of the system: (25-x) Bi_2O_3:20Li_2O:20ZnO:35 B_2O_3: xPr_6O_{11}. (Where x=1, 1.5,2 mol %) have been prepared by melt-quenching method. The amorphous nature of the glasses was confirmed by X-ray diffraction studies. The physical parameters like density, average molecular weight, dielectric constant, molar volume, reflection loss, electronic polarizability, molar polarizability, optical basicity, oxide ions polarizability have been evaluated. Dielectric constant, refractive index, electronic polarizability varies with increasing mole% of Pr_6O_{11} respectively. The theoretical value of electronic polarizability and oxide ion polarizability were calculated by using lorentz-lorentz formula. Theoretical optical basicity of the glasses is also evaluated based on equation proposed by Duffy and Ingram. The metallization criterion has been calculated on the basis of refractive index and energy gap. The large value of metallization criterion indicates that the glass materials are insulators.
Keywords*: praseodymium based glass; Optical basicity; Polarizability; Metallization criterion.*

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INTRODUCTION

Rare earth doped solid state materials have become an important class of solids, attracting much attention among researches as is evident from the abundance of studies that can be found in the literature. A substantial amount of work has been done on the lasing characteristics of rare earth doped solid state materials. The availability of high power infrared laser diodes has stimulated researches in the area of fiber lasers [1-4],optical amplifiers[5-7],frequency up convertors [8-11] and the potential application in areas such as three dimensional displays, high density optical data reading and storage, sensors, viewers and indicators among many. As a branch of visible luminescence up conversion fluorescence of rare earth ions catches more and more attention. Rare earth doped low phonon optical glasses [12, 13] are very useful materials because of their potential singnal amplification in telecommunication system, infrared lasers and optical broad band amplifiers.

Recently, Dimitrov and Komatsu [14] have investigated the polarizability approach of numerous oxide glasses by estimating the electronic oxide ion polarizability, optical basicity and metallization criterion based on the refractive index and energy gap.

The aim of the present study is to prepare the Pr^{3+}doped zinc lithium bismuth borate glass with different Pr_6O_{11}concentrations and to study the effect of Pr_6O_{11} content on the various physical parameters such as density, molar volume, refractive index. In addition the optical basicity and polarizability were theoretically determined.

EXPERIMENTAL TECHNIQUES

Preparation of glasses

The following Pr^{3+} doped zinc lithium bismuth borate glass samples (25-x) Bi_2O_3:20Li_2O:20ZnO: 35 B_2O_3: xPr_6O_{11} (where x=1, 1.5.2) have been prepared by melt-quenching method. Analytical reagent grade chemical used in the present study consist of Bi_2O_3, Li_2O, ZnO, and $B_2O_3$and Pr_6O_{11}. All weighed chemicals were powdered by using an Agate pestle mortar and mixed thoroughly before each batch (10g) was melted in alumina crucibles in silicon carbide based an electrical furnace.

Silicon Carbide Muffle furnace was heated to working temperature of 1050^{0}C, for preparation of Zinc Lithium Bismuth Borate glasses, for two hours to ensure the melt to be free from gases. The melt was stirred several times to ensure homogeneity. For quenching, the melt was quickly poured on the steel plate & was immediately inserted in the muffle furnace for annealing. The steel plate was preheated to100^{0}C.While pouring; the temperature of crucible was also maintained to prevent crystallization. And annealed at temperature of 350^{0}C for 2h to remove thermal strains and stresses. Every time fine powder of cerium oxide was used for polishing the samples. The glass samples so prepared were of good optical quality and were transparent. The chemical compositions of the glasses with the name of samples are summarized in Table 1

Table 1 Chemical composition of the glasses

Sample	Glass composition (mol %)
ZnLiBiB (Pr0)	25 Bi_2O_3:20Li_2O:20ZnO: 35 B_2O_3
ZnLiBiB (Pr1)	24 Bi_2O_3:20Li_2O:20ZnO: 35 B_2O_3: 1 Pr_6O_{11}
ZnLiBiB (Pr1.5)	23.5 Bi_2O_3:20Li_2O:20ZnO: 35 B_2O_3: 1.5 Pr_6O_{11}
ZnLiBiB (Pr2)	23 Bi_2O_3:20Li_2O:20ZnO: 35 B_2O_3: 2 Pr_6O_{11}

ZnLiBiB (Pr) -Represents Pr^{3+} doped Zinc Lithium Bismuth Borate glass specimens

RESULT AND DISCUSSION

XRD Measurement

Figure 1 presents the XRD pattern of the samples containing show no sharp Bragg's peak, but only a broad diffuse hump around low angle region. This is the clear indication of amorphous nature with in the resolution limit of XRD instrument.

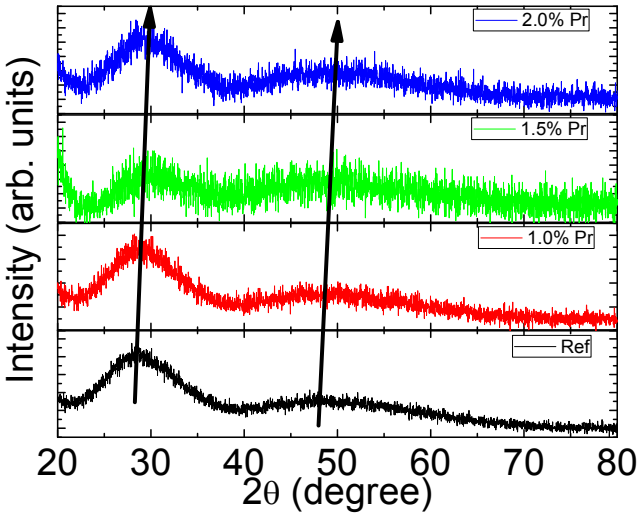

Fig. 1.X-ray diffraction pattern of Bi_2O_3: Li_2O: ZnO: B_2O_3: Pr_6O_{11} glasses.

Physical properties

Density measurement

The density of all glasses was measured by using Archimedes principle with xylene as immersing liquid. The relation used is

$$\rho(gm/cm^3) = \frac{W_a}{W_a - W_b} \times \rho_b \qquad (1)$$

Where W_a is the weight of glass sample in air, W_b is the weight of glass sample when immersed in xylene and ρ_b is the density of xylene(0.86gm/cm^3).

The molar volume of the glass samples can be calculated from following expression:

$$V_m = \frac{M_T}{\rho} \quad (2)$$

Where ρ is the density of the sample and M_T is the total molecular weight of the multi-component glass system given by

$$M_T = X_{Bi2O3} Z_{Bi2O3} + X_{Li2O} Z_{Li2O} + X_{ZnO} Z_{ZnO} + X_{B2O3} Z_{B2O3} + X_{Pr6O11} Z_{Pr6O11} \quad (3)$$

Where X_{Bi2O3}, X_{Li2O}, X_{ZnO}, X_{B2O3}, X_{Pr6O11} are the molar fraction of the constituent oxides and Z_{Bi2O3}, Z_{Li2O}, Z_{ZnO}, Z_{B2O3}, Z_{Pr6O11} are the molar weights of the constituent oxides.

Refractive index measurement

The refractive index were measured by using an Abbe refractometer with sodium vapor lamp as the light source emitting the light at a wavelength λ of 589.3nm and having mono-bromonaphthalene as the contact layer between the sample and prism of the refractometer.

Reflection loss

The reflection loss from the glass surface was computed from the refractive index using Fresnel's formula [15]

$$R_L = \left[\frac{(n-1)}{(n+1)}\right]^2 \quad (4)$$

Where n is the refractive index.

Molar refraction

The molar refractivity of the glass samples were calculated using the formula which is well known as Volf and Lorentz-Lorentz formula [16]

$$R_m = \left[\frac{(n^2-1)}{(n^2+2)}\right] \times V_m \quad (5)$$

Where n is the refractive index of the glass sample, V_m is the molar volume.

Energy gap

According to Duffy the energy gap is given by [17]

$$E_g = 20\left(1 - \frac{R_m}{V_m}\right)^2 \quad (6)$$

Molar electronic polarizability

The molar electronic polarizability of the material can be calculated from following expression [18]

$$\alpha_m = \frac{R_m}{2.52} \quad (7)$$

Dielectric constant

The dielectric constant was calculated using refractive index of the glass [19]

$$\epsilon = n^2 \quad (8)$$

Where n is the refractive index.

Optical dielectric constant

The optical Dielectric Constant refractive index of the glass [20]

$$p\frac{dt}{dp} = (\epsilon\text{-}1) = n^2\text{-}1 \quad (9)$$

Where ϵ is the dielectric constant.

Electronic polarizability

The electronic polarizability was cal calculated using the formula [21]

$$\alpha_e = \frac{3\left(n^2-1\right)}{4\Pi A_V\left(n^2+2\right)} \quad (10)$$

Where A_V is the Avogadro number.

Oxide ions polarizability

The Electronic polarizability of oxide ions has been calculated using the equation proposed by Dimitrov and Sakka[22]

$$\alpha_O{}^{2\text{-}(n)} = \left[\frac{R_m}{2.52} - \sum \alpha_i\right]\left(N_o^{2-}\right)^{-1} \quad (11)$$

Where $\sum \alpha_i$ In the above equation is molar cation polarizability and $N_O{}^{2-}$ is the number of oxide ions in the chemical formula. The molar cation Polarizability (α) values of Li^+,B^{3+},Zn^{2+},Bi^{3+} and Pr^{3+},ions are respectively $\alpha_{Li=}$.042Å^3, $\alpha_{B=}$.002 Å^3 ,$\alpha_{Zn=}$.283 Å^3 ,$\alpha_{Bi=}$1.508 Å^3 and $\alpha_{Pr=}$1.23 Å^3

Ionic concentrations

The ionic concentrations of the glass samples are determined using the following relation [23]

$$N\ (\text{ions}/\text{cm}^3) = \frac{(Avogadro's\ number)\ (glass\ density)}{(Average\ molecular\ weight\ )} \times (mol\%\ of\ rare\ earth) \quad (12)$$

Polaron radius

The polaron radius was calculated using the formula [24]

$$R_p = \frac{1}{2}\times\left(\frac{\Pi}{6N}\right)^{\frac{1}{3}} \quad (13)$$

Where N is the ionic concentrations.

Inter-ionic distance

Inter-ionic distance of the glass samples is given as [24]

$$R_i = \left(\frac{1}{N}\right)^{\frac{1}{3}} \quad (14)$$

Where R_i is the ionic concentrations.

Field strength

The field strength was calculated using the formula [25]

$$F\ (\text{cm}^3) = \left(\frac{Z}{R_p{}^2}\right) \quad (15)$$

Where Z is the thickness of the samples.

Oxygen packing density

The oxygen packing density of the glass samples were calculated using the following relation [26]

$$\text{O.P.D.} = n\left(\frac{\rho}{M}\right)\times 1000 \qquad (16)$$

Where ρ the density of desired glass samples, M is the molecular weight of the sample and n is the number of oxygen atoms in the composition.

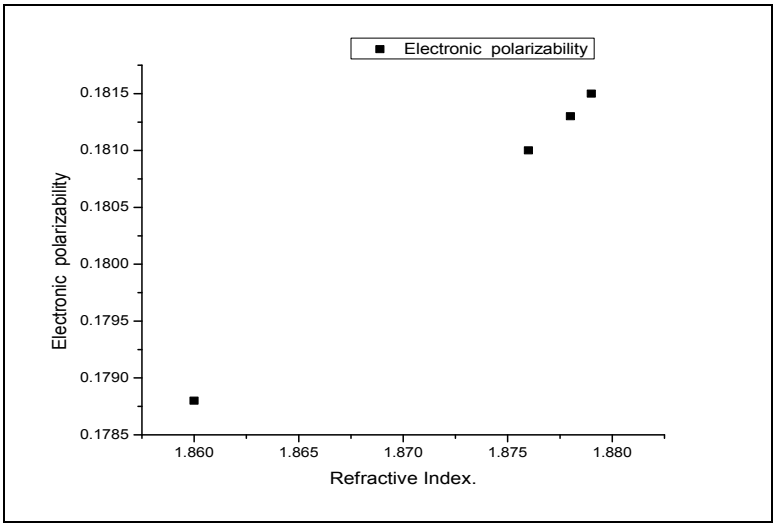

Fig.2. Varation of Electronic polarizability with Refractive Index.

Table 2: The physical and optical properties of Bi_2O_3: Li_2O: ZnO: B_2O_3: Pr_6O_{11} glasses

Physical properties	ZnLiBiB(Pr 0)	ZnLiBiB(Pr 01)	ZnLiBiB(Pr 1.5)	ZnLiBiB(Pr 02)
Refractive Index (n)	1.860	1.876	1.878	1.879
Density (ρ) $\left(gm/cm^3\right)$	3.2	4.568	4.651	4.742
Thickness(Z)	0 .235	0.244	0.233	0 .245
Averagemolecularweight M $\left(g\right)$	163.121	168.68	171.45	174.23
Rare earth ions concentratio(N)	--	1.630	2.451	3.279
Dielectric Constant (ϵ)	3.46	3.519	3.527	3.531
OpticalDielectricConstant $p\frac{dt}{dp}$	2.46	2.519	2.527	2.531
MolarVolume (V_m) $\left(gm/cm^3\right)$	50.975	36.926	36.863	36.742
Reflection losses(R_L)	9.042	9.277	9.307	9.322
Molar refractivity (R_m)	22.965	16.855	16.854	16.812
Polaron radius R_p $\left(A^0\right)$	--	3.424	2.986	2.692
Interionic distance(R_i) $\left(A^0\right)$	--	8.497	7.417	6.731

Electronic polarizability (α_e)	0.1788	0.1810	0.1813	0.1815
Field strength (F)	--	0.2081	0.2608	0.3381
Optical basicity (Λ)	0.7834	0.7838	0.7840	0.7842
Molarpolarizability(α_m)$\times 10^{-24}\, cm^3$	9.113	8.168	8.165	8.144
Oxide ions polarizability ($\alpha_{O^{2-(n)}}$) A^0	3.769	3.361	3.186	3.142
Oxygen packing density(OPD)	43.12	61.75	62.94	64.23
Metallization criterion (M)	0.5495	0.5435	0.5428	0.5424
Energy gap(E_g)	6.0387	5.909	5.892	5.885

Optical basicity

The optical basicity addresses the ability of oxide glass in contributing the negative charges in the glass matrix. In other words it defines the electron donating power of the oxygen in the oxides glass. The theoretical optical basicity can be calculated by the equation proposed by Duffy and Ingram [27]

$$\Lambda_{th} = X_1 \Lambda_1 + X_2 \Lambda_2 + X_3 \Lambda_3 + X_4 \Lambda_4 \qquad (17)$$

Where X_1, X_2, X_3 ,X_4, ……X_n are equivalent fraction based on the amount of oxygen each oxide contributes to the overall glass stoichometry and Λ_1, Λ_2 , Λ_3 ,Λ_4…… Λn are basicities assigned to the individual oxides. The values of optical basicity of each oxide are: Λ (B_2O_3) =0.42, Λ (Bi_2O_3) =1.19, Λ (Li_2O) =1.00, Λ (ZnO) =0.82, Λ (Pr_6O_{11}) =1.22.

It is clear that observed from Table 2 that the optical basicity increases when Bi_2O_3 is replaced by one of the trivalent metal praseodymium oxide. Increase in optical basicity in this work means the higher ability of oxide ions to transfer electrons to the surrounding cations.

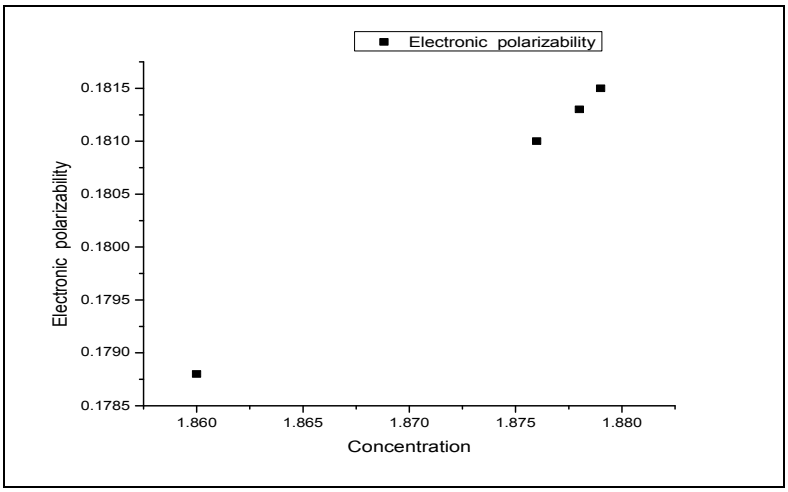

Fig.3. Variation of optical basicity with Pr_6O_{11} concentration

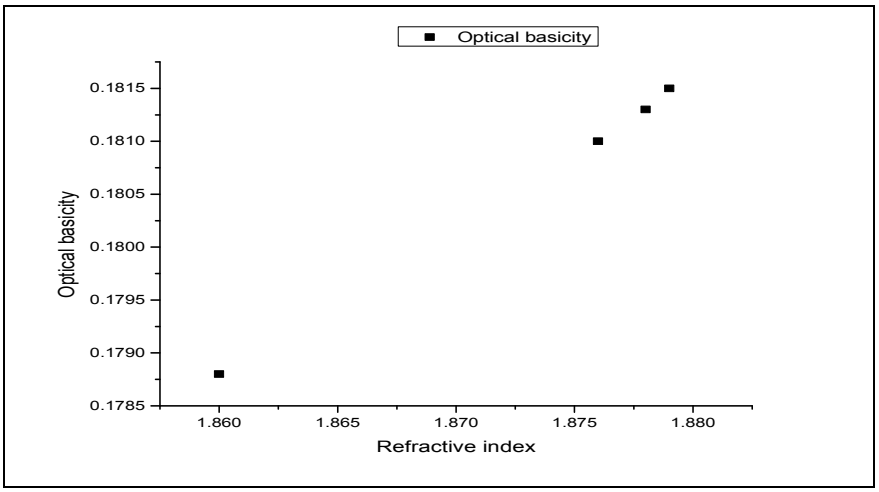

Fig.4. Variation of optical basicity with refractive index

Insulating nature

According to the Herzfeld theory of metallization, If $R_m/V_m > 1$ and $R_m/V_m < 1$ predicting metallic or insulating [28]. Subtracting by 1 gives the metallization (M)

Meena and Bhatia

$$M=\left(1-\frac{R_m}{V_m}\right) \quad (18)$$

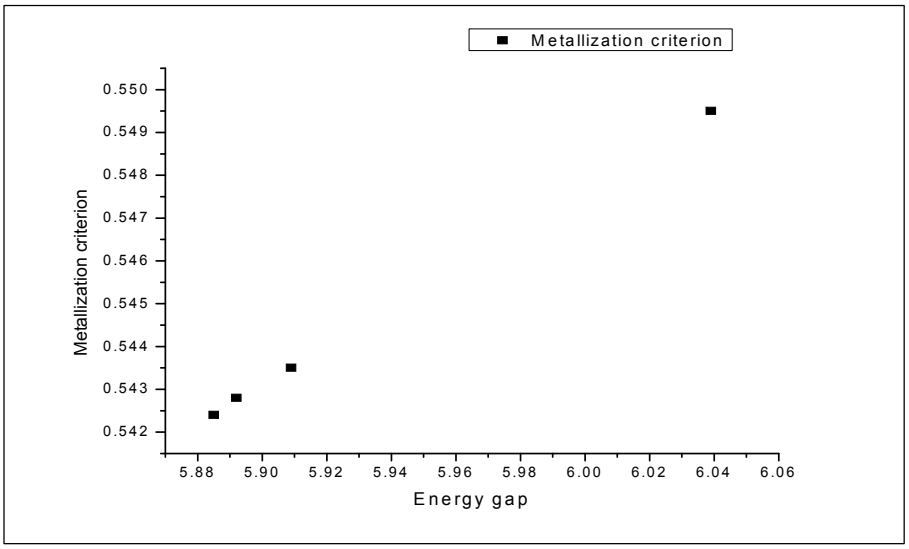

Fig.5. Variation of Metallization criterion with energy gap.

CONCLUSIONS

The Pr^{3+} doped Zinc lithium bismuth borate gasses were prepared at various doping concentration of Pr_6O_{11} and characterized for their physical properties. The density and refractive index increases with an increase in concentration of Pr_6O_{11}. The optical basicity also rises over the doping concentration. Increase in optical basicity results in increasing ability of oxide ions to denote electrons to surrounding cation. This suggests that the present glasses are more basic. The metallization parameter values of the present glasses are found to be less than one thus they exhibit insulating behaviour.

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