Polarizability and Optical Basicity of Sm^{3+} ions doped Yttrium Zinc Lithium Bismuth Borate Glasses

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Abstract

Glass of the system: (20-x) Bi_2O_3:15Li_2O:15ZnO:10 Y_2O_3: 40 B_2O_3:xSm_2O_3. (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, reflection loss, electronic polarizability, optical basicity, oxide ions polarizability have been evaluated. Refractive index, electronic polarizability varies with increasing mole% of Sm_2O_3 respectively. The theoretical value of average electronic polarizability and oxide ion polarizability were calculated by using lorentz-lorentz formula. The metallization criterion has been calculated on the basis of refractive index and energy gap. The decrease value of metallization criterion indicates that glass material is metalizing.

Keywords: Samarium based glass; Optical basicity; Polarizability; Metallization criterion.

Introduction

Bismuth borate glasses are very important because of their technological and scientific application [1-3].Rare earth doped transparent bismuth borate glasses and glass ceramics are of increasing interests in various optical applications, because of their superior optical properties, such as high refractive index, high density and high reflection losses [4-7]. The glasses containing rare earth in various forms such as network formers and modifiers are of great deal of interest for their unique optical, electrical and magnetic properties [8].Glass is one of the examples for the system application because of its superior properties of tunable nonlinear optical properties and low phonon cut energy. One of the most important properties in the field of electronic and optical is the electronic polarizability of ions [9].

The boron atom usually coordinates with their three or four oxygen atoms forming $(BO_3)^{3-}$ or $(BO_4)^{5-}$ structural units. Futhermore, these two fundamental units can be arbitrarily combined to form different B_xO_y structural groups [10]. In recent years, glasses doped with rare earth ions have drawn much attention due to their potential applications in solid state lasers and optical amplifiers [11-13].Moreover, bismuth oxide contained host glass matrix improves chemical durability of the glass [14]

Recently, Demitrov and Komatsu have investigated the polarizability approach of numerous oxide glasses by estimating the electronic oxide polarizability,optical basicity and metallization criterion based on their refractive index and energy gap[15].

The aim of the present study is to prepare the Sm^{3+}doped bismuth borate glass with different Sm_2O_3concentrations and to study the effect of Sm_2O_3content on density, molar volume, refractive index, polarizability of oxide ions and optical basicity.

Experimental Techniques

Preparation of glasses

The following Sm^{3+} doped yttrium zinc bismuth borate glass samples (20-x) Bi_2O_3:15Li_2O:15ZnO: 10Y_2O_3: 40 B_2O_3: x Sm_2O_3 (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, Y_2O_3 and $B_2O_3$and Sm_2O_3. 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 1050^0C, for preparation of yttrium zinc lithium bismuth borate glass samples, 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 to100^0C.While pouring; the temperature of crucible was also maintained to prevent crystallization. And annealed at temperature of 350^0C 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 %)
YZnLiBiB (Sm0)	20 Bi_2O_3:15Li_2O:15ZnO: 10Y_2O_3:40 B_2O_3
YZnLiBiB (Sm 1)	19 Bi_2O_3:15Li_2O:15ZnO: 10 Y_2O_3: 40 B_2O_3:1 Sm_2O_3
YZnLiBiB (Sm 1.5)	18.5 Bi_2O_3:15Li_2O:15ZnO: 10 Y_2O_3: 40 B_2O_3: 1.5 Sm_2O_3
YZnLiBiB (Sm2)	18 Bi_2O_3:15Li_2O:15ZnO: 10 Y_2O_3: 40 B_2O_3: 2 Sm_2O_3

YZnLiBiB (Sm) -Represents Sm^{3+} doped Yttrium 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.

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

$$M_T = X_{Bi2O3} Z_{Bi2O3} + X_{Li2O} Z_{Li2O} + X_{ZnO} Z_{ZnO} + X_{Y2O3} Z_{Y2O3} + X_{B2O3} Z_{B2O3} + X_{Sm2O3} Z_{Sm2O3} \quad (3)$$

Where X_{Bi2O3}, X_{Li2O}, X_{ZnO}, X_{Y2O3}, X_{B2O3}, X_{Sm2O3} are the molar fraction of the constituent oxides and Z_{Bi2O3}, Z_{Li2O}, Z_{ZnO}, Z_{Y2O3}, Z_{B2O3}, Z_{Sm2O3} are the molar weights of the constituent oxides.

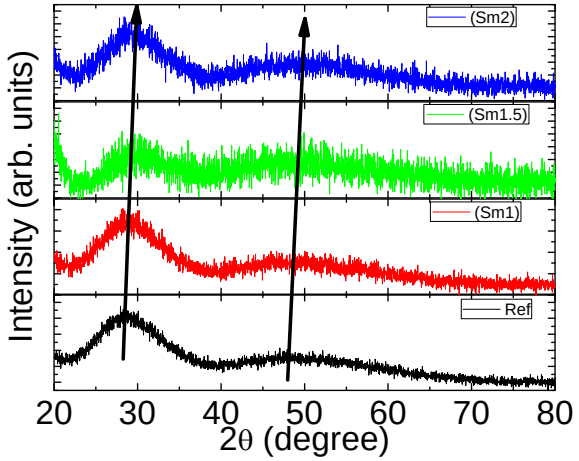

Fig. 1.X-ray diffraction pattern of Bi_2O_3: Li_2O: ZnO: B_2O_3: Y_2O_3: Sm_2O_3glasses.

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 [16]

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

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 [17]

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

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 [18]

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

Molar electronic polarizability

The molar electronic polarizability of the material can be calculated from following expression [19]

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

Dielectric constant

The dielectric constant was calculated using refractive index of the glass [20]

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

Where n is the refractive index.

Optical dielectric constant

The optical Dielectric Constant refractive index of the glass [21]

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

Where ϵ is the dielectric constant.

Electronic polarizability

The electronic polarizability was cal calculated using the formula [22]

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

Where A_V is the Avogadro number.

Electronic polarizability of oxide ions polarizability

The Electronic polarizability of oxide ions has been calculated using the equation proposed by Dimitrov and Sakka[23]

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

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 Sm^{3+},ions are respectively $\alpha_{Li=}$.042Å^3, $\alpha_{B=}$.002 Å^3 ,$\alpha_{Zn=}$.283 Å^3 ,$\alpha_{Bi=}$1.508 Å^3, α_Y =0.544 Å^3 and $\alpha_{Sm=}$ 2.435 Å^3

Ionic concentrations

The ionic concentrations of the glass samples are determined using the following relation [24]

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

Polaron radius

The polaron radius was calculated using the formula [25]

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

Where N is the ionic concentrations.

Inter-ionic distance

Inter-ionic distance of the glass samples is given as [25]

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

Where R_i is the ionic concentrations.

Field strength

The field strength was calculated using the formula [26]

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

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 [27]

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

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.

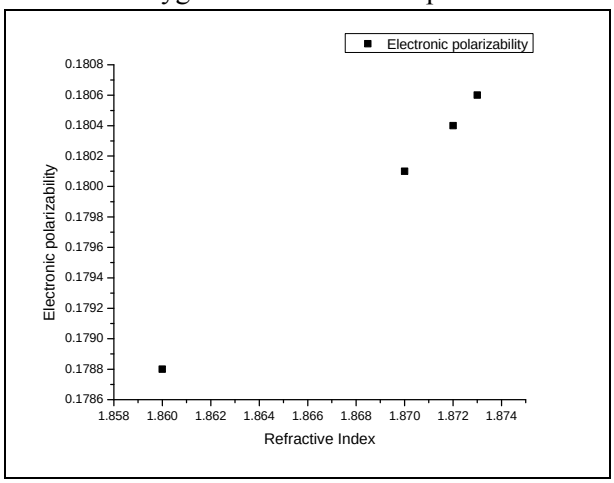

Fig.2. Varation of Electronic polarizability with Refractive Index.

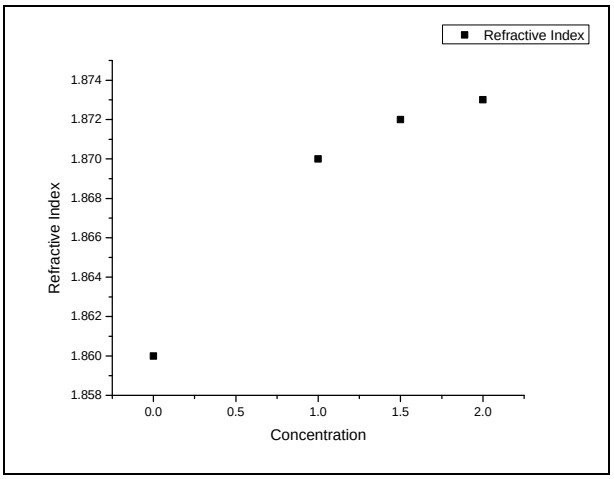

Fig.3. Varation of Refractive Index with Concentration.

Table 2: The physical and optical properties of Bi_2O_3: Li_2O: ZnO: B_2O_3: Y_2O_3: Sm_2O_3glasses

Physical properties	ZnLiBiB (Sm 0)	YZnLiBiB (Sm 01)	YZnLiBiB (Sm 1.5)	Y ZnLiBiB (Sm 02)
Refractive Index (n)	1.860	1.870	1.872	1.873
Density (ρ) $\left(gm/cm^3\right)$	3.2	4.250	4.325	4.420
Thickness(Z)	0 .235	0.263	0.261	0.262
AveragemolecularweightM $\left(g\right)$	163.121	159.14	158.56	157.97
Rare earth ions concentratio(N)	--	1.609	2.464	3.370
Dielectric Constant (ϵ)	3.460	3.479	3.504	3.508
OpticalDielectricConstant $p\frac{dt}{dp}$	2.460	2.479	2.504	2.508
MolarVolume ($V_{m)}$ $\left(gm/cm^3\right)$	50.975	41.406	40.552	39.548
Reflection losses(R_L)	9.042	9.189	9.219	9.233
Molar refractivity ($R_{m)}$	22.965	18.808	18.450	18.008
Polaron radius $R_p\left(A^0\right)$	--	4.722	5.442	6.041
Interionic distance(R_i) $\left(A^0\right)$	--	0.8534	0.7404	0.6670
Electronic polarizability (α_e)	0.1788	0.1801	0.1804	0.1806
Field strength (F)	--	0.1180	0.0881	0.0718
Optical basicity (Λ)	0.7834	0.7501	0.7486	0.7471
Molarpolarizability(α_m) $\times 10^{-24}\,cm^3$	9.113	7.463	7.321	7.146
Oxide ions polarizability ($\alpha_O{}^{2-(n)}$) A^0	3.769	2.784	2.721	2.644
Oxygen packing density(OPD)	43.12	57.963	59.183	60.686
Metallization criterion (M)	0.5495	0.5458	0.5450	0.5447
Energy gap(E_g)	6.0387	5.957	5.941	5.933

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 [28]

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

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) =0.95, Λ (Y_2O_3) =0.99, Λ (Sm_2O_3) =0.9476.

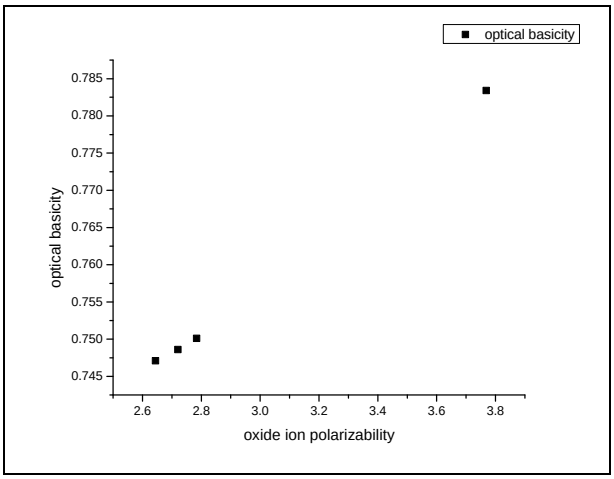

Fig.4. Variation of optical basicity with oxide ion polarizability .

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 [29]. Subtracting by 1 gives the metallization (M)

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

Conclusions

The Sm^{3+} doped Yttrium Zinc lithium bismuth borate gasses were prepared at various doping concentration of Sm_2O_3 and characterized for their physical properties. The density and refractive index increases with an increase in concentration of Sm_2O_3.The existence of trivalent electrons of samarium ions affects the structure of the glass system by increasing number of free electrons which leads to decreasing number of Energy gap.The decrease values of optical basicity indicate decrease in covalency. It also indicates the increase in non-bridging oxygen's (NBO's) in network. The decrease value of metallization criterion indicates that glass material is metalizing.

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