Thermal and Physical properties of Gd^{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: xGd_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, dielectric constant and electrical susceptibility have been evaluated. Dielectric constant, refractive index, electronic polarizability varies with increasing mole% of Gd_2O_3 respectively. The metallization criterion has been calculated on the basis of refractive index and energy gap. It was found to be decreased with increasing refractive index and decreasing energy gap. The large value of metallization criterion indicates that the glass materials are insulators.

***Keywords*: Gadolinium based glass;** *Electrical Susceptibility*; ***Metallization criterion*.**

INTRODUCTION

Among various glasses, borate glasses are excellent host matrices because boric oxide (B_2O_3) acts as a good glass former and flux material. Bismuth oxide contained host glass matrix improves chemical durability of the glass. Recently, many rare earth ions-doped glasses found important in the area of solid-state lasers, fiber laser, optical data storage and amplifier in optical communication [1-5]. In order to improve the glass quality and its optical performance a divalent oxide such as ZnO has been added separately beside the other property improving network modifier (NWF) namely Li_2O. These bismuth – borate glasses have high refractive index, good physical and chemical stability and large transmission windows in the near infrared regions [6-8].

Recently, bismuth borate glasses have received a great deal of attention due to their potential application in optical data transmission, detection, sensing and waveguide [9–12]. Bismuth borate glasses have attained great attention in synthesis, structure and physical properties due to their high refractive index, high density and high dielectric constant. The aim of the present study is to prepare the Gd^{3+}doped zinc lithium bismuth borate glass with different Gd_2O_3concentrations and to study the effect of Gd_2O_3content on the various physical parameters such as density, refractive index, molar refractivity, molar polarizability and oxygen packing density.

EXPERIMENTAL TECHNIQUES

Preparation of glasses

The following Gd^{3+} doped zinc lithium bismuth borate glass samples (25-x) Bi_2O_3:20Li_2O:20ZnO: 35 B_2O_3: xGd_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, B_2O_3 and Gd_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^{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 280^{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 (UD)	25Bi_2O_3:20Li_2O:20ZnO:35 B_2O_3
ZnLiBiB (GD 1)	24Bi_2O_3:20Li_2O:20ZnO:35 B_2O_3:1 Gd_2O_3
ZnLiBiB (GD 1.5)	23.5Bi_2O_3:20Li_2O:20ZnO:35 B_2O_3:1.5 Gd_2O_3
ZnLiBiB (GD 2)	23Bi_2O_3:20Li_2O:20ZnO:35 B_2O_3:2 Gd_2O_3

ZnLiBiB (UD) -Represents undoped Zinc Lithium Bismuth Borate glass specimens
ZnLiBiB (GD) -Represents Gd $^{3+}$ 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 within the resolution limit of XRD instrument.

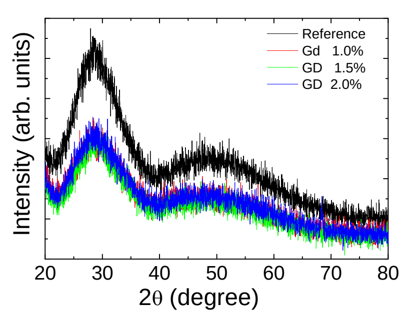

Figure 1 X-ray diffraction pattern of Bi_2O_3: Li_2O: ZnO: B_2O_3: Gd_2O_3 glasses.

Thermal Studies

Figure 2 depicts the DTA thermogram of powdered ZnLiBiB sample show an endothermic peak corresponding to glass transition event followed by an exothermic peak related to crystallization event. The glass transition temperature (T_g), onset crystallization temperature (T_x), crystallization temperature (T_c) were estimated to be 515 ^{0}C, 581^{0}C and 602^{0}C respectively. From the measured value of T_g, T_x and T_c , the glass stability factor ($\Delta T = T_x - T_g$) has been determined to be 66^{0}C indicating the good stability of the glass . Therefore, the present glass composition could also be used to draw fiber and used to determine the required heat temperatures applied to induce crystallization.

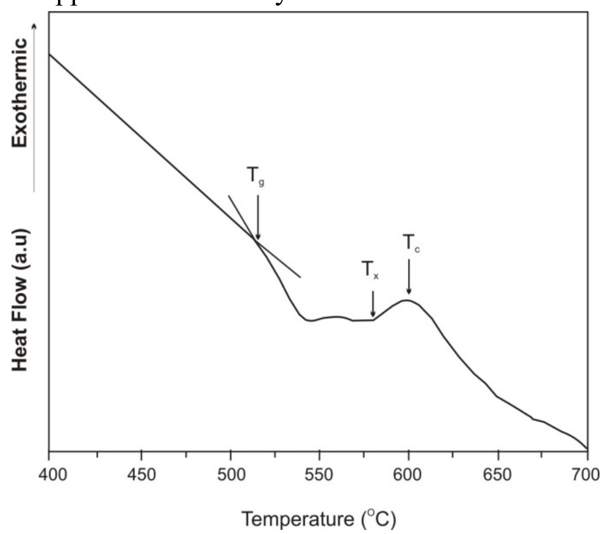

Figure 2. DTA thermogram of powdered ZnLiBiB sample.

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:

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

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

$$M_T = X_{Bi2O3} Z_{Bi2O3} + X_{Li2O} Z_{Li2O} + X_{ZnO} Z_{ZnO} + X_{B2O3} Z_{B2O3} + X_{Gd2O3} Z_{Gd2O3} \qquad (3)$$

Where X_{Bi2O3}, X_{Li2O}, X_{ZnO}, X_{B2O3}, X_{Gd2O3} are the molar fraction of the constituent oxides and Z_{Bi2O3}, Z_{Li2O}, Z_{ZnO}, Z_{B2O3}, Z_{Gd2O3} 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 [13]

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

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 [14]

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

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 [15]

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

Molar electronic polarizability

The molar electronic polarizability of the material can be calculated from following expression [16]

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

Dielectric constant

The dielectric constant was calculated using refractive index of the glass [17]

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

Where n is the refractive index.

Optical dielectric constant

The optical Dielectric Constant refractive index of the glass [18]

$$p\frac{dt}{dp} = (\varepsilon - 1) = n^2 - 1 \qquad (9)$$

Where ε is the dielectric constant.

Electronic polarizability

The electronic polarizability was cal calculated using the formula [19]

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

Where A_V is the Avogadro number.

Ionic concentrations

The ionic concentrations of the glass samples are determined using the following relation [20]

$$N(ions/cm^3) = \frac{(\text{Avogadro's number})(\text{glass density})}{(\text{Average molecular weight})} \times (\text{mol \% of rare earth}) \qquad (11)$$

Polaron radius

The polaron radius was calculated using the formula [21]

$$R_p = \frac{1}{2} \times \left(\frac{\Pi}{6N}\right)^{\frac{1}{3}} \qquad (12)$$

Where N is the ionic concentrations.

Inter-ionic distance

Inter-ionic distance of the glass samples is given as [21]

$$R_i = \left(\frac{1}{N}\right)^{\frac{1}{3}} \qquad (13)$$

Where R_i is the ionic concentrations.

Field strength

The field strength was calculated using the formula [22]

$$F\,(cm^3) = \left(\frac{Z}{R_p{}^2}\right) \qquad (14)$$

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 [23]

$$\text{O.P.D.} = n\left(\frac{\rho}{M}\right)\times 1000 \qquad (15)$$

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.

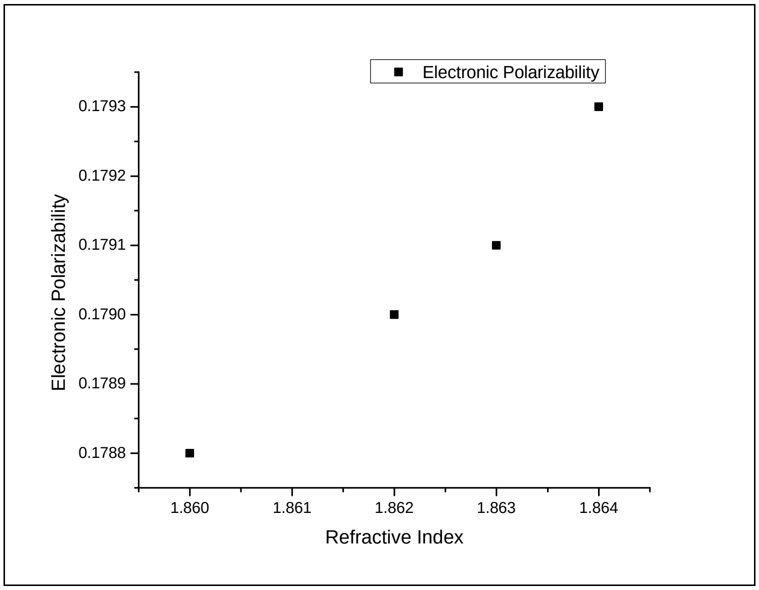

Figure 3. Varation of electronic polarizability with refractive index.

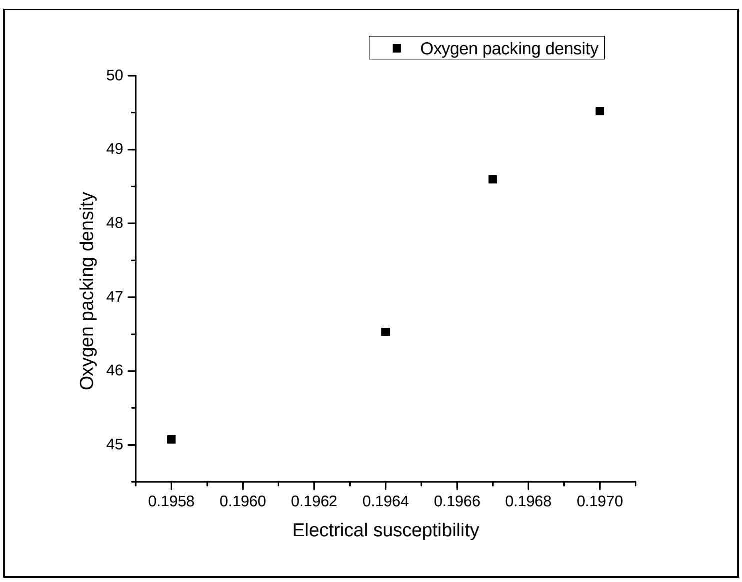

Fig.4. Variation of oxygen packing density with electrical susceptibility.

Table 2: The physical and optical properties of Bi_2O_3: Li_2O: ZnO: B_2O_3: Gd_2O_3 glasses

Physical properties	ZnLiBiB (UD)	ZnLiBiB (GD 01)	ZnLiBiB (GD1.5)	ZnLiBiB (GD 02)
Refractive Index (n)	1.860	1.862	1.863	1.864
Density (ρ) $\left(gm/cm^3\right)$	3.342	3.428	3.532	3.625
Thickness(Z)	0 .235	0.245	0.245	0.245
AveragemolecularweightM (g)	163.121	162.086	161.569	161.051
Rare earth ions concentratio(N)	--	1.274	1.975	2.711
Dielectric Constant (ϵ)	3.460	3.467	3.471	3.474
Optical Dielectric Constant $p\frac{dt}{dp}$	2.46	2.467	2.471	2.474
MolarVolume (V_{m}) $\left(gm/cm^3\right)$	48.809	47.283	45.270	44.428
Reflection losses(R_L)	9.042	9.071	9.086	9.101
Molar refractivity (R_{m})	21.989	21.337	20.445	20.082
Polaron radius R_p $\left(A^0\right)$	--	0.3718	0.3213	0.2891
Interionic distance(R_i) $\left(A^0\right)$	--	0.9225	0.7972	0.7174
Electronic polarizability (α_e)	0.1788	0.1790	0.1791	0.1793
Field strength (F)	--	1.772	2.373	2.931
Molarpolarizability(α_m) $\times 10^{-24} cm^3$	8.726	8.467	8.113	7.969
Oxygen packing density(OPD)	45.074	46.528	48.597	49.518
Metallization criterion (M)	0.5495	0.5487	0.5484	0.5480
Energy gap(E_g)	6.039	6.022	6.014	6.006
Electrical susceptibility (χ)	0.1958	0.1964	0.1967	0.1970

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

$$M = \left(1 - \frac{R_m}{V_m}\right) \qquad (16)$$

Electrical susceptibility (χ)

The Electrical susceptibility was calculated using the formula [25]

$$\chi = \left(\frac{n^2 - 1}{4\pi}\right) \qquad (17)$$

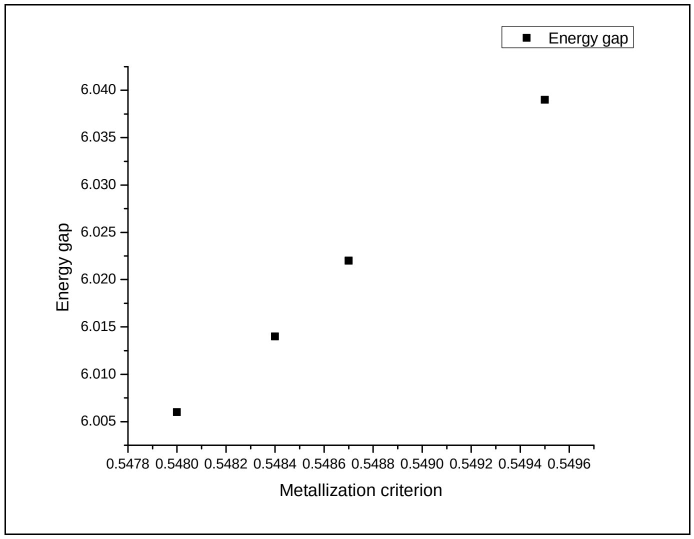

Fig.5. Variation of energy gap with metallization criterion.

CONCLUSIONS

The Gd^{3+} doped zinc lithium bismuth borate gasses were prepared at various doping concentration of Gd_2O_3 and characterized for their physical properties. The density and refractive index increases with an increase in concentration of Gd_2O_3.Increase in electronic polarizability results in increasing ability of oxide ions denote electrons to surrounding cation The results show that the refractive index of glass not only depends on the density but also on the electronic polarizability of the glass. The decrease value of metallization criterion indicates that the glass material is metalizing.

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