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Influence of Fe_2O_3 on structural, physical and optical properties of Lithium Sodium Bismuth Borate glasses

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Abstract: *In this paper, the Ferric oxide doped Lithium Sodium Bismuth Borate glass samples of composition* xFe_2O_3-$25Li_2O$-$5Na_2O$-$15Bi_2O_3$-$(55-x)B_2O_3$ *(where x = 0,2,4,6) have been prepared by melt quenching technique. Powder X-ray diffraction pattern confirmed the amorphous nature of the prepared glasses. Density measurements have been done with standard Archimedes principle. From the value of density, molar volume and OPD have been calculated. The DSC characterization was carried out to observe glass transition temperature. The FTIR spectral investigations exhibit characteristic vibrations of* BO_3, BO_4 *units, bending vibration of B-O-B linkages and in* BiO_6 *octahedral units Bi-O bonds exist. From the UV absorption spectra, direct optical band gap and refractive index have been calculated. The direct optical band gap values obtained lies in the range 1.06-1.87 eV. Density, molar volume, OPD, Tg, direct optical band gap energy and refractive index have shown interesting anomalous behavior.*

Keywords: *Bismuth Borate glasses, Ferric oxide, optical band gap, anomalous behavior.*

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I. INTRODUCTION

Glasses containing heavy metal oxide like Bi_2O_3 have drawn great attention because of their high density, high refractive index, high dielectric constant etc. These glasses have wide range of applications in the field of glass ceramics, layers for optical and electronic devices, reflecting windows, sensors etc. [1-3].The vitreous B_2O_3 structure consists of a random network of boroxyl rings and BO_3 triangles connected by B-O-B linkages. The addition of modifier oxide into the B_2O_3 structure changes some of BO_3 triangles to BO_4 tetrahedral units and some may change to various cyclic units [4].The addition of modifier oxides such as alkali, alkaline earth and transition oxides to borate glasses suggest that there will be change in the local configuration in the glass network and increase in the number of free carriers [5].The addition of transition metal oxide like Fe_2O_3 and V_2O_5 to borate glass makes semiconducting in nature [6,7].The ions of iron exist in more than one valence state, i.e., Fe^{2+} and Fe^{3+}[8]. The glasses containing Fe_2O_3 used in electrochemical, electronic, electro-optic and memory switching devices [9].The objective of present work is to study the structural, physical and optical properties of ferric oxide doped lithium sodium bismuth borate glasses.

II. EXPERIMENTAL DETAILS

Fe_2O_3 doped glass samples of composition $xFe_2O_3+25Li_2O+5Na_2O+15Bi_2O_3+(55-x)B_2O_3$ where (x=0,2,4,6) were prepared by melt quenching technique. Analytical grade chemicals Bi_2O_3, H_3BO_3, Li_2CO_3, Na_2CO_3 and Fe_2O_3.were used to prepare the glass samples. The mixture was homogeneously ground for 2 hrs in an Agate mortar. The ground powder was taken in a silica crucible and melted at 1100 C for 30 min in a furnace. The melt was stirred frequently to get homogeneity. The melt was suddenly quenched in air between two stainless steel plates at room temperature. The glasses so formed were annealed at 300 C for 3 hours to release the thermal stress in the glasses.

2.1 Glass characterization

The XRD spectral profiles of prepared glass samples were obtained using *PANalytical X'Pert Pro* powder X-ray diffractometer operated at 45 kV and 30 mA using Ni filtered Cu-K_α radiation. The non crystalline phase of the samples was conformed from XRD pattern by using Differential Scanning Calorimeter (*Model METTLER-TOLEDO DSC1*) at a heating rate of 10 C/min the prepared glass samples, glass transition temperature have been studied. The FTIR spectra were recorded using KBr pellets using *Thermo Nicolet 6700* FTIR spectrometer in the region 400-4000 cm^{-1}.UV-vis absorption spectra of glass samples were recorded by using *Analytik Jena SPECORD S-600* Spectrophotometer in the region 390–1050 nm. Density measurements were carried out at room temperature by standard principle of Archimedes with xylene (density 0.86 gm/cc) as an immersion liquid.

III. RESULTS AND DISCUSSION

3.1 *XRD Characterization*

The XRD confirms that the prepared glasses are amorphous in nature Fig (1) as it shows a broad hump at 2Θ ~30^0 and no crystalline phase exists in any of the composition of the glass samples.

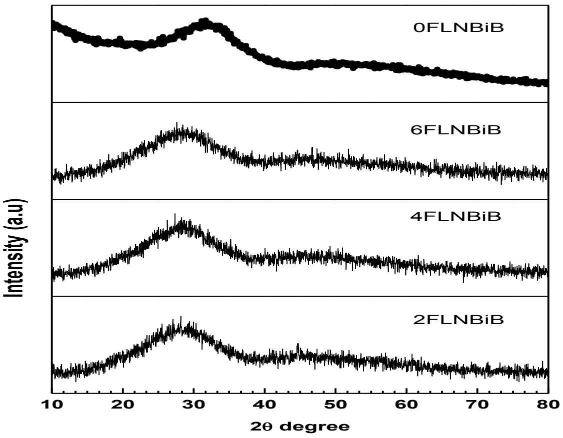


Fig (1) : XRD pattern of glass samples.

3.2. Physical properties

The density of prepared glass samples ρ was calculated by using

$$\rho = \frac{W_a \times 0.86}{W_a - W_b} \qquad (1)$$

where, W_a is the weight of the sample in air, W_b is the weight of the sample in xylene.

The molar volume V_m was calculated from

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

where, M is the molecular weight of the sample.

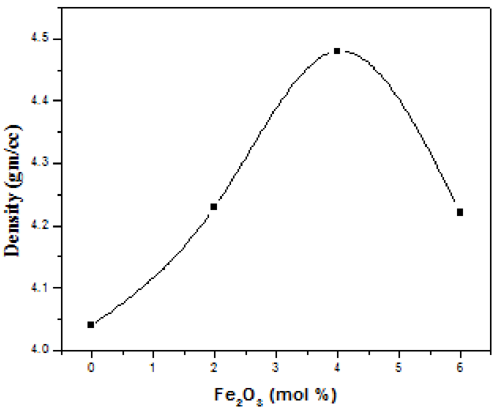
From the value of density and molar volume, oxygen packing density (OPD) was calculated by

$$OPD = C \times 1000 \left[\frac{\rho}{M}\right] \qquad (3)$$

where, C is the number of oxygen per formula unit. Density is a very important parameter to know the glass co-ordination, cross link, structure of glasses, geometrical configuration and compactness. From the density value, molar volume, OPD have been calculated and tabulated in the Table (1). The compositional variation of density, molar volume and OPD with Fe_2O_3 content are as shown in Fig (2), Fig(3) and Fig(4) respectively. The density increased up to x=4 mol% and then decreased, but the molar volume decreased up to x=4 mol% and again increased. Addition of Fe_2O_3 at x= 6mol% to borate glasses shows abrupt change which may be due to the boron anomaly. The increase in density gives an idea of creation of Non Bridging Oxygen’s (NBOs).

Table 1. Density, Molar volume (V_m), Oxygen packing density (OPD), glass transition temperature (T_g) for the glasses

Sample Code	Density **(g/cc)**	V_m **(cc/mol)**	Tg **(C)**	OPD (cm^3/mol)
0FLNBiB	4.04	33.57	447	71.41
2FLNBiB	4.23	32.57	423	73.70
4FLNBiB	4.48	31.17	412	76.97
6FLNBiB	4.22	33.53	420	71.50



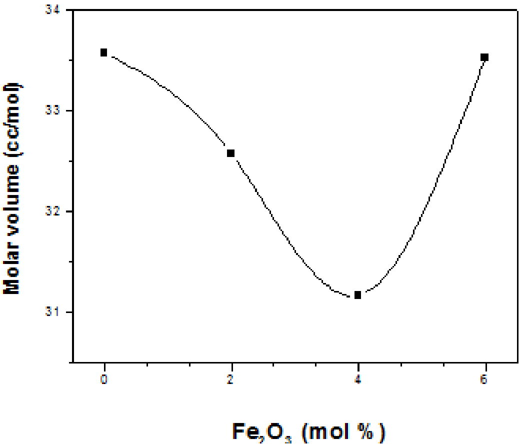


Fig (2): Compositional variation of density with Fe_2O_3. **Fig (3):**Compositional variation of molar volume With Fe_2O_3 .

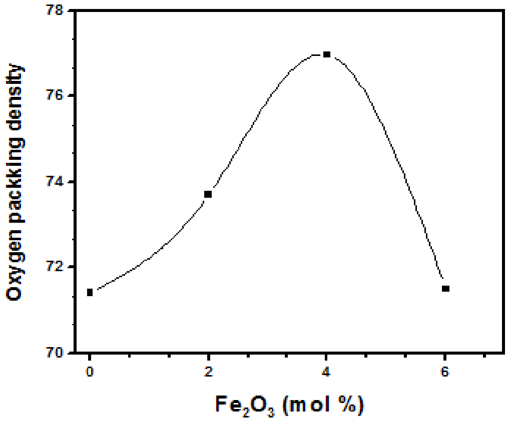


Fig (4) : Compositional variation of oxygen packing density with Fe_2O_3.

3.3. DSC Characterization

The DSC of the samples and glass transition temperature (T_g) with Fe_2O_3 content are shown in Fig(5) and Fig(6).The T_g of the glasses decreased up to x=4 % and then increased with increase of Fe_2O_3 content. The decrease in T_g indicates an increase in the number of NBO up to x=4%. The value of OPD increased up to x=4% and then decreased. An increase in the OPD up to x=4% of the prepared sample shows that the structure becomes tightly packed. The T_g and OPD have shown anomaly at x=4%.

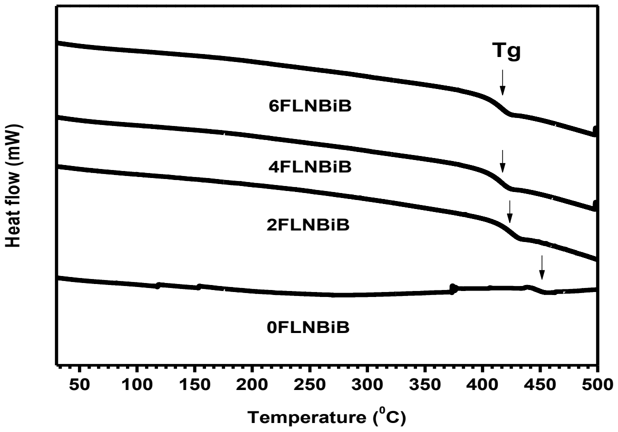


Fig (5):DSC of glasses.

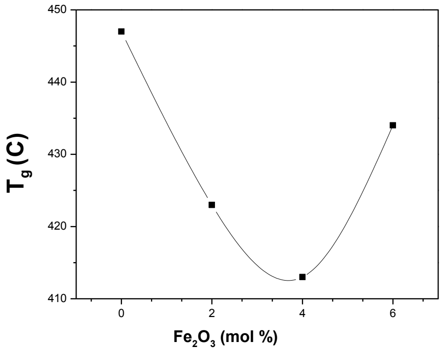


Fig (6) Compositional variation of T_g with Fe_2O_3 content.

3.4 FTIR analysis

In all the borate network glasses the vibrational modes are classified into three main IR active regions [10,11]. The band of first group of bands lies in the range 1200–1600 cm^{-1} which gave the information of the B–O bond asymmetric stretching relaxation of the trigonal BO_3 units.The second group band lies in the range 800–1200 cm^{-1} and that shows stretching of the B–O bond of tetrahedral BO_4 units. The band of third group of IR bands exist around 700 cm^{-1} and that gave an idea of B–O–B bending links are formed in the borate network. The absence of the band at 806 cm^{-1} signifies that no boroxyl ring was present. The absorption bands at around 507cm^{-1} to 512cm^{-1} are specific to the vibrations of Bi–O bonds in BiO_6 octahedral units [12-14].Due to the absence of absorption bands at 830 cm^{-1}expected only BiO_6 units will influence the glass matrix. The FTIR assignment peak bands of the present glasses are shown in Table(2).The bands from 706 cm^{-1} to 724 cm^{-1} signify B-O-B bending vibrations. The band around 977cm^{-1} to 1088 cm^{-1} indicates B-O stretching vibrations $BO_{4.}$ The band around 1385 cm^{-1} to 1436cm^{-1} specifies the B-O stretching vibrations of BO_3 as shown in Fig (7).The peaks observed at lower wave number of spectra are weak and well defined broad peak can be observed for higher wave number. For 6FLNBiB glass the peaks are observed broad at high wave number which gives the information of some structural change at this composition. The glass network nearly remains same at lower concentration of Fe_2O_3 while their doping affects at higher concentrations.

Table (2) Assignment of FTIR bands of glasses.

Sample code and Peak position				IR assignment
0FLNBiB	2FLNBiB	4FLNBiB	6FLNBiB	
508	510	507	512	Bi-O bonds in BiO_6 octahedral units
	706	724	714	B-O-B bending vibrations
990	-	-	977	In BO_4 there is B-O stretching vibrations
-	1088	1074	-	
1385	1383	1436	1415	In BO_3 there is B-O stretching vibrations

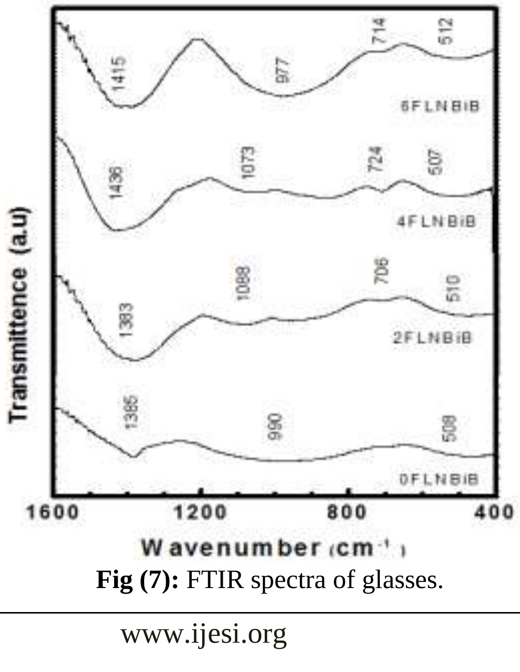


Fig (7): FTIR spectra of glasses.

3.5. UV-VIS Spectroscopy

From the near absorption edge of photon energies of glasses the absorption coefficient α (υ) can be determined by using the following relation [15,16].

$$\alpha(\nu) = \frac{2.303 \times A}{d} \tag{4}$$

where 'A' represents the absorbance and 'd' is the sample thickness.

In an optical transition there are two types. They are direct transition and indirect transition. These transitions occur in crystalline and non crystalline materials at the fundamental absorption edge which gives information regarding band structure and energy gap. To find absorption co-efficient α(υ) for the direct and indirect transitions formula proposed by Davis and Mott [17].

$$\alpha(\upsilon) = \frac{B(h\upsilon - E_{opt})^n}{h\upsilon} \tag{5}$$

where n=1/2 for allowed transitions is a constant and E_{opt} is the direct optical band gap. Plotting $(\alpha h\upsilon)^2$ vs (hυ) optical energy band gap can be obtained for direct transitions. The E_{opt} values are obtained for direct transitions by extrapolating to $(\alpha h\upsilon)^2 = 0$ respectively. The plots were drawn between $(\alpha h\upsilon)^2$ vs hυ and are shown in Fig (8).The calculated values of direct optical band gap and refractive index are as shown in Table(3).The compositional variation of direct optical band gap and refractive index with Fe_2O_3 content are as shown in Fig (9) (a) and (b).

Table 3. The values of direct optical band gaps and Refractive Index (n) of glasses.

Sample	Band gap (eV)	N
0FLNBiB	1.87	2.353
2FLNBiB	1.47	2.525
4FLNBiB	0.94	2.868
6FLNBiB	1.06	2.772

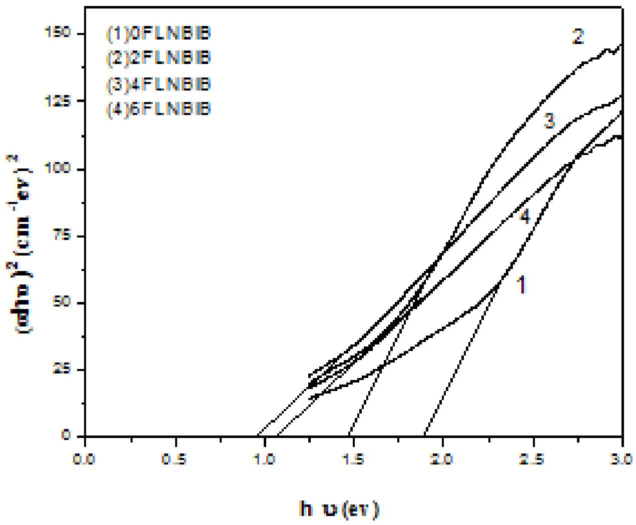
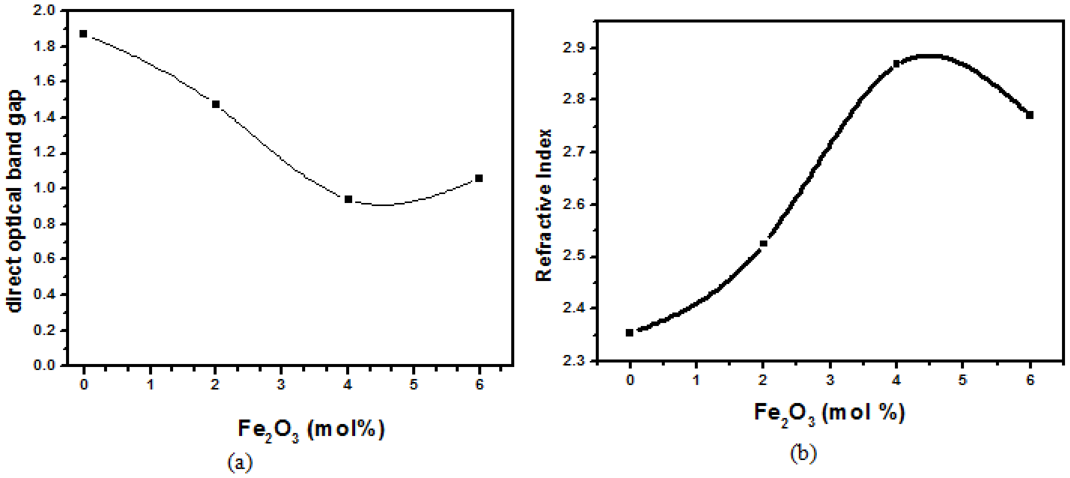


Fig (8): $(\alpha h\upsilon)^2$ vs hυ of glasses (direct transition)

The refractive index have been calculated using the following relation proposed by Dimitrov and Sakka [18,19].

$$\frac{n^2 - 1}{n^2 + 1} = 1 - \left[\frac{E_{opt}}{20}\right]^{1/2} \tag{11}$$

where n is the refractive index and E_{opt} is the direct optical band gap. The optical band gap energy decreased up to x=4 % with the addition of Fe_2O_3 content and further increased. The refractive index increased up to x=4% and then the decreased. Both optical band gap and refractive index shown anomalous behavior.



(a)

(b)

Fig (9): (a) and (b) are compositional variation of direct optical band gap and refractive index with Fe_2O_3 (mol%).

IV. CONCLUSIONS

In this paper, xFe_2O_3-$25Li_2O$-$5Na_2O$-$15Bi_2O_3$-$(55-x)B_2O_3$ (where x = 0,2,4,6) glasses have been prepared by melt quenching technique. X-ray diffraction confirmed that the prepared glasses are non crystalline in nature. The FTIR spectral investigations of glasses exhibit characteristic vibrations of BO_3 units, BO_4 units and bending vibration of B-O-B linkages and vibrations of Bi–O bonds in BiO_6 octahedral units. The absence of the band at 806 cm^{-1} signifies that no boroxyl rings were observed in the glass structure. From UV absorption spectra the direct optical band gap have been evaluated and they lie in the range 1.06-1.87 eV. Density, molar volume, OPD, Tg, direct optical band gap energy and refractive index have shown interesting anomaly behavior at x=6%.

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