Physical and Optical Properties of Fe_2O_3 Doped Lithium Zinc Borate Glasses

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Abstract

(50-x)B_2O_3-20Li_2O-30ZnO -x Fe_2O_3 glass system with x = 0,0.1,0.3 have been prepared by melt quenching. The samples were characterized by X-ray diffraction. XRD studies have confirmed that the prepared glasses were amorphous in nature. Physical properties (density, molar volume,) of these glasses have also been examined. The density of glass samples was found to be increased while the molar volume decreased with the increasing of concentration of Fe_2O_3.Thecompactness of the prepared glass system increase with the increase of Fe_2O_3 content. From the optical absorption, the UV cutoff was found to be increased from 315 to 400 nm by increasing Fe_2O_3. The optical band gap obtained decreases from 3.28 to 2.68 eV It indicates that Fe_2O_3 acts as a network modifier in this system. It was concluded that the prepared glasses are suitable for laser preventing applications such as UV laser production.

Key words: Fe_2O_3, amorphous, optical band gap, network modifier, UV laser production.

1. Introduction

Glass is an amorphous(non-crystalline)solid which exhibit 'glasstransition' All glasses are amorphous, but not all amorphous solids are necessarily be glasses[1]. Glass has a large variety of applications such as bioactive materials, sensor applications, radiation shielding window, scintillation counters, optoelectronic devices and solid-state ionic conductors. Glasses are generally prepared by melt-quenching method [2].Among the various glasses borate glasses play a significant role in various applications such as solid state lasers, optical and electrical applications, fiber optics, optical waveguides, and luminescence materials[3]. As borate glasses show high transparency, low melting point, high thermal stability and good glass forming nature, borate glasses are the best one for doping transition metal ions compared to several other conventional glassy systems. Glasses containing transition metals like Fe, Co, Cr, Mn etc., have semiconducting properties and hence they are used for several applications such as memory switching, electrical threshold. It is known that glass containing transition metal ions have many colors depending on the chemical composition of the glass system, the type of transition metals or the characteristics of the transition metal ions [4,5]. Iron present in glasses may occur in two valence states, namely Fe^{2+} and Fe^{3+} ions. It is reported that the trivalent iron ions can take two different coordination sites, i.e., either tetrahedral or octahedral sites in glasses[6].In the present paper, the physical and optical properties of Fe_2O_3 doped lithium zinc borate glasses, prepared by melt quench technique, were discussed.

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2.Experiment

The sample having the general chemical formula (50-x) B_2O_3-20Li_2O-30ZnO- x Fe_2O_3 with x = 0, 0.1and 0.5 mol% were prepared by melt quenching method. The starting materials are H_2BO_3, Li_2O, ZnO and Fe_2O_3. The glass starting materials were weighed using electronic balance after batch calculation and were weighted using digital balance. Then, the mixed powders were ground in agate mortars to obtain fine and homogeneous powders. The well mixed powders were melt in aluminum crucible using a lifting furnace. Melting is carried out at temperature 1100ºC for 1 hour. The molten sample is poured into a pre-heated steel mould .Then the glass samples were annealed at 300C for 3 hours to avoid the mechanical strain developed during the quenching process as shown in Figure 1. The photograph of prepared glass samples can be seen in Figure 2. These prepared glasses are labeled as BLZFe 0, BLZFe 1 and BLZFe 2 respectively. The detail of the prepared glass samples is listed in Table 1. The base glass(BLZFe0) was colourless and the glasses doped Fe_2O_3 were yellow in color. All samples are transparent and without bubbles. The colors of glass samples changed from yellow to dark yellow with increase of the iron oxide content. For each glass, parts of glass samples were grinded for XRD measurements. The amorphous nature of glasses was confirmed by X-Ray Diffractometer (XRD 1600 Shimazu @ Magway University) with Cu-Kα radiation, operating at 40 kV and 30 mA and the physical properties of glass sample were examined. Optical properties of glass samples have been characterized by UV-vis spectrophotometry (GENESYS 10S). The wavelength range of 200-900 nm was scanned with step interval of 5 nm.

Chemical Annealed at 1100° Poured into steel mold Anneal at 300° Glass sample

Figure 1. Photograph of the glass production process.

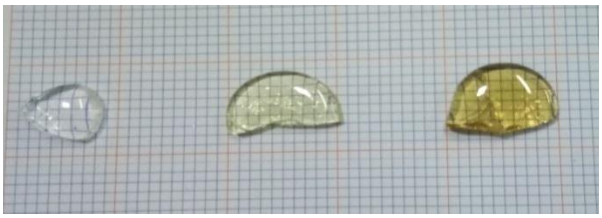


Figure 2. Photograph of Glass samples

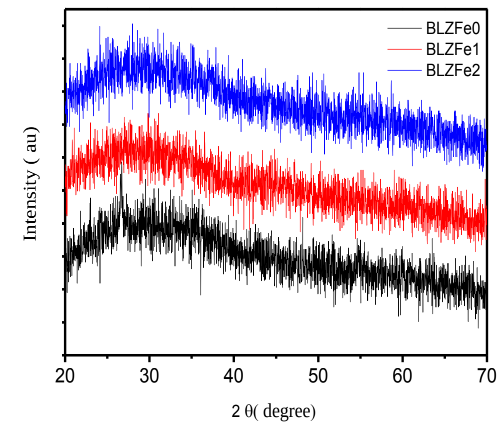
Table 1: Detail of Glass Samples

Glass	B_2O_3 (mol%)	Li_2O (mol%)	ZnO (mol%)	Fe2O3 (mol%)
BLZFe 0	50	20	30	0
BLZFe 1	49.9	20	30	0.1
BLZFe 2	49.7	20	30	0.3

3.Results and Discussion

3.1 XRD Analysis

Figure 3 shows the X-ray diffraction patterns of the prepared samples with different mol% of Fe_2O_3 content. The results of XRD studies of all samples show diffused scattering where broad humps can be observed. The absence of sharp peaks in the XRD patterns confirms the amorphous nature of the prepared samples. Moreover, the broad profiles around 2θ = 30 ° suggest the existence of some short-range order in the glass samples.



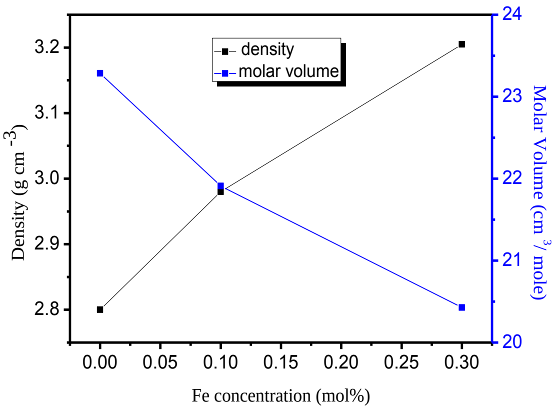


Figure 3. XRD Spectrum of Glasses

Figure 4.Variation of Density and Molar Volume of Glasses

3.2 Physical properties of glasses

The density and molar volume measurements are considered to be very important tools to detect the structural changes and the arrangement of the building units in the glass network[7]. The calculated values of the physical parameters of glass samples are listed in Table 2. The results indicate a linear increase in the density of the glass samples with increasing content of Fe_2O_3. However, the molar volume is found to have the opposite trend to that of the density as shown in Figure.4. The increase in density agrees qualitatively with that predicted by the composition relation in which the low density B_2O_3 was replaced by the high density Fe_2O_3 [8].

For better understanding of structural changes in samples, the ionic concentration of Fe ion(N), the inter-ionic distance(r_i),the polaron radius (r_p) and field strength (F) of Fe-O bond in the glass system can be determined using the following relations[7,9,10] and depticted in Table 2;

Concentration of ions, $N = (\text{mole \% of Fe}) \frac{N_A\ \rho}{(glass\ average\ molecular\ weight)}$ ....(1)

Interionic distance $r_i = \left[\frac{1}{N}\right]^{1/3}$ ....(2)

Polaron radius $r_p = \frac{1}{2}\left[\frac{\pi}{6N}\right]^{1/3}$ ....(3)

Field strength $F = \left[\frac{Z}{r_p^3}\right]$ ....(4)

It is observed that Fe-ion concentration increases whereas inter-ionic distance decreases with increasing concentration of Fe_2O_3 which is consistent with the obtained behavior of the density and molar volume. Moreover, the inter-ionic distance(r_i) and the polaron radius (r_p) decrease and field strength (F) increases with the increasing of Fe ions. These results support with the density results and confirm the compactness of glass structure with the increase in Fe_2O_3. Due to compactness of glass sample , there is decrease in delocalization of electrons which in turns the increase in donor centers[10].

Table 2 Physical Parameters of Glass Samples

Parameters	Glass Code		
	BLZFe 0	BLZFe 1	BLZFe 2
Density(ρ)g cm^{-3}	2.8	2.94	3.05
Molar volume(V) $cm^3\ mol^{-1}$	23.29	22.21	21.47
Ion concentration (N) $\times 10^{20}$ ions cm^{-3}	-	29.83	92.59
Interionic radius (r_i) $\dot{A}$	-	8.19	5.63
Polaron radius (r_p) $\dot{A}$	-	3.31	2.28
Field strength (F) $\times 10^{16}$ cm^{-2}	-	5.12	10.80

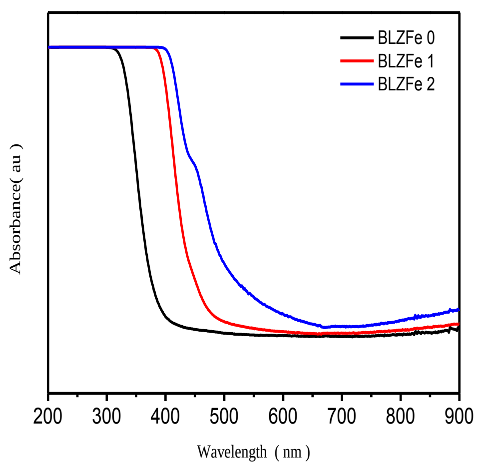
3.3 Optical Properties of Glasses

Figure 5 shows the optical absorption spectra of the glass samples over the wavelength range (200–900 nm) for different mole% of Fe_2O_3. It is evident that all samples exhibit an optical absorption band in both the visible-near infrared region and fundamental optical absorption edge in the ultraviolet region The absorption edge observed at 315nm for base glass(0 mole%) and it is shifted towards to higher wavelength with increase of the iron oxide content. Figure 6 shows the optical transmission spectra of the glass samples in the wavelength range 200–900 nm for different mole% of Fe_2O_3. The transmission spectra are consistent with the absorption data. As shown in Fig. 5 and listed in Table 3, the UV cutoff is found to be increased from 315 to 400 nm by increasing Fe_2O_3 content. It can be concluded that the present study offers an excellent optical material for preventing the whole UV range. The glass samples can be used for UV preventing applications such as UV-Laser protection.

The optical band gap, E_g of the glass samples was determined using the relation [11]:

$$\alpha h\nu = B(h\nu - E_g)^n \qquad \text{..........(5)}$$

where B is a constant,α is absorption coefficient and hν is the photon energy, E_g is the optical energy gap and n is an index. The values of n are 1/2 and 2 for direct and indirect transitions, respectively. To estimate the optical energy band gap values for direct transitions $(\alpha h\nu)^2$ as a function of hν had been plotted. The optical band gap energy was obtained by extrapolating the linear region of the curve to the hν axis as shown in Figure. 7 and the values of energy gaps for glass samples are listed in Table 3. The optical band gap energy decreases from 3.28 to 2.68 with the increasing of Fe_2O_3 concentration. This is because of increasing in donor centers. These results were agreed with the results of physical properties. From these optical results, it can be concluded that Fe_2O_3 acts as a network modifier in the glass system and the prepared glasses are suitable for using as optical device for UV protection.



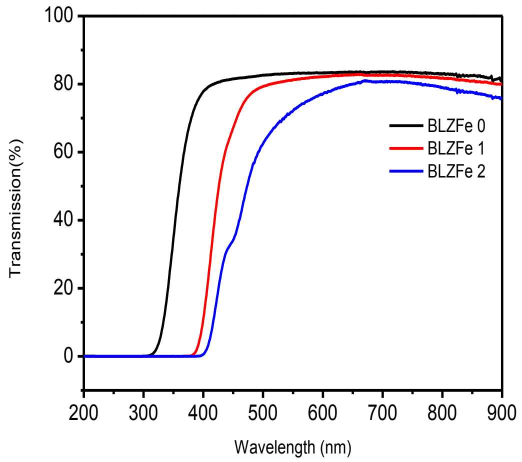


Figure 5.Optical Absorption Spectra of Glasses

Figure 6. .Optical Transmission Spectra of Glasses

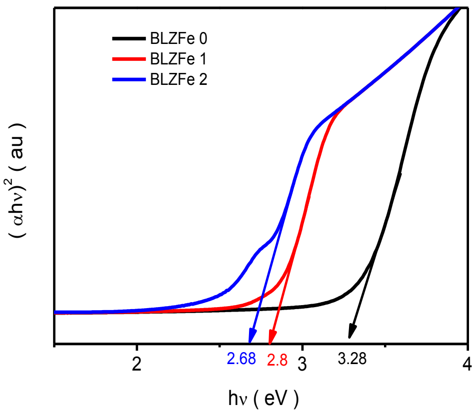


Figure 7. Plots for Direct Optical Band Gap of Glasses

Table 3: Summary of data of optical properties of glass samples

Glass Code	Cut-off Wavelength (nm)	Band gap energy (eV)
BLZFe 0	315	3.28
BLZFe 1	380	2.8
BLZFe 2	400	2.68

4.Conclusion

(50-x)B_2O_3-20Li_2O-30ZnO -x Fe_2O_3 glass system with x = 0,0.1,0.3 have been prepared by melt quenching method. The XRD pattern showed that the prepared glasses are amorphous in nature. Physical properties (density, molar volume, etc.) of these glasses have also been examined. The density of glass samples was found to be increased while the molar volume decreased with the increasing of concentration of Fe_2O_3. It can be concluded that the more compact the glass structure with the increase in Fe_2O_3. From the optical absorption, the UV cutoff was found to be increased from 315 to 400 nm by increasing Fe_2O_3. The results indicate that the prepared glass system is a good candidate for optical device with excellent band stop in UV range. So, the prepared glasses are suitable for using as optical devices for UV laser production. Moreover, the optical band gap obtained was found to be decreased from 3.28 to 2.68 eV with the increase of Fe_2O_3. The optical studies had concluded that Fe_2O_3 acts as a network modifier with the lithium zinc borate glass.

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