Research Article

Fe₂O₃ Modified Physical, Structural and Optical Properties of Bismuth Silicate Glasses

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Iron-containing bismuth silicate glasses with compositions $60\text{SiO}_2 \cdot (100 - x)\text{Bi}_2\text{O}_3 \cdot x\text{Fe}_2\text{O}_3$ have been prepared by conventional melt-quenching technique. The amorphous nature of the glass samples has been ascertained by the X-ray diffraction. The density (d) has been measured using Archimedes principle, molar volume (V_m) has also been estimated, and both are observed to decrease with the increase in iron content. The glass transition temperature (T_g) of these iron bismuth silicate glasses has been determined using differential scanning calorimetry (DSC) technique, and it increases with the increase in Fe₂O₃ content. The IR spectra of these glasses consist mainly of [BiO₆], [BiO₃], and [SiO₄] structural units. The optical properties are measured using UV-VIS spectroscopy. The optical bandgap energy (E_{op}) is observed to decrease with the increase in Fe₂O₃ content, whereas reverse trend is observed for refractive index.

1. Introduction

The heavy metal oxide glasses have attracted the attention due to their optoelectronic and photonic applications because of their optical properties such as refractive index, optical nonlinearity, and infrared transmission to develop more efficient lasers and fibre optic amplifiers at longer wavelength than other oxide glasses [1]. Bi₂O₃, attracted the attention of scientific community which is of current interest because of its important applications in glass ceramics, thermal and mechanical sensors, layers for optical and electronic devices, and so forth and as transmitting windows in the IR region [2–4]. Due to high polarizability and small field strengths of Bi³⁺ ions, Bi₂O₃ is not a classical glass former although in the presence of other oxides such as B₂O₃, PbO, SiO₂, and V₂O₅, it may form a glass network of [BiO₃] and [BiO₆] pyramids [1, 5]. Silicate glasses, because of their favourable physical, chemical, and optical characteristics, are used in numerous applications: in optics as lenses or beam splitters, in telecommunications as optical fibres, in micro- and optoelectronics, and in near-IR windows due to their

low optical attenuation and optical dispersion [6, 7]. Oxide glasses containing transition metal oxides such as Fe₂O₃ are used in electrochemical, electronic, and electro-optic devices [8]. The presence of transition metal oxides (in addition to Bi₂O₃) gives new possibilities to extend the properties of these materials. Due to the presence of different valence states of Fe, it participates in glass matrix as Fe²⁺ and Fe³⁺ and results in various modified structural units [9]. The addition of Fe₂O₃ in these glasses enhances the chemical durability and their stability. Keeping in the view the effect of transition metal ions in modifying the structure and their wide range of applications, it is of interest to carry out the detailed study of the effect of Fe₂O₃ on the physical, structural, and optical properties of heavy metal oxide containing bismuth silicate glasses.

2. Experimental Details

Glass samples of compositions $60\text{SiO}_2 \cdot (100 - x)\text{Bi}_2\text{O}_3 \cdot x\text{Fe}_2\text{O}_3$ ($x = 0, 1, 3, 5, 10, 15$, and 20) were prepared using analar grade chemicals Fe₂O₃, Bi₂O₃, and SiO₂. The

appropriate amount of these chemicals were thoroughly mixed in an agate pestle mortar. Silica crucible containing the mixture was put in an electrically heated muffle furnace, and the temperature was raised slowly to 1000–1150°C depending on the composition. The temperature was maintained for 1 hour, and the melt was shaken frequently to ensure proper mixing and homogeneity. The melt was then poured onto a stainless steel block and was pressed immediately by another stainless steel block at room temperature. X-ray diffraction (XRD) patterns of the synthesized glass samples were recorded by using Rigaku tabletop X-Ray diffractometer. Density (d) of the samples was measured by Archimedes' principle using xylene as immersion liquid. The values of glass transition temperature (T_g) of different glass samples were measured using the DSC technique by TA Instruments, Model no. Q600 SDT. The studies were carried out at a heating rate of 20°C/min in nitrogen atmosphere. The room temperature absorption spectra and IR spectra of the glass samples were, respectively, recorded using double beam UV-visible spectrophotometer and Shimadzu IR affinity-I 8000 Fourier transform infrared (FT-IR) spectrophotometer in the wavelength range of 4000–400 cm⁻¹ using KBr as a standard reference material.

3. Results and Discussion

The X-ray diffractograms (XRD) of the prepared glass samples 60SiO₂·(100 - x)Bi₂O₃ · x Fe₂O₃ are shown in Figure 1. The perusal of XRD patterns shows the presence of broad hump and absence of any sharp peaks. In XRD patterns, the presence of a broad diffuse scattering at low angles instead of crystalline peaks, confirms a long range structural disorder characteristic of amorphous network.

The values of the characteristic glass transition temperature (T_g) of these glasses have been estimated using differential scanning calorimetry (DSC) at a rate of 20°C/min. It is observed that the glass transition temperature increases from 469°C to 513°C and provide greater glass stability. The addition of Fe₂O₃ can act as an intermediate and a glass modifying oxide and can be present in both the Fe²⁺ and Fe³⁺ states in the glass network [10]. This observation suggests that the addition of Fe₂O₃ leads to the growth and densification of the Bi₂O₃ glass matrix. The increase of T_g with iron content indicates that the glass network becomes more stable. The increasing trend in the T_g with the increase in the iron content indicates that when Fe₂O₃ is substituted for Bi₂O₃, the Fe–O–Bi and Bi–O–Bi bonds are broken and new bonds such as Fe–O–Fe bonds are probably formed [11]. Therefore, drastic changes in the T_g cannot be expected with the increase in the Fe₂O₃ content indicating the isostructural units of nearly same bond strength.

3.1. Physical Properties. The density “ d ”, of the glasses in present system, was determined at room temperature using Archimedes principle with xylene (density is taken as 0.865 gm/mL) as an inert immersion liquid [12]. The molar volume (V_m) of samples was calculated using the following

FIGURE 1: X-ray diffractograms of the different compositions of 60SiO₂·(100 - x)Bi₂O₃ · x Fe₂O₃ glass system.

relation [13]

$$V_m = \frac{\sum x_i M_i}{d}, \quad (1)$$

where x_i is the molar fraction, M_i is the molecular weight of the i th component, and d is the density of sample. The density (d) and molar volume (V_m) both decrease with the increase in iron content. The measured values of density and calculated values of molar volume for the system are listed in Table 1. The perusal of data from Table 1 shows that the topology of the network is significantly changed with composition and the glass structure becomes less tightly packed with the increase in the Fe₂O₃ concentration [14]. This type of behavior is explained simply as the replacement of the heavier Bi₂O₃ by the lighter Fe₂O₃, and this indicates that Fe₂O₃ plays the role of the glass modifier, and it introduces excess structural free volume [4].

3.2. FTIR Spectroscopy. The FTIR spectra of glass compositions 60SiO₂·(100 - x)Bi₂O₃ · x Fe₂O₃ with different values of x are shown in Figure 2(a), and the magnified version of typical FTIR spectrum for composition $x = 15$ is presented in Figure 2(b). Two broadbands at 420–540 cm⁻¹ and 860–1120 cm⁻¹ are observed in the spectra of all compositions, while weakband at around 730–780 cm⁻¹ exists in the spectra of all compositions. The band at 420–540 cm⁻¹ is attributed to the Bi–O bending vibrations of BiO₆ structural units [15]. On increasing the concentration of Fe₂O₃, small kinks at ~410–430 cm⁻¹, 430–460 cm⁻¹, and 470–530 cm⁻¹ start appearing within the broadband [16]. The increase in concentration of Fe₂O₃ some bands at ~550–660 cm⁻¹ in compositions with $x > 5$ mole% appears and is attributed due to the vibrations of Fe–O bonds of FeO₆ structural units, and FeO₄ structural units and it indicates that some iron ions occupy the glass network modifier and glass former positions [17]. The shifting of bands towards higher wave number a side with the increase in Fe₂O₃ content indicates the formation of FeO₄ units at the expense of FeO₆ octahedral units. The dip of broad band between ~730–780 cm⁻¹ centred at around 752 cm⁻¹ increases with the increase in the concentration of Fe₂O₃ and may be attributed to the symmetric stretching vibration of Si–O–Si bonds of SiO₄ tetrahedra [18]. The band at around

FIGURE 2: (a) FTIR spectra for different glass compositions in spectral range 400–1200 cm^{-1} of the glass system $60\text{SiO}_2 \cdot (100-x)\text{Bi}_2\text{O}_3 \cdot x\text{Fe}_2\text{O}_3$. (b) Amplified IR spectra excluding region of maximum transparency for glass sample with $x = 15$.

TABLE 1: Density (d), molar volume (V_m), glass transition temperature (T_g), optical band gap energy (E_{op}), and refractive index (n) of $60\text{SiO}_2 \cdot (100-x)\text{Bi}_2\text{O}_3 \cdot x\text{Fe}_2\text{O}_3$ glasses for different values of x .

Parameters	$x = 0$	$x = 1$	$x = 3$	$x = 5$	$x = 10$	$x = 15$	$x = 20$
d (gm/cm^3) ($\pm 0.01 \text{ gm}/\text{cm}^3$)	6.22	6.16	6.08	5.97	5.73	5.52	5.26
V_m (cm^3/mole) ($\pm 0.01 \text{ cm}^3/\text{mole}$)	35.71	35.61	35.04	34.66	33.42	31.92	30.62
T_g ($^{\circ}\text{C}$) ($\pm 1^{\circ}\text{C}$)	469	471	476	481	505	510	513
E_{op} (eV) ($\pm 0.01 \text{ eV}$)	2.95	2.47	2.22	2.02	—	—	—
n (± 0.01)	2.41	2.55	2.64	2.72	—	—	—

$860\text{--}1120 \text{ cm}^{-1}$ is assigned to Si–O–Si asymmetric vibrations of SiO_4 tetrahedra in polymerized network dominated Si–O–Si bridging links. The width of this band slowly goes on decreasing with the increase in concentration of Fe_2O_3 [19]. As the concentration of the SiO_2 is kept constant in all compositions, the symmetry of silicate network goes on increasing with Fe_2O_3 concentration. These increases in symmetry indicate the increase in the strength of network and hence increase in the glass transition temperature.

3.3. Optical Transmittance. The optical transmission spectra of the glass samples $60\text{SiO}_2 \cdot (100-x)\text{Bi}_2\text{O}_3 \cdot x\text{Fe}_2\text{O}_3$ with different values of x are shown in Figure 3. The absorption edge is observed towards longer wavelength side with the increase in the iron content. As the concentration of Fe_2O_3 increases beyond 5 mol% (i.e., $x = 10, 15$, and 20 mol%) the colour of the glass samples becomes opaque (blackish in colour), and transmittance becomes nearly zero.

The optical band gap energy of the glasses can be calculated from the UV absorption edge using the well-known Tauc law relation [20]

$$\alpha h\nu = A(h\nu - E_{\text{op}})^m, \quad (2)$$

where α is the absorption coefficient, $h\nu$ is the incident photon energy, A is constant, E_{op} is the optical band gap energy, and the exponent m is a parameter which depends on the type of electronic transition responsible for absorption. The Tauc plots were plotted for various values of m , that is, $1/2$, 2 , $1/3$, and 3 corresponding to direct allowed, indirect allowed, direct forbidden, and indirect forbidden transitions respectively. The fitting is most suitable corresponding to $m = 1/2$ and shown in Figure 4. The value of optical band gap energies (E_{op}) are determined from the linear region of the curve after extrapolating to meet the $h\nu$ axis at $(\alpha h\nu)^2 = 0$ and are presented in Table 1.

The values of refractive index for various compositions have been determined from the optical energy band gap using the relation proposed by Dimitrov and Sakka [21]:

$$\frac{n^2 - 1}{n^2 + 2} = 1 - \frac{\sqrt{E_{\text{op}}}}{20}. \quad (3)$$

The decrease in optical band gap may be due to the increase in concentration of the nonbridging oxygen (NBO) atoms with the increase in Fe_2O_3 [22]. Similarly, the increase in refractive index with the increase in iron content due to the

FIGURE 3: Optical transmission spectra of different compositions of synthesized glass samples of $60\text{SiO}_2 \cdot (100 - x)\text{Bi}_2\text{O}_3 \cdot x\text{Fe}_2\text{O}_3$ system.

FIGURE 4: Tauc's plot for different glasses samples of $60\text{SiO}_2 \cdot (100 - x)\text{Bi}_2\text{O}_3 \cdot x\text{Fe}_2\text{O}_3$ system for $m = 1/2$.

presence of nonbridging oxygens which have an effect on the refractive index because the polarity of the nonbridging oxygen is higher than that of the bridging oxygen [23]. The variation in optical band gap energy and refractive index as a function of Fe_2O_3 is shown in Figure 5.

4. Conclusions

Glasses with compositions $60\text{SiO}_2 \cdot (100 - x)\text{Bi}_2\text{O}_3 \cdot x\text{Fe}_2\text{O}_3$; $x = 0, 1, 3, 5, 10, 15$, and 20 have been successfully prepared by conventional rapid melt-quenching technique. The glassy

FIGURE 5: The variation of E_{op} and n with different compositions of Fe_2O_3 (x).

nature is confirmed by the X-ray diffractograms. Values of the physical properties like density and molar volume decrease with the increase in the iron content, whereas glass transition temperature shows reverse trend. The analysis of the FTIR shows that SiO_2 in these glass compositions exists in SiO_4 tetrahedral structural units, and the symmetry of the silicate network goes on increasing with the increase in Fe_2O_3 concentration. Bismuth plays the role of network modifier and exists in BiO_6 octahedral units. Iron plays the role of network modifier as well as glass former and exists in FeO_6 octahedral structural units and FeO_4 tetrahedral units, respectively. The band gap energy decreases with increase in iron concentration, and refractive index increases with the increase in the Fe_2O_3 content. In all glass samples, the symmetry of silicate network goes on increasing with Fe_2O_3 content and hence it modifies the physical and structural properties of these glasses.

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