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Fe_2O_3Enhanced Bismuth Silicate Glasses Physical, Structural, and Optical Properties

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Abstract:
Iron-containing $60SiO_2{\cdot}(100\text{-}x)Bi_2O_3\,.xFe_2O_3$ silicate glasses with compositions were prepared using traditional melt-quenching technique. The X-ray diffraction has ascertained the amorphous nature of the glass samples. The density (d) was calculated using the Archimedes method, molar volume (V_m) was also estimated, and both were observed to decrease with the iron content increase. The glass transition temperature (T_g) of these iron bismuth silicate glasses has been calculated using the technique of differential calorimetry scanning (DSC) and increases with the rise in Fe_2O_3 contents. The IR spectra of these glasses consists mainly of structural units [BiO_6], [BiO_3], and [SiO_4]. Using UV-VIS spectroscopy, we test the optical properties. With the increase in Fe_2O_3 material, the optical bandgap energy (E_{op}) is observed to decrease, whereas the reverse trend is observed for refractive index.

***Keywords*—**$60SiO_2{\cdot}(100\text{-}x)Bi_2O_3\,.xFe_2O_3$, optical dispersion, FTIR Spectroscopy, Dimitrov and Sakka, optical band gap energy.

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I. INTRODUCTION

Because of their optoelectronic and photonic applications, the heavy metal oxide glasses have attracted attention due to their optical properties such as refractive index, optical nonlinearity and infrarot transmission to produce more powerful lasers and fiber optic amplifiers at longer wavelengths than other oxide glasses[1]. Bi_2O_3 has attracted the attention of the scientific community, which is of current interest due to its important applications in glass ceramics,thermal and mechanical sensors, optical and electronic system layers, and so on and as transmitting windows in the IR region[2–4]. Bi_2O_3 is not a classical glass former because of its high polarizability and small field strengths of Bi^{3+} ions, although it may form a glass network of [BiO_3] and [BiO_6] pyramids[1, 5] in the presence of other oxides such as B_2O_3, PbO, SiO_2, and V_2O_5. Silicate glasses are used in numerous applications due to their favorable physical, chemical and optical characteristics: 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]. For electrochemical, electronic, and electro-optic applications, oxide glasses containing transition metal oxides such as Fe_2O_3 are used[8].The presence of transition metal oxides (besides Bi_2O_3) provides new possibilities for extending the properties of these materials. Due to the presence of different valence states of Fe, it participates in glass matrix as Fe^{3+} and F^{2+} results in various modified structural units [9]. Adding Fe_2O_3 to these glasses increases the chemical longevity and its stability. It is of interest to carry out a detailed study of the impact of Fe_2O_3 on the physical, structural and optical properties of heavy metal oxide containing bismuth silicate glasses in view of the role of transition metal ions in changing the structure and their wide range of applications.

II. EXPERIMENTAL DETAILS

Glass samples of compositions $60SiO_2$.(100-x)Bi_2O_3.xFe_2O_3(x=0, 1, 3, 5, 10, 15, and 20) were prepared using analar grade chemicals Fe_2O_3, Bi_2O_3, and SiO_3. The required quantity of these chemicals was thoroughly mixed in a pestle mortar with agate. The silica crucible containing the mixture was put in an electrically heated muffle furnace, and depending on the composition, the temperature was gradually raised to 1000–1150 ° C. 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.Rigaku tabletop X-Ray diffractometer was used to record patterns of the synthesized glass samples. The density (d) of the samples was calculated using xylene as immersion liquid using the Archimedes principle. TA Instruments, Model No, used DSC technique to calculate the glass transition temperature values (T g) of various glass samples. SDT Q600. The experiments were conducted in a nitrogen atmosphere at a heating rate of 20 ° C / min. The room temperature absorption spectra and the IR spectra of the glass samples were recorded using the double beam UV-visible spectrophotometer and the Shimadzu IR affinity-I 8000 Fourier transform infrared (FT-IR) spectrophotometer in the 4000–400 cm^{-1} wavelength range using KBr as the standard reference material.

III. RESULT AND DISCUSSION

The X-ray diffractograms (XRD) of the prepared glass samples $60SiO_2$.(100-x) Bi_2O_3.xFe_2O_3 are shown in Figure 1. The perusal of XRD patterns reveals the presence of large hump and no sharp peaks. For XRD trends, the presence of a large diffuse scattering at low angles rather than crystalline peaks suggests an amorphous network characteristic of a long-range structural disorder.

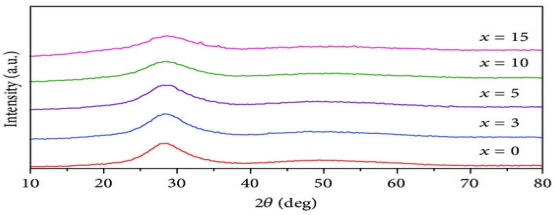

Fig 1 $X-ray\ diffactogram$ different composition of $\mathbf{60}\boldsymbol{siO_2}.(\mathbf{100}-\boldsymbol{x})\boldsymbol{Bi_2O_3}.\boldsymbol{xFe_2O_3}$ glass system[24]

The characteristic glass transition temperature (T_g) values of these glasses were measured at a rate of 20 °C / min using differential calorimetry scanning (DSC). It is found that the temperature of the glass transition rises from 469 °C to 513 °C and gives greater stability to glass. The addition of Fe_2O_3 can act as an oxide-modifying intermediate and glass, and can be present in both the state Fe^{2+} and Fe^{3+} in the glass network[10]. This result indicates that the addition of Fe_2O_3 contributes to the Bi_2O_3 glass matrix rising and densifying. The increase of T g with iron content shows the glass network becoming more stable. The growing trend in iron content increases suggests that when Fe_2O_3 is substituted with Bi_2O_3, the bonds of Fe–O–Bi and Bi–O–Bi are broken and new bonds such as Fe–O–Fe bonds are likely to be formed[11]. Consequently, drastic changes in the T_g can not be expected with an increase in the content of Fe_2O_3 suggesting isostructural units of almost the same bond strength.

A. Physical properties

Glass density "d" has been determined at room temperature using the Archimedes principle with xylene (density taken as 0.865 gm/mL) as an inert immersion liquid[12].The molar volume (V_m) of samples was calculated using the following relation [13]

$$V_m = \frac{\Sigma x_i M_i}{d},$$

Where x_i is the molar fraction, is the molecular weight of the ith component, and d is the density of sample. The density (d) and molar volume (V_m) both decrease with the increase in iron content.Table 1 lists the estimated density values and the determined molar volume values for the device. The perusal of Table 1 data shows that the topology of the network is significantly changed with composition, and the structure of the glass becomes less tightly packed with the rise in concentration of Fe_2O_3 [14].This type of behavior is explained simply by replacing the heavier Bi_2O_3 with the lighter Fe_2O_3, which suggests that Fe_2O_3 plays the role of the

glass multiplier, and it introduces excess structural free volume[4].

Table 1 Density ($\boldsymbol{d}$), molar volume ($\boldsymbol{V_m}$), glass transition temperature ($\boldsymbol{T_g}$), optical band gap energy ($\boldsymbol{E_{op}}$), and refractive index ($\boldsymbol{n}$) of $\boldsymbol{60SiO_2.(100-x)Bi_2O_3.xFe_2O_3}$ glasses for different values of $\boldsymbol{x}$.[24]

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

B. FTIR spectroscopy

The FTIR spectra of glass compositions $60SiO_2$.(100-x) $Bi_2O_3.xFe_2O_3$ with different values of 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 weak band 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 BiO_6 structural units [15]. On increasing the concentration of Fe_2O_3, small kinks at ~410–430cm^{-1} , 430–460 cm^{-1} , and 470–530 cm^{-1} start appearing within the broadband [16].The increase in concentration of Fe_2O_3 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 FeO_6 structural units, and FeO_4 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 Fe_2O_3 content indicates the formation of FeO_4 units at the expense of FeO_6 octahedral units. The dip of broad band between ~730–780 cm^{-1} centered at around 752 cm^{-1} increases with the increase in the concentration of Fe_2O_3 and may be attributed to the symmetric stretching vibration of Si–O–Si bonds of SiO_4 tetrahedra [18]. The band at around 860–1120 cm^{-1} is allocated to Si – O – Si asymmetric SiO_4 tetrahedra vibrations controlled by Si – O – Si bridging ties in polymerized network. This band's width gradually continues to decrease with Fe_2O_3 concentration increase[19]. Since the SiO_2 concentration is kept constant in all compositions, the silicate network symmetry is continuing to increase with the concentration of Fe_2O_3. This changes in symmetry suggest an increase in network intensity and hence an increase in the temperature for the glass transition.

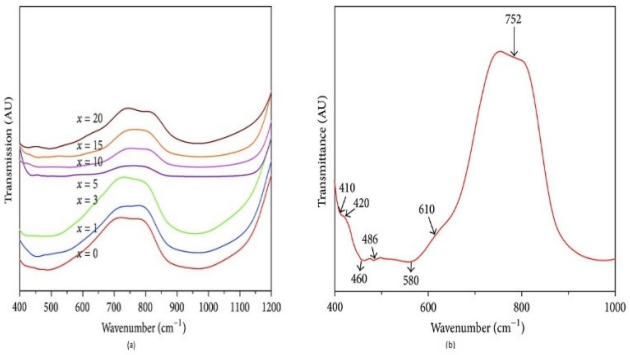

Fig 2(a) *FTIR spectra* for different glass compositions in spectral range 400–1200$\boldsymbol{cm^{-1}}$ of the glass system $\boldsymbol{60SiO_2.(100-x)Bi_2O_3.xFe_2O_3}$. (b) *Amplified IR spectra* excluding region of maximum transparency for glass sample with $\boldsymbol{x = 15}$.[24]

C. Optical transmittance

The optical transmission spectra of the glass samples $60SiO_2$.(100-x)$Bi_2O_3.xFe_2O_3$ with different values of x are shown in Figure 3. With the rise in iron content, the absorption edge is observed towards longer wavelength side.As the concentration of Fe_2O_3 increases beyond 5 mol% (i.e.,$x = 10, 15$, and 20 mol%) the color of the glass samples becomes opaque (blackish in color), and transmittance becomes nearly zero.

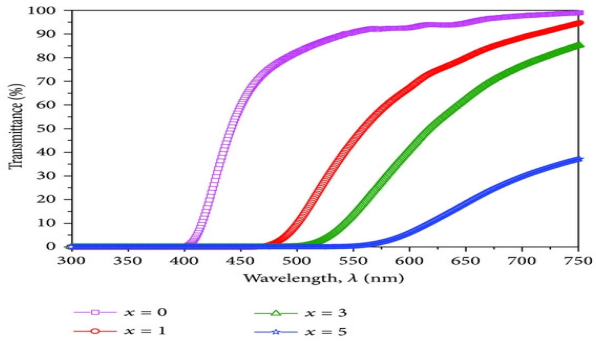

Fig 3*Optical transmission* spectra of different compositions of synthesized glass samples of $\boldsymbol{60SiO_2.(100-x)Bi_2O_3.xFe_2O_3}$ system.[24]

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

$$\alpha h\upsilon = A\left(h\upsilon - E_{op}\right)^{m},$$

Where α is the absorption coefficient, hυ 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 , 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 axis at $(\alpha h\upsilon)^2$ and are presented in Table 1.

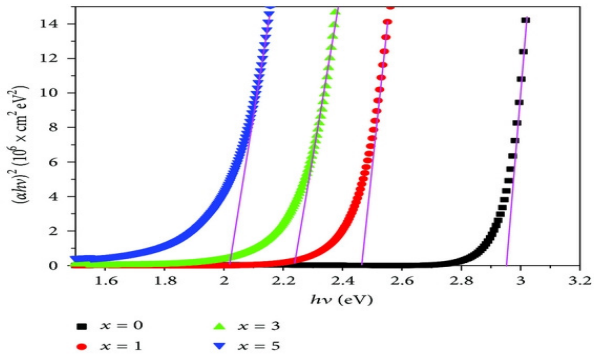

Fig 4*Tauc's plot* for different glasses samples of $60SiO_2.(100-x)Bi_2O_3.xFe_2O_3$ system for $m = 1/2$.[24]

From the optical energy band gap the refractive index values for various compositions were calculated using the relationship proposed by Dimitrov and Sakka[21]

$$\frac{n^2-1}{n^2+1} = 1 - \frac{\sqrt{E_{op}}}{20}.$$

The decrease in the optical band gap may be due to the increase in non-bridging oxygen (NBO) atom concentration with the increase in Fe_2O_3 [22].Likewise, the increase in the refractive index with the increase in iron content due to the presence of non-bridging oxygen that affects the refractive index because the non-bridging oxygen polarity is higher than that of the oxygen bridging [23].The difference in the energy gap of optical bands and the refractive index as a function of Fe_2O_3 is shown in Figure 5.

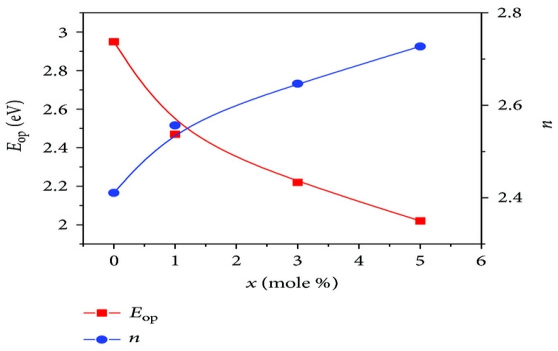

Fig 5 The variation of E_{op} and n with different compositions of Fe_2O_3 (x).[24]

IV. CONCLUSIONS

Glasses with $60SiO_2$.(100-x)Bi_2O_3.xFe_2O_3 ;x=0, 1, 3, 5, 10, 15, and 20 formulations were successfully prepared using traditional rapid melt-quenching techniques.The X-ray diffractograms support the glassy existence. Values of physical properties such as density and molar volume decrease as iron content increases, whereas glass transition temperature shows a reverse trend.The FTIR analysis shows that SiO_2 occurs in the SiO_4 tetrahedral structural units in these glass compositions, and the symmetry of the silicate network continues to increase with the rise in Fe_2O_3 concentration. Bismuth plays the role of multiplier of the network and occurs in octahedral units BiO_6. In FeO_6 octahedral structural units and FeO_4 tetrahedral units, respectively, iron plays the role of network modificator as well as glass former and exits. With the rise in iron concentration, the band gap energy decreases, and the refractive index increases with the increase in Fe_2O_3 content. The symmetry of the silicate network continues to increase with the content of Fe_2O_3 in all glass samples and thus modifies the physical and structural properties of those glasses.

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