Enhanced Bismuth Silicate Glasses
Physical, Structural, and Optical Properties

Md. Khademul Basher
Department of Physics, University of Rajshahi, Bangladesh
Email: basher4366@gmail.com

Abstract:
Iron-containing \(60\text{SiO}_2\cdot(100-x)\text{Bi}_2\text{O}_3\cdot x\text{Fe}_2\text{O}_3\) 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 \(\text{Fe}_2\text{O}_3\) contents. The IR spectra of these glasses consists mainly of structural units \([\text{BiO}_3]\), \([\text{BiO}_6]\), and \([\text{SiO}_4]\). Using UV-VIS spectroscopy, we test the optical properties. With the increase in \(\text{Fe}_2\text{O}_3\) material, the optical bandgap energy \((E_{\text{op}})\) is observed to decrease, whereas the reverse trend is observed for refractive index.

Keywords—\(60\text{SiO}_2\cdot (100-x)\text{Bi}_2\text{O}_3\cdot x\text{Fe}_2\text{O}_3\), optical dispersion, FTIR Spectroscopy, Dimitrov and Sakka, optical band gap energy.

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]. \(\text{Bi}_2\text{O}_3\) 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]. \(\text{Bi}_2\text{O}_3\) is not a classical glass former because of its high polarizability and small field strengths of \(B\)\(^{3+}\) ions, although it may form a glass network of \([\text{BiO}_3]\) and \([\text{BiO}_6]\) pyramids[1, 5] in the presence of other oxides such as \(\text{B}_2\text{O}_3\), \(\text{PbO}\), \(\text{SiO}_2\), and \(\text{V}_2\text{O}_5\). 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 \(\text{Fe}_2\text{O}_3\) are used[8]. The presence of transition metal oxides (besides \(\text{Bi}_2\text{O}_3\)) 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 \(Fe^{2+}\) results in various modified structural units [9]. Adding \(\text{Fe}_2\text{O}_3\) to these glasses increases the chemical longevity and its stability. It is of interest to carry out a detailed study of the impact of \(\text{Fe}_2\text{O}_3\) 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 60SiO₂ .(100-x)Bi₂O₃,xFe₂O₃(x=0, 1, 3, 5, 10, 15, and 20) were prepared using analar grade chemicals Fe₂O₃, Bi₂O₃, and SiO₃. 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 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 (Tg) values of various glass samples. SDT Q600. The experiments were conducted in a nitrogen atmosphere at a heating 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 Fe₂O₃ can act as an oxide-modifying intermediate and glass, and can be present in both the state Fe²⁺ and Fe³⁺ in the glass network[10]. This result indicates that the addition of Fe₂O₃ contributes to the Bi₂O₃ glass matrix rising and densifying. The increase of Tg with iron content shows the glass network becoming more stable. The growing trend in iron content increases suggests that when Fe₂O₃ is substituted with Bi₂O₃, 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 Tg cannot be expected with an increase in the content of Fe₂O₃ 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 (Vₘ) of samples was calculated using the following relation[13]

\[ V_m = \frac{\sum x_i M_i}{d} \]

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 (Vₘ) 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 Fe₂O₃ [14]. This type of behavior is explained simply by replacing the heavier Bi₂O₃ with the lighter Fe₂O₃, which suggests that Fe₂O₃ plays the role of the...
B. FTIR spectroscopy

The FTIR spectra of glass compositions $60SiO_2$ $\cdot$ $(100-x)Bi_2O_3$ $\cdot$ $xFe_2O_3$ 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 spectrum 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$_3$ structural units [15]. On increasing the concentration of Fe$_2$O$_3$, small kinks at $\sim 410-430$ cm$^{-1}$, $430-460$ cm$^{-1}$, and $470-530$ cm$^{-1}$ start appearing within the broadband [16]. The increase in concentration of Fe$_2$O$_3$ some bands at $\sim 550-660$ cm$^{-1}$ in compositions with $x > 5$ mol% appears and is attributed due to the vibrations of Fe–O bonds of FeO$_4$ 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$_2$O$_3$ content indicates the formation of FeO$_4$ units at the expense of FeO$_6$ octahedral units. The dip of broad band between $\sim 730-780$ cm$^{-1}$ centered at around $752$ cm$^{-1}$ increases with the increase in the concentration of Fe$_2$O$_3$ 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$_2$O$_3$ 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$_2$O$_3$. This changes in symmetry suggest an increase in network intensity and hence an increase in the temperature for the glass transition.

C. Optical transmittance

The optical transmission spectra of the glass samples $60SiO_2$ $\cdot$ $(100-x)Bi_2O_3$ $\cdot$ $xFe_2O_3$ 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$_2$O$_3$ 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.

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

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

Where $\alpha$ 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 (\( E_{\text{opt}} \)) are determined from the linear region of the curve after extrapolating to meet the axis at \((\alpha h\nu)^2\) and are presented in Table 1.

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

\[
\frac{n^2 - 1}{n^2 + 1} = 1 - \frac{\sqrt{E_{\text{opt}}}}{20}.
\]

The decrease in the optical band gap may be due to the increase in non-bridging oxygen (NBO) atom concentration with the increase in \( \text{Fe}_2\text{O}_3 \) [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 \( \text{Fe}_2\text{O}_3 \) is shown in Figure 5.

**Fig 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 \( m = 1/2 \).[24]

**Fig 5** The variation of \( E_{\text{opt}} \) and \( n \) with different compositions of \( \text{Fe}_2\text{O}_3 \) \( (x) \).[24]

**IV. CONCLUSIONS**

Glasses with \( 60\text{SiO}_2 \cdot (100-x)\text{Bi}_2\text{O}_3 \cdot x\text{Fe}_2\text{O}_3 \) :\( x=0, 1, 3, 5, 10, 15, \) and 20 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 \( \text{SiO}_2 \) occurs in the \( \text{SiO}_4 \) tetrahedral structural units in these glass compositions, and the symmetry of the silicate network continues to increase with the rise in \( \text{Fe}_2\text{O}_3 \) concentration. Bismuth plays the role of multiplier of the network and occurs in octahedral units \( \text{BiO}_6 \). In \( \text{FeO}_6 \) octahedral structural units and \( \text{FeO}_4 \) tetrahedral units, respectively, iron plays the role of network modifier 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 \( \text{Fe}_2\text{O}_3 \) content. The symmetry of the silicate network continues to increase with the content of \( \text{Fe}_2\text{O}_3 \) in all glass samples and thus modifies the physical and structural properties of those glasses.

**ACKNOWLEDGMENT**

I am thankful to my parents for supporting me a lot. I also thankful to my friends Musabbir who support me a lot with share his knowledge about research with
me and suggest me in many ways to doing this research

REFERENCES


