SPECTROSCOPIC & MAGNETIC PROPERTIES OF PbO-Bi₂O₃-B₂O₃ GLASSES DOPED WITH FeO

Mohammad Ehasanulla, K. Srikanth, A. Veerabhadra Rao and K. A. Emmanuel*
Department of Chemistry, Sir C R Reddy (A) College, Eluru, A.P., India.
*E-mail: emmikola@gmail.com

ABSTRACT
PbO-Bi₂O₃-B₂O₃ glasses containing different concentrations of FeO have been prepared. The glasses are characterized by XRD and differential thermal analysis. The results of these studies have been analyzed in the light of different oxidation states of iron with the aid of the data on IR, ESR, optical absorption and magnetic susceptibility measurements. The analysis shows that iron ions exist mainly in Fe³⁺ state, occupy tetrahedral positions if FeO is present in smaller concentrations. However, if FeO is present in higher concentrations in the glass matrix, (i) the intensity and the half width of the ESR signal has been observed to decrease and (ii) the value of magnetic moment (evaluated from magnetic susceptibility) has been observed to drop to a value of 4.60 µΒ from 5.82 µΒ. From these results it has been concluded that in this concentration range, iron ions exist mainly in divalent state.

Keywords: A. Glasses; Optical absorption, ESR and IR spectra.

INTRODUCTION
Heavy metal oxide-based glasses such as Bi₂O₃ have been quite extensively investigated due to their manifold applications in optical and optoelectronic devices such as ultrafast switches, infrared windows and optical isolators1-3. The physical properties of the Bi₂O₃–B₂O₃ glass system have attracted a great deal of research interest owing to their possible use as waveguides in the infrared region4. These glasses exhibit high optical transmission into the far-infrared region (in the range 0.5–8.7 mm), possess a high refractive index and exhibit non-linear optical behaviour. Recently, optical Kerr shutter switching and degenerated four wave mixing experiments have been performed on bismuth borate glasses using femtosecond lasers1–3. The nonconventional glass forming oxide Bi₂O₃, participates in the glass structure with two possible coordinations [BiO₃] pyramidal and [BiO₆] octahedral units2, 3, 5, 6.

Further, bismuth ion was found to be an efficient luminescent activator with applications in lasers as a sensitizer for some rare earth ions7, 8. Kityk et al.9–12 have carried out extensive work on Bi₂O₃-based glasses along these lines in recent years. The modifier oxide, PbO, when added to bismuth borate glasses, the glasses are expected to become highly stable against devitrification and chemically inert13, since PbO, in contrast with the conventional alkali/alkaline earth oxide/halide modifiers, form the stable glasses due to its dual role—one as modifier (with PbO₆ structural units) and the other as glass network former in both covalent and ionic bondings with PbO₄⁴⁷ pyramidal units connected in puckered layers13, 14. There has been an increasing demand for the development of materials suitable for ultra broadband optical amplifiers to revolutionize telecommunication systems. Although rare earth ion-doped glasses were considered as suitable candidates for such applications, the optical amplification bandwidth in these materials is narrowed, due to the fact that the emission bands of the 4f–4f transition of the rare earth ions are very narrow.

The addition of ferrous oxide to lead bismuth borate glasses increases the chemical durability and corrosion resistance in aqueous environments11. These ions exist in different valence states with different coordinations in glass matrices; for example, as Fe³⁺ in both tetrahedral and octahedral environments, and as Fe²⁺ in the octahedral environment12. The content of iron in different environments and in different
valence states in the glass depends on the properties of the modifiers and glass formers, such as the size of the ions in the glass structure, their field strength, the mobility of the modifier cation, etc. Hence, the connection between the state and the position of the iron ion and the physical properties of lead bismuth borate glass is expected to be very interesting. Both Fe\(^{3+}\) and Fe\(^{2+}\) ions are well-known paramagnetic ions. Fe\(^{2+}\) ion exhibits a large magnetic anisotropy owing to the strong spin–orbit interaction of the 3d orbital, whereas the magnetic anisotropy energy of Fe\(^{3+}\) ions is small because its orbital angular momentum is zero. Recent studies on valence states and the influence of iron ions on the physical properties of a number of glasses are available in the literature\(^{13}\). Day and co-workers\(^{14, 15}\) have carried out extensive investigations, including Mössbauer spectra and dc conductivity studies, on a variety of glasses containing iron ions. The majority of studies on Bi\(_2\)O\(_3\)-based glasses are related to understanding their structure via spectroscopic, DTA and other physical measurements.

The present study is aimed at understanding the structural role of iron ions in the PbO–Bi\(_2\)O\(_3\)–B\(_2\)O\(_3\) glass system via dielectric measurements over a moderately wide range of frequency and temperature coupled with spectroscopic studies (ESR, infrared and optical absorption) and magnetic susceptibility studies.

**EXPERIMENTAL**

Within the glass forming region of PbO-Bi\(_2\)O\(_3\)-B\(_2\)O\(_3\) glass system, the following compositions with successive increase in the concentration of FeO are chosen for the present study:

- \(F_0\): 40PbO-10Bi\(_2\)O\(_3\)-50B\(_2\)O\(_3\)
- \(F_1\): 40PbO-10Bi\(_2\)O\(_3\)-49.9B\(_2\)O\(_3\): 0.1 FeO
- \(F_2\): 40PbO-10Bi\(_2\)O\(_3\)-49.8B\(_2\)O\(_3\): 0.2 FeO
- \(F_3\): 40PbO-10Bi\(_2\)O\(_3\)-49.7B\(_2\)O\(_3\): 0.3 FeO
- \(F_4\): 40PbO-10Bi\(_2\)O\(_3\)-49.6B\(_2\)O\(_3\): 0.4 FeO
- \(F_5\): 40PbO-10Bi\(_2\)O\(_3\)-49.5B\(_2\)O\(_3\): 0.5 FeO

Appropriate amounts (all in mol %) of reagent grades of Bi\(_2\)O\(_3\), PbO, H\(_3\)BO\(_3\) and FeO powders were thoroughly mixed in an agate mortar and melted in a platinum crucible in the temperature range 950-1000 °C in a PID temperature controlled furnace for about 1 h until a bubble free transparent liquid was formed. The resultant melt was then poured in a brass mould and subsequently annealed at 300 °C. The amorphous state of the glasses was confirmed by X-ray diffraction and scanning electron microscopy studies.

The differential thermal analysis on these samples was carried out using STA 409C, Model DTA-TG with a programmed heating rate of 10 °C / min in the temperature range of 30-1000 °C. The samples were then ground and optically polished. The final dimensions of the samples used for dielectric and optical studies were about 1 cm x 1 cm x 0.2 cm. The density \(d\) of these glasses was determined to an accuracy of 0.001 by standard principle of Archimedes' using o-xylene (99.99% pure) as the buoyant liquid.

The IR spectra of the glasses were recorded by KBr pellet method. Glass powders (2 mg) were mixed with anhydrous potassium bromide powder (150 mg) and pressed into pellets at 2000 kg cm\(^{-2}\). The spectra were recorded using a FT-IR Digital Excalibur 3000 Spectrophotometer with a resolution of 0.1 cm\(^{-1}\) in the range 400-2000 cm\(^{-1}\). The optical absorption spectra of these glasses were recorded at room temperature in the wavelength range 350-900 nm up to a resolution of 0.1 nm using Shimadzu UV-VIS-NIR Spectrophotometer Model 3101.

The ESR spectra of the fine powders of the samples were recorded at room temperature on JES-FA 200 (\(v = 9.21\) GHz) ESR spectrometer with 100 KHz field modulation. The magnetic susceptibility measurements were made at room temperature by Guoy’s method using fine powders of these glasses.

**RESULTS AND DISCUSSION**

Our visual examination, the absence of peaks in the X-ray diffraction pattern shown in Fig. 1, the SEM photographs of all samples shown in Fig. 2, the existence of glass transition temperature \(T_g\) and
crystalline temperature \( T_c \) in the DTA traces, indicate that the samples prepared were of amorphous in nature.

From the measured values of density \( d \) and calculated average molecular weight \( M \), various physical parameters such as iron ion concentration \( \text{Fe} \) and mean ion separation \( r_i \) of these glasses are evaluated using the conventional formulae and are presented in Table 1.

Fig. 3 shows typical traces of differential thermal analysis of all the glasses under study. The curves exhibit an endothermic effect due to glass transition temperature \( T_g \); the value of \( T_g \) is evaluated from the point of inflection of this change. At still higher temperatures, an exothermic peak \( T_c \) due to the crystal growth followed by an endothermic effect due to the melting effect denoted by \( T_m \) are also observed. The values of \( T_g, T_c \) and \( T_m \) obtained for all the glasses are furnished in Table 2. The appearance of single peak due to the glass transition temperature in DTA pattern of all the glasses indicates the good homogeneity of the glasses prepared. For \( \text{FeO} \) doped glasses, the quantity \( (T_c-T_g) \), which is proportional to glass forming ability, is found to decrease where as the quantity \( (T_m-T_g) \) which is inversely proportional to glass forming ability is found to increase (Table 2) with increase in the content of \( \text{FeO} \). From the measured values of \( T_g, T_c \) and \( T_m \), the parameters \( T_g/T_m \), \( (T_c-T_g)/T_g \), \( (T_c-T_g)/T_m \) and glass forming ability parameter known as Hruby’s parameter \( (T_c-T_g)/(T_m-T_g) \) are evaluated and presented in Table 2. The variation of the parameter \( (T_c-T_g)/(T_m-T_g) \) with the concentration of \( \text{FeO} \) shows the maximum value for glass \( F_1 \) (Table 2) indicating its highest glass forming ability among all the glasses under investigation.

The infrared transmission spectra of pure \( \text{PbO-Bi}_2\text{O}_3 \) glasses have exhibited two main groups of bands: (i) in the region 1300-1400 cm\(^{-1} \), (ii) in the region 1100-1200 cm\(^{-1} \) and another band at about 712 cm\(^{-1} \) (Fig.4); these bands are identified due to the stretching relaxation of B-O bond of the trigonal \( \text{BO}_3 \) units, vibrations of \( \text{BO}_4 \) structural units and due to the bending vibrations of B-O-B linkages respectively. A band due to \( \text{PbO}_4 \) structural units is also observed in the spectra of all the glasses at about 520 cm\(^{-1} \). A band due to \( \text{PbO}_4 \) structural units was also observed in the spectra of all the glasses at about 485 cm\(^{-1} \). In the same region, a band due to symmetrical bending vibrations of \( \text{BiO}_4 \) units have also been reported. In view of this, we may also expect the presence of \( \text{Bi}–\text{O}–\text{Pb} \) linkages in the glass network.

With the introduction of \( \text{FeO} \) (0.1 mol \%) into the glass network, the intensity of second group of bands (bands due to \( \text{BO}_4 \) units) is observed to increase with a shifting of meta-center towards slightly lower wavenumber, where as, the intensity of the first group of bands (bands due to the \( \text{BO}_3 \) structural units) is observed to decrease. For further increase of \( \text{FeO} \), the intensity of the first group of bands is observed to increase at the expense of second group of bands (inset of Fig. 4).

The optical absorption spectra of \( \text{PbO-Bi}_2\text{O}_3 \) glasses recorded in the wavelength region 350-1100 nm are shown in Fig. 5. The absorption edge observed at 406 nm for the glass \( F_0 \) is observed to shift to 393 nm with the introduction of \( \text{FeO} \) (0.1 mol \%). For further increase in the concentration of \( \text{FeO} \), the edge is observed to shift gradually towards higher wavelength. The spectra of the glasses have exhibited absorption bands at 785, 581 and 539 nm due to \( \text{Fe}^{3+} \) ion transitions and another band at 955 nm due to \( \text{Fe}^{2+} \) ions. With increase in the concentration of \( \text{FeO} \) beyond 0.2 mol \%, the bands due to \( \text{Fe}^{3+} \) ions have been observed to fade away slowly where as the intensity of the band due to \( \text{Fe}^{2+} \) ions is observed to increase gradually.

From the observed absorption edges, we have evaluated the optical band gaps \( (E_o) \) of these glasses by drawing Urbach plot between \( (\alpha \ h \ \omega)^{1/2} \) and \( h \ \omega \) as per the eqn.:

\[
(\alpha (\omega) h \ \omega = C (h \ \omega - E_o)^2.
\]

Fig. 6 represents the Urbach plots of all these glasses in which a considerable part of each curve is observed to be linear. The values of optical band gap \( (E_o) \) obtained from the extrapolation of the linear portions of these plots are presented in Table 3. The value of \( E_o \) is found to decrease with the increase in concentration of \( \text{FeO} \) from 0.1 mol \%.

The ESR spectra of \( \text{PbO-Bi}_2\text{O}_3 \) glasses recorded at room temperature are shown in Fig. 7. The intense line centered at about \( g = 2.0 \) could clearly be seen in the spectra of these glasses. The intensity of this signal is however observed to decrease gradually with increase in the concentration of
FeO in the glass matrix. Additionally a weak signal at g=4.3 could also be detected in the spectra of glasses F1 and F2.

Magnetic susceptibility of PbO-Bi₂O₃-B₂O₃: FeO glasses measured at room temperature is observed to decrease with increase in FeO content in the glass composition (Table 4). From the values of magnetic susceptibilities, the effective magnetic moments (μ\(_{\text{eff}}\)) are evaluated and presented in Table 4. The value of μ\(_{\text{eff}}\) is found to decrease gradually from a value of 5.82 (for glass F1) to a value of 4.6 μ\(_B\) for the glass containing 0.5 mol % of FeO.

It is well known fact that the effect of introduction of modifiers like PbO, Bi₂O₃ into B₂O₃ network is to convert the sp\(^2\) planar BO\(_3\) into more stable sp\(^3\) tetrahedral BO\(_4\) units in addition to non-bridging oxygens (NBO’s). Each BO\(_4\) unit is linked to two such other units and one oxygen from each unit with a metal ion giving rise to a structure that leads to the formation of long chain tetrahedrons. The presence of such BO\(_4\) units in the present glass system is evident from infrared spectral studies.

PbO in general is a glass modifier and enters the glass network by breaking up the B-O-B bonds (normally the oxygens of PbO break the local symmetry while Pb\(^{2+}\) ions occupy interstitial positions) and introduces coordinate defects known as dangling bonds along with non-bridging oxygen ions. Bi₂O₃ is an incipient glass network former and as such does not readily form glass, but does so in the presence of modifiers like PbO with triangular BiO\(_3\) pyramids. The coordination of bismuth in the glass network can be viewed as tetrahedrons with the oxygen at three corners and 6s\(^1\) stereo chemically active electronic lone pair at the fourth corner. However, Bi₂O₃ also takes part octahedral positions in the glass network with BiO\(_6\) structural units. The addition of FeO to the bismuth borate glass network is accompanied by a change in the boron coordination from three to four or vice versa depending upon its concentration and also on other ingredients of the glass matrix. A schematic illustration of bismuth borate network containing Fe\(^{2+}\) in octahedral and tetrahedral positions is shown in Fig. 8.

To form octahedral units, Pb should be sp\(^3\)d\(^2\) hybridized (6s, 6p and 6d orbitals)\(^{13}\). However, PbO may also participate in the glass network with PbO\(_4\) structural units when lead ion is linked to four oxygens in a covalency bond configuration. In such a case the network structure is considered to build up from PbO\(_4\) and BO\(_4\) pyramidal units, which are linked together by B-O-Pb bonds. Iron ions are expected to exist mainly in Fe\(^{3+}\) state in the present PbO-Bi₂O₃-B₂O₃ glass network. However, regardless of the oxidation state of the iron in the starting glass batch, the final glass contains both Fe\(^{2+}\) and Fe\(^{3+}\) ions\(^{19, 20}\). The speciation of iron in these glasses is controlled by the following reversible reaction:

\[
4\text{Fe}^{2+}{\text{melt}} + \text{O}_2{\text{melt atm.}} \xrightleftharpoons{} 4\text{Fe}^{3+}{\text{melt}} + 2\text{O}^{2-}{\text{melt}}
\]

The optical absorption spectra of PbO-Bi₂O₃-B₂O₃: FeO glasses recorded in the wavelength region 350-1100 nm have exhibited three absorption bands at 785, 581 and 539 nm. Using Tanabe-Sugano- diagrams for d\(^1\) ion, the spectra have been analyzed and the bands are assigned to \(6A_1 (t_{2g}^3e_g^2) \rightarrow a^6T_1(t_{2g}^4e_g^2)\), \(6A_1 (t_{2g}^3e_g^2) \rightarrow a^4T_2(t_{2g}^4e_g^2)\) and \(6A_1 (e^2t_{2g}^3) \rightarrow a^4T_1(e^3t_{2g}^2)\) (spin forbidden) transitions of Fe\(^{3+}\) ions respectively\(^{21}\) with LF parameters D\(_q\) (crystal field splitting energy) = 1250 cm\(^{-1}\) and Racah interelectronic repulsion parameters B = 845 cm\(^{-1}\). Theses values are consistent with those reported for other glass systems like phosphate, alkali borate etc.,\(^{22, 23}\)

More precisely, based on selection rules and ligand field calculations, the first two bands are identified due to FeO\(_6\) group and the third band is due to FeO\(_4\) group\(^ {24}\). Both of these Fe\(^{3+}\) sites can be considered as subjected to interaction between its external orbitals and the p-orbitals of the neighbouring oxygens\(^ {25}\).

With increase in the concentration of FeO, these bands slowly fade away and a new absorption band at 955 nm (Fig. 4) is observed to grow at the expense of these bands. This band is identified due to \(5T_{2g} \rightarrow 5E_g\) transition of Fe\(^{2+}\) (d\(^3\)) ions\(^ {26}\). Further, these Fe\(^{2+}\) ions are expected to occupy only interstitial positions since the ratio of cation-oxygen radii is 0.63 for Fe\(^{3+}\) ion, which is far from the value of 0.19 to be possessed by an ion to occupy tetrahedral or substitutional sites\(^ {27}\).
ESR spectra of PbO-Bi$_2$O$_3$-B$_2$O$_3$: FeO glasses recorded at room temperature (Fig. 7) exhibited an intense spectral line centered at about $g = 2.0$. The intensity of this signal is observed to decrease with increase in the concentration of FeO. Additionally, a weak signal at about $g = 4.3$ (identified due to the isolated Fe$^{3+}$ ions in the orthorhombic crystal field) could be detected in the spectra of glasses F$_1$ and F$_2$. The $^6S_{5/2}$ ground state of Fe$^{3+}$ ($d^5$) free ion is expected to split into three Kramers doublets $\{\pm 5/2\}, \{\pm 3/2\}$ and $\{\pm 1/2\}$ with separation normally greater than the microwave quantum. The weak symmetric and isotropic line observed at $g = 4.3$ in the spectra of glasses F$_1$ and F$_2$ is due to the middle Kramers doublets containing an admixture of different $|m\rangle$ that are identified due to the low symmetry term $E(S_x^2 - S_y^2)$ in the Hamiltonian, where as the signal at $g = 2.0$ is attributed to Fe$^{3+}$-O-Fe$^{3+}$ spin pair. The diminishing intensity of the ESR signal with the increase in the concentration of FeO indicates a gradual decrease in the concentration of Fe$^{3+}$ ions in the glass network. The effective value of $g$ obtained from ESR spectra show a slight decrease (Table 4) with increase in the concentration of FeO in the glass matrix. Such an observation indicates a negligible contribution of orbital angular momentum to the magnetic moment of Fe$^{3+}$ ions.

The magnetic properties of these glasses arise from the paramagnetic Fe$^{3+}$ ($3d^5$) and Fe$^{2+}$ ($3d^6$) ions. The value of the effective magnetic moment (5.82 $\mu_B$) obtained for glass F$_1$ confirms the highest concentration of Fe$^{3+}$ ions in this glass. The decrease in the value of $\mu_{\text{eff}}$ from 5.82$\mu_B$ to a value of 4.60 $\mu_B$ (for glass F$_5$) indicates a gradual growing concentration of Fe$^{2+}$ ions that take modifying positions in the glass network. Such Fe$^{2+}$ ions may increase the degree of disorder in the glass network.

Recollecting the data on IR spectra, with the raise in the concentration of FeO, the intensity of the bands due to BO$_3$ structural units has been observed to increase at the expense of the bands due to BO$_4$ units. This observation suggests, a gradual increase in the concentration of divalent iron ions in the glass network that acts as modifiers; as modifiers, these ions create more disorder in the glass network. Normally, the oxygens of FeO break the local symmetry while Fe$^{2+}$ ions occupy the interstitial positions.

These conclusions are supported by (i) decrease in the glass transition temperature $T_g$ and related parameters with FeO concentration, (ii) decrease in the intensity of band in the IR spectra, due to BO$_4$ structural units, (iii) the shifting of absorption edge towards higher wavelength (or decrease in the value of optical band gap $E_o$) and (iv) a decrease in the value of effective magnetic moment from 5.82$\mu_B$ to 4.60 $\mu_B$ (a value corresponds to the magnitude expected for Fe$^{2+}$ ions).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Average molecular weight</th>
<th>Density</th>
<th>Ni (10$^{21}$)</th>
<th>Ri (10$^8$)</th>
<th>Rp (10$^8$)</th>
<th>Fi (10$^{15}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F$_0$</td>
<td>170.670</td>
<td>7.128</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>F$_1$</td>
<td>170.675</td>
<td>7.224</td>
<td>2.55</td>
<td>7.32</td>
<td>2.95</td>
<td>2.3</td>
</tr>
<tr>
<td>F$_2$</td>
<td>170.677</td>
<td>7.315</td>
<td>5.16</td>
<td>5.79</td>
<td>2.33</td>
<td>3.68</td>
</tr>
<tr>
<td>F$_3$</td>
<td>170.679</td>
<td>7.398</td>
<td>7.83</td>
<td>5.04</td>
<td>2.03</td>
<td>4.86</td>
</tr>
<tr>
<td>F$_4$</td>
<td>170.682</td>
<td>7.425</td>
<td>10.5</td>
<td>4.57</td>
<td>1.84</td>
<td>5.90</td>
</tr>
<tr>
<td>F$_5$</td>
<td>170.684</td>
<td>7.498</td>
<td>13.2</td>
<td>4.23</td>
<td>1.70</td>
<td>6.89</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Glass</th>
<th>$T_g$ (K)</th>
<th>$T_c$ (K)</th>
<th>$T_m$ (K)</th>
<th>$T_g/T_m$</th>
<th>$(T_c-T_g)/T_g$</th>
<th>$(T_c-T_g)/T_m$</th>
<th>$(T_c-T_g)/(T_m-T_g)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>F$_0$</td>
<td>417</td>
<td>568</td>
<td>880</td>
<td>0.474</td>
<td>0.362</td>
<td>0.172</td>
<td>0.484</td>
</tr>
</tbody>
</table>

Table-1: Summary of data on Physical Parameters of PbO-Bi$_2$O$_3$-B$_2$O$_3$: FeO glasses

Table-2: Summary of data on differential thermal analysis of PbO-Bi$_2$O$_3$-B$_2$O$_3$: FeO glasses
Table-3: Summary of data on optical absorption spectra of PbO-Bi₂O₃-B₂O₃: FeO glasses

<table>
<thead>
<tr>
<th>Glass</th>
<th>$F_0$</th>
<th>$F_1$</th>
<th>$F_2$</th>
<th>$F_3$</th>
<th>$F_4$</th>
<th>$F_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^6A_1(t^2_g e^2_g)\rightarrow a^3T_1(t^2_g e^2_g)$</td>
<td>---</td>
<td>539</td>
<td>539</td>
<td>539</td>
<td>539</td>
<td>539</td>
</tr>
<tr>
<td>$^6A_1(t'^2_g e^2_g)\rightarrow a^3T_2(t'^2_g e^2_g)$</td>
<td>---</td>
<td>---</td>
<td>5810</td>
<td>581</td>
<td>581</td>
<td>581</td>
</tr>
<tr>
<td>$^6A_1(t'^2_g e^2_g)\rightarrow a^3T_1(e^1 t^2_g)$</td>
<td>---</td>
<td>---</td>
<td>785</td>
<td>789</td>
<td>785</td>
<td>784</td>
</tr>
<tr>
<td>Cut-off wavelength (nm)</td>
<td>406</td>
<td>393</td>
<td>408</td>
<td>414</td>
<td>417</td>
<td>419</td>
</tr>
<tr>
<td>Optical band gap (eV)</td>
<td>1.93</td>
<td>2.06</td>
<td>1.85</td>
<td>1.73</td>
<td>1.65</td>
<td>1.60</td>
</tr>
</tbody>
</table>

Table-4: Data on magnetic properties of PbO-Bi₂O₃-B₂O₃: FeO glasses

<table>
<thead>
<tr>
<th>Glass</th>
<th>Conc. of FeO (mol %)</th>
<th>$g$</th>
<th>Susceptibility, $\chi$ ($10^{-5}$, emu)</th>
<th>$\mu$ ($\mu_B$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_1$</td>
<td>0.1</td>
<td>2.042</td>
<td>21.3</td>
<td>5.82</td>
</tr>
<tr>
<td>$F_2$</td>
<td>0.2</td>
<td>2.037</td>
<td>14.8</td>
<td>5.51</td>
</tr>
<tr>
<td>$F_3$</td>
<td>0.3</td>
<td>2.025</td>
<td>7.2</td>
<td>4.75</td>
</tr>
<tr>
<td>$F_4$</td>
<td>0.4</td>
<td>2.003</td>
<td>4.6</td>
<td>4.63</td>
</tr>
<tr>
<td>$F_5$</td>
<td>0.5</td>
<td>2.002</td>
<td>3.6</td>
<td>4.60</td>
</tr>
</tbody>
</table>

Fig.1. X-Ray diffraction pattern of PbO-Bi₂O₃-B₂O₃ glasses doped with different conc. of FeO
CONCLUSION

The summary of conclusions drawn from the study of various properties of PbO-Bi₂O₃-B₂O₃ glasses doped with FeO is as follows:

1. The optical absorption and ESR spectral studies indicate the presence of part of iron ions in Fe³⁺ state occupy tetrahedral positions, if FeO is present in lower concentrations; when the concentration of FeO is in higher quantities (> 0.1 %), these ions seems to exist in Fe²⁺ state.

2. The magnetic moment, evaluated from magnetic susceptibility measurements of the glasses, decreases from 5.82 to 4.60 µB with increasing concentration of FeO in the glass matrix. This result has been attributed to the gradual conversion of iron ions from Fe³⁺ state to Fe²⁺ state.

3. The IR spectral investigations indicate that with the increase in the concentration of FeO in the glass matrix, a gradual increase in the concentration of divalent iron ions that occupy octahedral positions and enhance disorderliness in the glass network.

Summarising, the properties with optical absorption, ESR, IR and magnetic susceptibilities of PbO-Bi₂O₃-B₂O₃: FeO glasses indicate that when the concentration of FeO in the glass network is low, iron ions seems to exist mainly in Fe³⁺ state and occupy network forming positions and strengthen the glass structure; if the concentration is increased gradually, these ions seems to exist mainly in Fe²⁺ state and occupy modifying positions and increase disorder in the glass network.

ACKNOWLEDGEMENTS

The authors are indebted their sincere thanks to the Correspondent Sri Jasti Raja Rama Mohana Rao and Principal Sri A B Lakshmi Narayana for their constant help and encouragement during the course of this work in the college. The authors are expressing their thanks to Dr. K. Balakrishna Rao, HOD, Dept of Physics for allowing the team to carry out research in their Materials Science Research Laboratory.
Fig. 3. Differential Thermal Analysis patterns of PbO-Bi$_2$O$_3$-B$_2$O$_3$: FeO glasses

Fig. 4. IR spectra of PbO-Bi$_2$O$_3$-B$_2$O$_3$:FeO glasses. Inset shows the variation of intensity of BO$_4$ and BO$_3$ units with concentration of FeO
Fig. 5. Optical absorption spectra of PbO-Bi$_2$O$_3$-B$_2$O$_3$: FeO glasses.

![Graph showing optical absorption spectra with annotations and labels.]

Fig. 6: A plot for evaluating the optical band gap of PbO-Bi$_2$O$_3$-B$_2$O$_3$: FeO glasses.

![Graph showing a plot with hv vs. (αhv)$^{1/2}$ where hv is the energy in eV and α is the absorbance.]

Optical density

Wavelength, (nm)

390 490 590 690 790 890 990 1090 1190
Fig. 7. ESR spectra of PbO-Bi$_2$O$_3$-B$_2$O$_3$: FeO glasses

Fig. 8: A Schematic illustration of PbO-Bi$_2$O$_3$-B$_2$O$_3$ containing Fe ions in Octahedral and Tetrahedral positions.

REFERENCES

Adopt GREEN CHEMISTRY
Save Our Planet.
We publish papers of Green Chemistry on priority.

If you think that you may be a potential reviewer in field of your interest, write us at rasayanjournal@gmail.com with your detailed resume and recent color photograph.