Spectroscopic and dielectric studies of BaO-Bi$_2$O$_3$-B$_2$O$_3$ glasses
doped with Fe$_2$O$_3$

5.1 Introduction

Iron ions have strong bearing on electrical, optical and magnetic properties of glasses. A large number of interesting studies are available on the environment of iron ion in various inorganic glass systems *viz.*., silicate, borate, phosphate, germinate, tellurite glasses [1-5]. Many of the recent studies on the glasses containing FeO and Fe$_2$O$_3$ indicate, that the iron ions exist in different valence states with different coordinations in glass matrices, for example, Fe$^{3+}$ occupy both tetrahedral and octahedral sites, whereas Fe$^{2+}$ occupy only octahedral positions [6-16]. The content of iron in diverse environments with different valence states that exist in the glass, depends on the quantitative properties of modifiers and glass formers, size of the ions in the glass structure, their field strength, mobility of the modifier cation etc., Hence, the correlation between the state and the position of the iron ion in the glass network and its physical properties are expected to be highly interesting. Both Fe$^{3+}$ and Fe$^{2+}$ ions are well known paramagnetic ions. Fe$^{2+}$ ion possesses a large magnetic anisotropy due to its strong spin-orbit interaction of the 3d orbital whereas such anisotropic energy of Fe$^{3+}$ ions is small as the orbital angular momentum of these ions is zero. Further, it is also quite likely, for iron ions to have link with borate groups that may strengthen the glass structure and raise the chemical resistance of the glass. BaO is a modifier oxide and enters the glass network by breaking up the random network. Normally the oxygens of these oxides break the local symmetry while the cations (Ba$^{2+}$ ions) take the
interstitial positions. Literature survey on Ba-B₂O₃ glasses shows that there are a considerable number of studies available on these glasses (including iron doped); however, majority of them are restricted to structural investigations by means of spectroscopic studies etc. Virtually, no devoted studies on spectroscopic (EPR, optical absorption and FTIR) and dielectric properties such as dielectric constant \( \varepsilon' \), loss (\( \tan \delta \)), a.c conductivity \( \sigma_{ac} \) of \( \text{Fe}_2\text{O}_3 \) containing \( \text{BaO}-\text{Bi}_2\text{O}_3-\text{B}_2\text{O}_3 \) glasses, are available. Such studies help in assessing the structural aspects of these glasses and may also throw some light on the insulating character and structural aspects of the glass system.

The compositions chosen for the present study are: 10BaO-(20-x) Bi₂O₃-70 B₂O₃: xFe₂O₃ x in the range 0 ≤ x ≤ 2.0 wt%.

The details are:
- F0: 10SrO-20Bi₂O₃-70B₂O₃
- F5: 10SrO-20Bi₂O₃-69.5B₂O₃: 0.5 Fe₂O₃
- F10: 10SrO-20Bi₂O₃-69.0B₂O₃: 1.0 Fe₂O₃
- F15: 10SrO-20Bi₂O₃-68.5B₂O₃: 1.5 Fe₂O₃
- F20: 10SrO-20Bi₂O₃-68.0B₂O₃: 2.0 Fe₂O₃

As shown in Fig 5.1 with initial 0.5 wt% doping of Fe₂O₃ green colored sample is obtained and the green color is turned to brown colored glasses while the iron free glass is pale yellow in color.

![Fig 5.1 Physical appearance of the glass samples of 1.0 mm thickness.](image-url)
5.2 Brief review of the previous work on the glasses containing iron ions

El-Samanoudy et al [17] have studied optical absorption and infrared spectra of Fe₂O₃ containing TeO₂-GeO₂ glasses; they showed that the fundamental absorption edge is a function of composition and the validity of the Urbach rule is investigated. Tanaka et al [18] have investigated the local structure around iron ions in the Bi₂O₃-Fe₂O₃ glasses by means of ESR studies. They have ascribed the ESR lines centered at \( g = 4.3 \) and \( g = 2.0 \) to isolated Fe³⁺ in the orthorhombic crystal field and Fe³⁺-O-Fe³⁺ spin pair respectively. The electrochemical behaviour of Fe²⁺/Fe³⁺ redox couple in sodium disilicate glasses has been studied by Maric et al [19]; from the results they have concluded that Fe³⁺ acts both as network former and network modifier while Fe²⁺ acts as network modifier. Sanad et al [20] have reported structural and magnetic properties of Fe₂O₃ containing CaO-P₂O₅ glasses. They have concluded that iron exists in both Fe²⁺ and Fe³⁺ states and the infrared measurements showed that the increase in the iron content of glass matrix caused a change in the coordination of iron from FeO₆ to FeO₄. Ardelean and Rusu [21] studied FT-IR and Raman spectra to get the information regarding the local structure of \( x\text{Fe}_2\text{O}_3.(100-x)\text{Bi}_2\text{O}_3 \) and \( x\text{Fe}_2\text{O}_3 \) \((100-x)[\text{Bi}_2\text{O}_3-\text{MO}] \) glass systems with MO=CdO, As₂O₃ and GeO₂ and interestingly pointed out the role of every component in the formation of the glass structure.

Dance et al [22] have investigated ESR of Fe³⁺ ions in fluoro aluminate glasses and attributed the single line centered at \( g = 4.3 \) in the ESR spectrum to the presence of Fe³⁺ ions in sites of fully rhombic symmetry. Baiocchi et al [23] have studied the optical and magnetic properties of iron ions in lead silicate glasses; they have assigned
the bands observed in the optical absorption spectrum to the corresponding transitions by taking into account the selection rules and on the basis of ligand field energy calculations. They have also concluded that the four-fold coordination of Fe$^{3+}$ ions is more common than the six fold in silicate glasses. Stefan and Simon [24] have reported EPR of Fe$^{3+}$ ions doped in bismuth borate glasses and their studies indicate various sites for Fe$^{3+}$ ions in environments characterized by different crystalline field intensities. Hazra and Ghosh [25] have studied structural and physical properties of Fe$_2$O$_3$ doped lead vanadate glasses; they have concluded that there is a strong role of iron both in the glass network and in the conduction mechanism of the glasses.

### 5.3 Results and discussion:

#### 5.3.1 X- Ray diffraction and SEM:

Fig 5.2 shows X-ray diffraction pattern of pure and 0.5 wt% Fe$_2$O$_3$ doped glass samples.

*Fig 5.2 XRD patterns of (a) BaBiBO$_4$ and (b) 0.5 wt% Fe$_2$O$_3$ doped BaBiBO$_4$ glasses*
The absence of sharp Bragg peaks in the XRD pattern confirmed the amorphous character of the present glasses since glassy or amorphous materials do not have long-range order, a diffraction pattern containing sharp peaks is not expected as in crystalline materials. Figure 5.3 shows SEM micrograms of Fe$_2$O$_3$ doped glasses in which it is found that the existence of some clusters in the glass matrix. From the literature there is some evidence that formation of colloids of Pb, As, Sb, and Bi metal atoms is quite easy even in glass which are not phase separated [26].

Fig 5.3 (a), (b), (c) and (d) shows the SEM images of F5, F10, F15 and F20 samples respectively
In the present investigation such clusters are due to agglomeration of bismuth metal atoms (Bi\(^0\)). A considerable number of such colloidal species of Bi\(^0\) caused green coloration of F5 glass samples and lack of such agglomeration reasoned the brown coloration at higher concentration of iron. Formation of colloidal clusters at 0.5wt% of Fe\(_2\)O\(_3\) is explained as follows:

Colloids are usually formed by producing the glass with the metal in ionic form and subsequently reducing the ions to form atoms. These atoms diffuse though the glass until they encounter other such atoms. The atoms then agglomerate to form nuclei, which grow to form the final colloids. In the present investigation it is found that such colloids occur only at 0.5 wt% of Fe\(_2\)O\(_3\) and metal atoms at higher concentration of dopant. Besides such tiny clusters or colloids are absent in iron free sample. As H\(_3\)BO\(_3\) was taken as an initial component of the raw materials, it is not possible to eliminate the trace amounts of ‘OH’ ions in the glass matrix. Such ‘OH’ ions react with the active centers of ferric ions in the glass matrix and reduce to ferrous state as follows.

\[ 2Fe^{3+} + 2(OH)^- \rightarrow 2Fe^{2+} + O_2 \uparrow + H_2 \uparrow \]  

----- (5.1)

The above Fe\(^{2+}\) acts as a redox partner of Bi\(^{3+}\) and reduce it to Bi\(^0\). This leads to a green color of sample F5. Reduction, therefore, can result from a redox reaction of Bi\(^{3+}\) ions with ferrous ions exists in the glass matrix as follows.

\[ Bi^{3+} + 3Fe^{2+} \rightarrow Bi^0 + 3Fe^{3+} \]  

----- (5.2)
5.3.2 Physical Parameters:

In the light of physico-chemical properties such as density, molar volume, refractive index, boron-boron separation, molar refraction, electronic refraction some relations could be estimated which describe the concentration of structural units as a function of modifier oxide concentration. The measured density value of F0 glass is found to be 4.5331 g/cm$^3$ and is decreased with initial 0.5 wt% doping of Fe$_2$O$_3$ and then increased to 4.6713 g/cm$^3$ (for F15 glass). However, at 2.0 wt% of Fe$_2$O$_3$ the density is slightly decreased to 4.6238 g/cm$^3$. A similar trend in refractive index and reverse trend in molar volume is observed as given in Table 5.1. The decrease in density at initial (0.5 wt%) and at higher (2.0 wt%) concentrations of Fe$_2$O$_3$ is attributed to one of the following (i) formation of octahedral Fe$^{3+}$ [0.645 Å] than tetrahedral Fe$^{3+}$ [0.49 Å] (ii) formation of electron and/or hole centers in the glass network [27]. The observed increase in density by the replacement of B$^{3+}$ by Fe$^{3+}$ can be expected due to replacement of a lighter cation by heavier one since the density of a glass is very sensitive to the ionic size and atomic weight [26]. From the Table 5.1 it is clear that as Fe$_2$O$_3$ increases from 0.5 to 2.0 wt% in the investigated glass samples an increase in the glass density is seen followed by a decrease in the molar volume values which suggest that the glass network become more compact when compared to F20 and F5 glasses. Using density and molar volume values some important physical parameters like Fe$^{3+}$ ion concentration Ni, mean Fe$^{3+}$ ion separation R$_i$, polaron radius R$_p$ are calculated and are given in Table 5.1. Besides this the average boron-boron
Table 5.1 The density $\rho$, molar volume $V_m$, refractive index $\mu$, Fe$^{3+}$ ion concentration $N_i$, mean Fe$^{3+}$ ion separation $R_i$ Polaron radius $R_p$ and average boron-boron seperation, molar refraction $R_m$ and molar electronic polarizability $\alpha_m$ of the glasses 10BaO.20Bi$_2$O$_3$.($70-x$)B$_2$O$_3$.x Fe$_2$O$_3$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\rho$ (g/cm$^3$)</th>
<th>$V_m$ (cm$^3$/mole)</th>
<th>$\mu$ (±0.0001)</th>
<th>$N_i \times 10^{21}$ (ions/cm$^3$) (±0.001)</th>
<th>$R_i$ (Å) (±0.001)</th>
<th>$R_p$ (Å) (±0.001)</th>
<th>$\langle d_{B-B} \rangle$ (nm) (±0.0001)</th>
<th>$R_m$ (Cm$^3$ mol$^{-1}$)</th>
<th>$\alpha_m$ (Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_0$</td>
<td>4.5331</td>
<td>30.560</td>
<td>1.7830</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>0.4578</td>
<td>18.088</td>
<td>7.178</td>
</tr>
<tr>
<td>$F_5$</td>
<td>4.4097</td>
<td>35.764</td>
<td>1.7725</td>
<td>8.42</td>
<td>4.92</td>
<td>1.98</td>
<td>0.4600</td>
<td>18.493</td>
<td>7.338</td>
</tr>
<tr>
<td>$F_{10}$</td>
<td>4.6145</td>
<td>34.275</td>
<td>1.7835</td>
<td>8.79</td>
<td>4.85</td>
<td>1.95</td>
<td>0.4511</td>
<td>17.878</td>
<td>7.095</td>
</tr>
<tr>
<td>$F_{15}$</td>
<td>4.6713</td>
<td>33.954</td>
<td>1.7840</td>
<td>8.87</td>
<td>4.83</td>
<td>1.95</td>
<td>0.4472</td>
<td>17.718</td>
<td>7.031</td>
</tr>
<tr>
<td>$F_{20}$</td>
<td>4.6238</td>
<td>34.400</td>
<td>1.7835</td>
<td>8.75</td>
<td>4.85</td>
<td>1.96</td>
<td>0.4468</td>
<td>17.718</td>
<td>7.121</td>
</tr>
</tbody>
</table>
separation $\langle d_{B-B} \rangle$ is also evaluated [28], to get more insight into the glass network, using the following Eq:

$$\langle d_{B-B} \rangle = \left[ \frac{V_m^B}{N_A} \right]^{1/3} \quad \text{----- (5.3)}$$

where $N_A$ is Avogadro’s number, $6.0228 \times 10^{23}$ mol$^{-1}$ and $V_m^B$ is the volume containing one mole of boron atoms in the given glass network. Since boron is central atom of BO$_{3/2}$ and BO$_{4/2}$ units, $V_m^B$ is given by

$$V_m^B = \frac{V_m}{2(1-x_B)} \quad \text{----- (5.4)}$$

Where $x_B$ refers to the molar fraction of B$_2$O$_3$. The calculated values of the average boron-boron separation are given in Table 5.1. Generally $V_m^B$ depends on the cations present in the glass network and hence depends on the radius of the modifier ions present in the system. With the incorporation of Fe$_2$O$_3$ at the expense of B$_2$O$_3$ leads to a substantial decrease in boron-boron separation from F5 to F20. Among the investigated samples the boron-boron separation is minimum for F20 and maximum for F5 glass.

Based on the refractive index and density Volf et al and Lorenz et al [29-30] derived the formula for molar refraction ($R_m$) as given below:

$$R_m = \left[ \frac{n_D^2 - 1}{n_D^2 + 1} \right] \left( \frac{m}{\rho} \right) \quad \text{----- (5.5)}$$

Where $n_D$ is the refractive index at sodium D1 line, $\rho$ is the density and $m$ is the molecular weight of the glass samples. The ratio $\left[ \frac{n_D^2 - 1}{n_D^2 + 1} \right]$ is known as the reflection
loss. Using the Classius-Mosotti relation, the structural related molar electronic polarizability (in cm$^3 \times 10^{-24}$) is proportional to molar refraction as follows:

$$\alpha_m = \left( \frac{3}{4\pi N} \right) R_m$$

----- (5.6)

The obtained values are also included in Table 5.1 from which both molar refraction and molar electronic polarizability values are minimum for F5 sample among the investigated samples.

### 5.3.3 Electron Paramagnetic Resonance:

Fig 5.4 shows the typical EPR spectra of as prepared glasses at room temperature. A small isotropic EPR line centered at $g=2.0047$ is observed for BaBiBO$_4$ pure. It confirmed the presence of few radicals in the sample (explained later in optical absorption). With 0.5 wt% doping of Fe$_2$O$_3$ to barium bismuth borate glass network a broad resonance signal at $g\approx2.1\pm0.1$ and an intense signal at $g\approx4.2\pm0.1$ along with a shoulder in the region of $g\approx6.82$. With increase in concentration of Fe$_2$O$_3$ the intensity of signals at 4.2 and 2.0 is found to decrease and a new signal around $g \approx 2.9$ is noticed in F20 glass sample.

In general, the magnetic properties of these glasses arise from the paramagnetic Fe$^{3+}$ and Fe$^{2+}$ ions with 3d$^5$ and 3d$^6$ electrons, respectively. As the iron ions are in Fe$^{3+}$ state belong to d$^5$ configuration with 6S as ground state in the free ion and there is no spin–orbit interaction [31]. The g value is expected to lie very near the free-ion value. However, a g value very much greater than 2.0 often occurs; in particular an isotropic g value at 4.2 occurs and these large g values arises due to
presence of certain symmetry elements in the glass matrix. The theory of these large g values is usually expressed by the spin-Hamiltonian [32]

\[
H = g \beta BS + D \left[ S_Z^2 - \left\{ \frac{S(S+1)}{3} \right\} \right] + E (S^2_x - S^2_y) \quad --- (5.7)
\]

Where \( S = 5/2 \). Here D and E are the axial and rhombic structure parameters, \( \lambda = E/D \) lies within the limits \( 0 < \lambda < 1/3 \) [33].

Fig 5.4 EPR spectra of iron doped BaBiBO\(_4\) glasses at room temperature. Inset shows the ESR spectrum of iron free BaBiBO\(_4\) glass sample.
The EPR spectra of Fe$^{3+}$ ions containing glasses are generally characterized by the appearance of resonance signals at $g = 2.1$, $g = 4.2$ and $g = 6.82$ with their relative intensities being strongly dependent on composition [34-37]. This feature at $g = 4.2$ is due to rhombic distortions of the crystal field around Fe$^{3+}$ ions [37]. In a large number of glasses containing Fe$^{3+}$ ions a symmetric and isotropic line at $g \approx 4$ to 4.2 is observed. Castner et al. [38] explained it as when Fe$^{3+}$ ions are placed in a crystal field environment, the 6S ground state splits into three Kramers doublets $|\pm 1/2>$, $|\pm 3/2>$ and $|\pm 5/2>$. The resonance signal at $g \approx 4.2$ is due to the middle Kramers doublet $|\pm 3/2>$.

In the present study, the ESR spectra of all doped glasses mainly consists of a broad resonance signal at $g \approx 2.1$, an intense resonance signals at $g \approx 4.2$ and a shoulder in the region of $g \approx 6.82$. The resonances at $g \approx 4.2$ is attributed to the isolated Fe$^{3+}$ ions predominantly situated in rhombically distorted octahedral sites where as $g \approx 6.82$ resonance arise from axially distorted sites, respectively. The $g \approx 2.0$ resonance may be attributed to either Fe$^{3+}$ions interacting by dipole–dipole interaction in sites of less distorted octahedral field or to their super exchange interactions within the pairs of Fe ions. Interestingly, though the concentration of Fe$_2$O$_3$ is increased from F5 to F20 the decrease in intensity and area of the resonance signals around $g \approx 2.1$ and $g \approx 4.2$ indicating the decrease of Fe$^{3+}$ ions concentration in the glass matrix. The reasons for such observations are given below:

(i) The compositions containing not only B but simultaneously Bi, exhibited a definite Curie-Weiss behavior [39]. Samples with Bi and Fe probably contained cations’ multivalency as a result of their broader distribution showing their
various degree of incorporation into the glass network, which shows a mixture of paramagnetism and antiferromagnetism resulting a very special behavior i.e., so called speromagnetism, probably caused by canted spins (not fully antiparallel moment ordering, where there is mutually little angle between magnetic moments) in the anti ferromagnetic sub-lattice (possibly place in the Fe-Bi-O) [40]. In Fe₂O₃ rich compositions, therefore, there is an increased interaction of incorporated transition metal ions via the intermediating oxygen, which may result in their anti ferromagnetic pair ordering thus substantially lowering the contribution of number of particles participating in resonance.

(ii) The spin moment of covalently bound Fe³⁺ ions may be lowered due to the transition of high-spin Fe³⁺ state to low-spin state, which may cause the formation of a new resonance signal at $g \approx 3.015$ [less than 4.2].

(iii) Whenever dopant is increased in the glass network, the glass-forming ability associates with the cation compatibilities alters due to various levels of B₂O₃, consequently reduction of Fe³⁺ cations to Fe²⁺ ions (Fe³⁺ + e⁻ → Fe²⁺) happens during melting and annealing process since the reduction takes place only with $E^0 = 0.77$ eV [41].

The observed $g$ values for all the present samples are given in Table 5.2. From the Table the $g$ value is positive shifted from free electron $g$ value. This shifting of $g$ value is due to coupling of the iron orbitals involved in molecular orbitals containing the unpaired electrons, with the filled ligand orbitals. From F5 to F20 this shifting is increased, which is consequence of amount of unpaired electron density at the donor
sites of the oxide ions. Therefore, the covalency of Fe-O bond should decrease as $\Delta g$ value is increased [42].

Table 5.2 Cutoff wavelength ($\lambda_c$), Optical band gap ($E_g$), Urbach energy ($\Delta E$), theoretical optical basicity ($\Lambda_{th}$) and $g$ values of the glasses $10\text{BaO}.20\text{Bi}_2\text{O}_3.(70-x)\text{B}_2\text{O}_3.x\text{Fe}_2\text{O}_3$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\lambda_c$ (nm) $\pm$0.1</th>
<th>$E_g$ (eV) $\pm$0.0001</th>
<th>$\Delta E$ (eV) $\pm$0.001</th>
<th>$\Lambda_{th}$</th>
<th>$g$ value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_0$</td>
<td>365.5</td>
<td>3.1069</td>
<td>0.2097</td>
<td>0.4540</td>
<td>--</td>
</tr>
<tr>
<td>$F_5$</td>
<td>415.0</td>
<td>2.5845</td>
<td>0.2949</td>
<td>0.4542</td>
<td>2.003</td>
</tr>
<tr>
<td>$F_{10}$</td>
<td>427.0</td>
<td>2.5417</td>
<td>0.2154</td>
<td>0.4545</td>
<td>2.032</td>
</tr>
<tr>
<td>$F_{15}$</td>
<td>441.5</td>
<td>2.3507</td>
<td>0.2317</td>
<td>0.4548</td>
<td>2.056</td>
</tr>
<tr>
<td>$F_{20}$</td>
<td>474.5</td>
<td>2.2610</td>
<td>0.4529</td>
<td>0.4551</td>
<td>2.099</td>
</tr>
</tbody>
</table>

5.3.4 Optical Absorption:

The optical absorption spectra of BaBiBO$_4$ glasses doped with different concentrations of Fe$_2$O$_3$, at room temperature in the wavelength region 350-1400 nm is shown in Fig 5.5. The absorption spectrum of F0 glass has exhibited a band around 848 nm and is blue shifted to 832 nm with 0.5 wt% doping of Fe$_2$O$_3$. In addition a broad band around 604 nm along with a small peak at 712 nm and a small broad hump at 987 nm is also observed. However, the bands around 604 and 712 nm are not found at higher concentrations of dopant. Moreover, with further addition of iron the band at 832 nm is slightly red shifted and the band at 987 nm is blue shifted. At higher
concentration of dopant both the peaks are observed to merged into single band at 912 nm.

The absorption band around 848 nm in undoped F0 glass has been attributed to the $^3P_0$ to $^3P_2$ electronic transition of Bi$^+$ radicals [43], which is supported by a small resonance signal observed in ESR spectra of F0 sample. The blue shift of the above band with 0.5 wt% doping of Fe$_2$O$_3$, indicates that iron ions react with the bismuth radicals.

**Fig 5.5** Optical absorption spectra of 10BaO.20Bi$_2$O$_3$.($70-x$)B$_2$O$_3$.xFe$_2$O$_3$ glasses.

By recollecting the ESR data there is an evidence for the existence of Fe$^{3+}$ ions in all BaBiBO$_4$:Fe glasses. It is known, from the famous Tanabe-Sugano diagram of d$^5$ ions,
Fe$^{3+}$ ions never show any spin-allowed transitions and generally gives only spin-forbidden transitions. Many researchers observed the feeble absorption bands around 408 and 424 nm in iron containing glasses and assigned to $^6A_{1g}(S)\rightarrow^4A_{1g}(G)$, $^4E_g(G)$ of Fe$^{3+}$ ions with distorted octahedral symmetry [44]. In all the present doped glasses no such peaks are found and it may be due to the less intensity of spin forbidden transitions. However, an absorption band around 987 nm in all doped glasses is attributed to $^5T_{2g}\rightarrow^5E_g$ transition of Fe$^{2+}$ (d$^6$) ions [45]. The increase in intensity along with blue shift of this band is clearly indicating the increase in Fe$^{2+}$ ions concentration through the reduction of Fe$^{3+}$ ions, which also support the decrease in ESR signal intensity around $g\approx4.2$. The blue shift of the absorption band is clearly due to increase of energy separation between the $^5T_{2g}$ and $^5E_g$ energy levels ($E_{s_{2g}}-E_{s_{2g}}$) is equal to the amount 10Dq [46], where $D=\frac{35Ze^2}{4a^2}$ (a being Fe-O bond length) is a factor that depends on the ligand oxygen ions and $q=\left(\frac{2}{105}\right)\langle r^4 \rangle$ (r being the radial position of the electron). Therefore, the blue shift of the band is a consequence of either increase of D (decrease of a) and/or increase in the radial position of electron cloud. Further, these Fe$^{2+}$ ions are expected to occupy only interstitial positions since the ratio of cation–oxygen radii is 0.63 for Fe$^{2+}$ ion, which is far from the value of 0.19 to be possessed by an ion to occupy tetrahedral or substitutional sites [41]. The FeO$_6$ octahedrons may be viewed as entwined with BiO$_3$ pyramids forming FeBiO$_8$ structural units where all the oxygens are bridging as shown in Fig 5.6. The peculiar green color (with small clusters) of F5 sample, which exhibited less density and two absorption bands around
604 and 712 nm, in the visible region, are ascribed to colloidal Bi\(^{0}\) metal atoms and Bi\(^{+}\) radical respectively as follows:

\[ \text{Fig 5.6 The local structure of FeO\textsubscript{6} octahedron entwined with BiO\textsubscript{3} pyramids} \]

The presence of magnetic cations such as Fe\(^{3+}\)/Fe\(^{2+}\) in the bismuth borate glasses exhibits their interactions with surrounding oxygen. The details of these interactions depend on the type of oxygen polyhedral around the ferric and/or ferrous cations [47]. Certainly, it is plausible for the formation of colloidal metal colors in the glass network, by the redox reaction of ionic form metal to atomic form with other components of the glass [26]. By comparing the atomic spectral data of Bi\(^{0}\) with the observed absorption spectrum of F5 glass sample it is found that the occurrence of coincidence between these two is very well. The absorption band at 604 nm is assigned to \(^{4}S_{3/2}\rightarrow^{2}D_{5/2}\) transitions of Bi\(^{0}\) where as the band at 712 nm is assigned to \(^{3}P_{0}\rightarrow^{1}D_{2}\) transition of Bi\(^{+}\) ions [43, 48]. The presence of bismuth colloids of Bi\(^{0}\) metal atoms as well as bismuth radical Bi\(^{+}\) provides great versatility in the production of broad band
NIR emission systems, which are of particular interest for communicating purpose [49].

5.3.5 Optical band gap and Urbach energy:

The fundamental absorption edge provides very useful information on the band structure around the energy gap. The fundamental short wavelength absorption edge (SWAE) or cut-off wavelength $\lambda_c$, which shows the rapid rise in the absorption coefficient, of F0 sample is observed at 365.5 nm and is gradually red shifted to 474.5 nm with increase in concentration of iron. Fig 5.7 represents the plots corresponding to $(\alpha h\nu)^{1/2}$ vs $h\nu$ for the present glasses, to evaluate the most useful data of optical band gap $E_g$ according to Mott & Davis [50].

**Fig 5.7** $(\alpha h\nu)^{1/2}$ vs $h\nu$ plots to determine optical band gaps of the BaBiBO$_4$:Fe glasses
As mentioned in Table 5.2 all the \( E_g \) values are measured by extrapolating the linear region of the graph to meet X-axis i.e, \((ahu)^{1/2} = 0\). Among all the investigated samples the \( E_g \) value is maximum for F0 (3.1069 eV) and is gradually decreased to 2.2610 eV with increase in \( \text{Fe}_2\text{O}_3 \) concentration. The decrease in \( E_g \) values by the successive replacement of \( \text{B}^{3+} \) with \( \text{Fe}^{3+} \) suggests that formation of large number of non bridging oxygens (NBOs) occurs by the incorporation of cations of \( \text{Fe}_2\text{O}_3 \) into \( \text{BaBiBO}_4 \) glass network, which predictably affects the structural properties. Presumably, the addition of \( \text{Bi}_2\text{O}_3 \) to the \( \text{B}_2\text{O}_3 \) matrix prefers to undertake web incorporations in the form of \( \text{BiO}_3^{3-} \) groups, their negative charge being compensated by pushing transition metals to bond within the network. Thus the concentration of BO is decreased. Such effect is very strong due to the higher deformability of the larger radius of Bi-ions. The decrease of optical band gap with further addition of \( \text{Fe}_2\text{O}_3 \) is also explained on the basis of ratios of \( \text{Fe}^{3+} / \text{Fe}^{2+} \) and/or \( \text{Fe}^{3+}/\Sigma\text{Fe} \) which are controlled by the glass-modifying admixtures of the glass composition, which generally affecting the level of NBO. Several researchers [51, 52] observed that NBO content in the melt increase with decrease of \( \text{Fe}^{3+} / \text{Fe}^{2+} \) ratio. In compliance with decrease of ESR signal corresponds to \( \text{Fe}^{3+} \) ions and increase of absorption band corresponds to \( \text{Fe}^{2+} \), the decrease of optical band gap is ascribed to increase of NBO due to decrease of \( \text{Fe}^{3+} / \text{Fe}^{2+} \) ratio. The decrease in band gap is also explained on the basis of color centers/defects in the doped glasses which provide energy states, in the forbidden gap, derived from their outer orbitals [53]. The Urbach energy (\( \Delta E \)) values are determined by taking the reciprocals of the slopes of the linear portion of the \( \ln \alpha(u) \) vs. \( h\nu \) plots as shown in Fig 5.8.
Fig 5.8 Urbach plots for tail gap energy of $10\text{BaO}.20\text{Bi}_2\text{O}_3.(70-x)\text{B}_2\text{O}_3.x\text{Fe}_2\text{O}_3$ glasses

Fig 5.9 The variation of optical band gap ($E_g$) and Urbach energies ($\Delta E$) with concentration of $\text{Fe}_2\text{O}_3$
These values are included in Table 5.2 and the effect of iron ion concentration on $E_g$ and $\Delta E$ values of present glasses is shown in Fig 5.9. From the figure it is clear that the $\Delta E$ value is minimum (0.2097 eV) for F0 glass and maximum (0.4529) for F20 glass sample. The observed minimum Urbach energy for F0 (0.2097 eV) indicates the least width of the tails among investigated samples. The increase in $\Delta E$ value of F5 than F10 can be explained in reminiscent with the observed colloidal Bi$^0$ metal atoms in the glass matrix. The increase of Urbach energy from F10 to F20 is due to formation of defects like wrong bonds and fluctuations in bond angle distortions [53]. The additional factor contributing to edge broadening is static disorder which increases the density of localized states $N(E_F)$ of these defects.

5.3.6 Theoretical Optical basicity($\Lambda_{th}$):

From Table 5.2, it is observed that with the gradual doping of Fe$_2$O$_3$ in the BaBiBO$_4$ glass network the value of theoretical optical basicity is increased. The gradual increase in theoretical optical basicity ($\Lambda_{th}$) is explained as follows: since, the optical basicity of a chemically complex glass is represented by the mean polarization state of the ligands [O$^{-2}$] and their mean ability to transfer fractional charges to the central cation [54], increase in $\Lambda_{th}$ suggests that an increase of localized donor pressure on cations of glass matrix. In other words, the covalence of the glass network decreases, which is also supported by increase of +ve shift of g factor from ESR study. Besides depending on the role of network formers and modifiers, optical basicity will change. The network formers interact covalently with oxygen, while the modifiers are the elements that interact ionically. Moreover, Duffy et al [55] concluded that the
polarizability of oxygen ions is directly proportional to the optical basicity. The increase in the polarizability of oxygen ions is another indication that the concentration of NBOs increases [56]. By increasing the number of NBOs, the $O^{2-}$ (electron donor power) will also increase, and the same is also supported by the observed decrease in $E_g$ and increase in $\Delta E$ values.

5.3.7 FTIR:

Fig 5.10 represents the IR transmission spectra of as prepared BaBiBO$_4$:Fe glasses.

![FTIR spectra of BaBiBO$_4$:Fe glass samples](image)

Fig 5.10 FTIR spectra of BaBiBO$_4$:Fe glass samples

The obtained band positions and their corresponding assignments are presented in Table 5.3. From the figure the observed broad bands are due to the convolution of
individual bands with one another. Three principle bands are observed at 1384, 943 and 684 cm$^{-1}$ with shoulders around 1501, 1225 and 1070 cm$^{-1}$ for BaBiBO$_4$ glass along with a week band around 495 cm$^{-1}$. By the doping of Fe$_2$O$_3$ (from F5 to F20) the centers of the bands around 1501, 1225, 1070 and 684 are gradually blue shifted to 1531, 1245, 1078 and 691 cm$^{-1}$ and the band at 1384 cm$^{-1}$ is almost unchanged while the bands around 943, 495 cm$^{-1}$ are red shifted to 925 and 487 cm$^{-1}$ respectively (for F20 glass sample). To augment the understanding of structural changes in the present glass network, it is helpful to analyze the IR spectra in the light of bismuth borate glasses.

**Table 5.3 Assignment of absorption bands in the infrared spectra (with a probable error of ±0.1cm$^{-1}$) of the glasses 10BaO.20Bi$_2$O$_3$.((70-x)B$_2$O$_3$.xFe$_2$O$_3$).**

<table>
<thead>
<tr>
<th>F$_0$</th>
<th>F$_5$</th>
<th>F$_{10}$</th>
<th>F$_{15}$</th>
<th>F$_{20}$</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>495</td>
<td>493</td>
<td>490</td>
<td>489</td>
<td>487</td>
<td>A doubly degenerate vibrations of Bi-O bonds BiO$_6$ octahedral units and Fe-O bonds of FeO$_6$ octahedral units</td>
</tr>
<tr>
<td>684</td>
<td>685</td>
<td>686</td>
<td>686</td>
<td>691</td>
<td>B-O-B bend</td>
</tr>
<tr>
<td>943</td>
<td>938</td>
<td>932</td>
<td>928</td>
<td>925</td>
<td>B-O stretch in BO$_4$ units from diborate groups and/or stretching vibrations of Bi-O bonds in BiO$_6$ units</td>
</tr>
<tr>
<td>1070</td>
<td>1073</td>
<td>1076</td>
<td>1076</td>
<td>1078</td>
<td>Stretching vibrations of B-O bonds in BO$_4$ units from tri, tetra and penta borate groups.</td>
</tr>
<tr>
<td>1225</td>
<td>1230</td>
<td>1238</td>
<td>1240</td>
<td>1245</td>
<td>B-O$_{\text{sym}}$ stretch in BO$_3$ units from pyro and ortho borate groups</td>
</tr>
<tr>
<td>1384</td>
<td>1384</td>
<td>1384</td>
<td>1384</td>
<td>1389</td>
<td>B-O$_{\text{sym}}$ stretch in BO$_3$ units from varied types of borate groups</td>
</tr>
<tr>
<td>1501</td>
<td>1506</td>
<td>1506</td>
<td>1514</td>
<td>1531</td>
<td>B-O$^-$ stretch in BO$_2$O$^-$ units from varied types of borate groups</td>
</tr>
</tbody>
</table>

It is widely accepted [57] that incorporation of Bi$_2$O$_3$ into B$_2$O$_3$ leads to conversion of SP$^2$ planar BO$_3$ units to more stable SP$^3$ tetrahedral BO$_4$ units and also
create non bridging oxygens. Each BO$_4$ unit is linked to two other similar units and the structure leads to the formation of long tetrahedron chains. However, addition of alkaline earth oxide (BaO) into glass network transfers the BO$_4$ tetrahedral into BO$_3$, by forming a BaO$_n$ polyhedron when it is surrounded by several BO$_4$ tetrahedrons [58]. This structure behaves like a defect in the bismuth borate network. In the present investigation the observed broad bands in the regions from 1500 – 1100 cm$^{-1}$ and from 1100 – 800 cm$^{-1}$ are assigned to the stretching vibrations of both triangular BO$_3$ and tetrahedral BO$_4$ units respectively. The band at 684 cm$^{-1}$ is attributed to B-O-B bending vibration and a feeble band around 495 cm$^{-1}$ is ascribed to degenerate vibrational bands of Bi-O bonds from BiO$_6$ units and Fe-O bonds of FeO$_6$ units. At the initial doping concentration (0.5 wt%) of Fe$_2$O$_3$ the area of the bands around 1384 and 1225 cm$^{-1}$ are observed to increase and is clearly indicating that the conversion of some BO$_4$ units into BO$_3$ units occurs. Interestingly, with further addition of Fe$_2$O$_3$ at the expense of B$_2$O$_3$ the band intensity corresponds to BO$_3$ and BO$_2$O$^-$ units is further increased. Meanwhile the intensity of the band around 938 cm$^{-1}$ is also increased, which may due to increase of BiO$_6$ octahedral symmetry units in the glass network at higher concentration of Fe$_2$O$_3$. At the same time the intensity and area of the band around 684 cm$^{-1}$ is increased with blue shift of the band center to 691 cm$^{-1}$ as well as the band at 943 cm$^{-1}$ is red shifted to 925 cm$^{-1}$. This type of band shifting is due to the formation of new bridging bonds, like Bi-O-B and Fe-O-B [59-60]. This new bonds might have been formed due to the inducement of the electric field of the high polarizing nature of Bi$^{3+}$ ions. As stretching force constant of Bi-O and Fe-O bonds is differed from that of B-O
bond, the effective force constant of Bi-O-B and Fe-O-B bonds is changed. Hence the increase in band intensity at 943 cm\(^{-1}\) and 495 cm\(^{-1}\) could be reasonably attributed to the formation or gradual increase of BiO\(_6\) and/or FeO\(_6\) units. At the same time the red shift of band centers at 495 cm\(^{-1}\) to 487 cm\(^{-1}\) is ascribed to increase of either Bi-O or Fe-O bond lengths due to increase of ionic radii which increases the BiO\(_6\) and FeO\(_6\) units, which is also confirmed by blue shift of Fe\(^{2+}\) absorption band. In compliance with the structural changes inferred from IR studies, the observed decrease in band gap and increase in \(\Delta E\) [Table 5.2] induced by the doping of Fe\(_2\)O\(_3\) in BaBiBO\(_4\) glass might be explained by the increase of BiO\(_6\) and FeO\(_6\) structural units along with the increase of NBOs (with increase of B-O\(^-\) bonds).

5. 3. 7 Dielectric studies:

The temperature dependence of dielectric constant \(\varepsilon'\) in the temperature range 30-400\(^{0}\)C at 100 KHz is shown in Fig 5.11. Though \(\varepsilon'\) is increased in the whole temperature range its rate of increase is very small upto 100 \(^{0}\)C. Inset of Fig 5.11 shows the variation of \(\varepsilon'\) with temperature at different frequencies for F10 sample. From which it is observed that the dielectric constant is decreased with increase in frequency. F0 sample has shown a minimum \(\varepsilon'\), 5.6, at 100 KHz and 30 \(^{0}\)C. By the doping of Fe\(_2\)O\(_3\) its value is found to increase. A maximum \(\varepsilon'\) 60, is observed for F20 glass at 400 \(^{0}\)C and 100 KHz. All investigated samples has been exhibited a broad dielectric dispersion. Iron free F0 sample showed a small dielectric dispersion at 220 \(^{0}\)C at 10 KHz and been shifted to lower temperature region by the doping of Fe\(_2\)O\(_3\). From the inset of Fig 5.11, the dispersion is shifted to higher temperature region with increase in frequency. Fig
Fig 5.11 Variation of dielectric constant $\varepsilon'$ with temperature at 100 KHz for BaBiBO$_4$ glasses doped with different concentrations of Fe$_2$O$_3$. Inset shows the variation of $\varepsilon'$ with temperature for different frequencies of F10 sample.

Fig 5.12 Variation of dielectric loss Tan$\delta$ with temperature at 10 KHz for BaBiBO$_4$:Fe glasses. Inset shows the variation of Tan$\delta$ with temperature at different frequencies of F20 sample.
5.12, shows the variation of dielectric loss \((\tan\delta)\) with temperature for BaBiBO\(_4\):Fe\(_2\)O\(_3\) glasses at 10 KHz. And its inset represents the loss \((\tan\delta)\) of F20 sample, with temperature at different frequencies. Moreover the loss maxima is shifted to lower temperature side and broadened with the increase of Fe\(_2\)O\(_3\) doping. Using the following Eq 5.8 the effective activation energy of dipoles \((W_d)\) of the present glass samples have been calculated [61] and presented in Table 5.4.

\[
f = f_0 \exp\left\{\frac{-W_d}{KT}\right\}
\]

----- (5.8)

Where \(f\) is the frequency and \(f_0\) is a constant. F0 sample is exhibited maximum \(W_d\) 4.92 eV and is decreased to 3.72 eV by the doping of Fe\(_2\)O\(_3\).

**Table 5.4 Summary of the data on dielectric loss of BaO-Bi\(_2\)O\(_3\)-B\(_2\)O\(_3\): Fe\(_2\)O\(_3\) glasses at100 kHz**

<table>
<thead>
<tr>
<th>Glass</th>
<th>((\tan\delta)_{ma})</th>
<th>Temp. region of relaxation (±1 °C)</th>
<th>AE for dipoles (±0.01) eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>F0</td>
<td>0.0978</td>
<td>220-265</td>
<td>4.92</td>
</tr>
<tr>
<td>F5</td>
<td>0.1421</td>
<td>165-235</td>
<td>4.25</td>
</tr>
<tr>
<td>F10</td>
<td>0.1685</td>
<td>160-240</td>
<td>4.07</td>
</tr>
<tr>
<td>F15</td>
<td>0.1916</td>
<td>140-230</td>
<td>3.89</td>
</tr>
<tr>
<td>F20</td>
<td>0.2214</td>
<td>130-225</td>
<td>3.72</td>
</tr>
</tbody>
</table>

The a.c electrical conductivity \((\sigma_{ac})\) of as prepared glasses has been evaluated [61] by following Eq.

\[
\sigma_{ac} = \omega \varepsilon \varepsilon_0 \tan \delta
\]

----- (5.9)
Fig 5.13 Variation of $\sigma_{ac}$ with $1000/T$ for different frequencies of F15 sample. Inset shows the variation of $\sigma_{ac}$ with $1000/T$ at 100 KHz for BaBiBO$_4$:Fe glasses.

Table 5.5 Summary of the data on ac. conductivity of BaO-Bi$_2$O$_3$-B$_2$O$_3$ : Fe$_2$O$_3$ glasses at 500 kHz

<table>
<thead>
<tr>
<th>Glass</th>
<th>$\sigma_{ac}$ at 90°C ($10^5$) (Ω·cm)$^{-1}$</th>
<th>N(E$_F$) ($10^{21}$ eV$^{-1}$/cm$^3$)</th>
<th>Activation energy for conduction (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Austin</td>
<td>Butcher</td>
</tr>
<tr>
<td>F0</td>
<td>6.41</td>
<td>5.44</td>
<td>2.27</td>
</tr>
<tr>
<td>F5</td>
<td>13.8</td>
<td>7.98</td>
<td>3.33</td>
</tr>
<tr>
<td>F10</td>
<td>23.2</td>
<td>10.3</td>
<td>4.32</td>
</tr>
<tr>
<td>F15</td>
<td>32.3</td>
<td>12.2</td>
<td>5.09</td>
</tr>
<tr>
<td>F20</td>
<td>42.5</td>
<td>14.0</td>
<td>5.84</td>
</tr>
</tbody>
</table>
where all the terms have their usual meaning. The variation of \( \log(\sigma_{ac}) \) with respect to 1000/T at different frequencies 10, 100 and 500 KHz for F15 glasses is shown in Fig 5.13 and its inset is shown the \( \log(\sigma_{ac}) \) dependence on 1000/T at 100 KHz of all the present glass samples.

In the higher temperature region (the linear region) of \( \log(\sigma_{ac}) \) vs 1000/T plots the values of activation energy for conduction are evaluated, as reported in the literature [61, 62]. The values of activation energy for conduction at 500 KHz are given in Table 5.5 and is highest 0.865 eV for F0 sample. By the doping of Fe\(_2\)O\(_3\) the values are found to decrease.

By the gradual doping of Fe\(_2\)O\(_3\) in the glass matrix, the values of \( \varepsilon' \), loss (\( \tan\delta \)) and \( \sigma_{ac} \) are found to increase at any temperature and frequency. Generally for amorphous materials like glasses space charge polarization is responsible for the increase of dielectric constant with increase in temperature at any frequency. The modifying ions in the present study Ba\(^{2+}\), Bi\(^{3+}\) and Fe\(^{3+}\) units with octahedral coordinations generate bonding defects (dangling bonds), structural defects (disorder in ideal random structure), donor and ionized donor pairs (like Bi\(^{3+}\)-Bi\(^{5+}\)). These defects create easy pathway for the migration of charges and build up space-charge polarization and facilitate an increase in the dielectric parameters [63]. Furthermore the activation energy for conduction is observed to decrease. These results are indication of increase in the space charge polarization, which in turn caused by the increase in modifying nature of Fe\(^{3+}\) ions with FeO\(_6\) octahedral units. In BaO mixed glasses the observed dielectric relaxation and its shifting with frequency suggests existence of
dipoles in these glasses. These dipoles may be formed by the association of reduced Bi$^{3+}$ radicals with their cationic vacancies in BaO mixed glasses. Further spreading of relaxation region with Fe$_2$O$_3$ doping is due to formation and/or increase in dipolar interaction of additional dipoles through Fe$^{3+}$-O-Fe$^{3+}$ bonds in the glass network. In general the observed decrease in activation energy and increase in conductivity is an obvious change [64]. It can be understood by correlating activation energy with mean separation ($R_i$) of Fe$^{3+}$ ions. As presented in Table 5.1 with the doping of Fe$_2$O$_3$ the mean site-to-site separation between Fe$^{3+}$ ions decreases which in turn causes decrease in activation energy $W_d$ and increase of $\sigma_{ac}$. The observed positive correlation agrees with the results suggested by several researchers [65].

The density of energy states $N(E_F)$ near the Fermi level, has been evaluated using the following equation and presented in Table 5.5.

$$\sigma(\omega) = \eta_e^2 kT[N(E_F)]^2 \alpha^{-5} \omega \left[ \ln \left( \frac{v_{ph}}{\omega} \right) \right]^4$$

(5.10)

where for Austin $\eta = \pi/3$, Butcher $\eta = 3.66 \pi^2/6$ and Pollack $\eta = \pi^4/96$ with the usual meaning of remaining symbols reported [66]. It suggests that, increase in doping of Fe$_2$O$_3$, increases the disorder and hence modifying nature in the glass network. Therefore, the number of localized states near Fermi level is found to increase and is supported by the increase of Urbach energy $\Delta E$ values at higher concentrations of dopant Fe$_2$O$_3$ in the glass matrix (Table 5.2).
References


