Influence of iron ions and alkaline earth oxides on spectroscopic and dielectric studies of alkali borate glasses

3.1 Introduction

Alkali /alkaline earth oxy borate glasses are well known due to their applications in phosphors, solar energy converters and in a number of electronic devices. These glasses are relatively moisture resistant; possess high electrical insulating and mechanical strength when compared with the pure borate glasses. Extensive studies have been done on various properties like electrical, magnetic, optical properties of various alkali borate glasses doped with different transition and rare earth metal ions [1,2]. Spectroscopic studies on alkali metal borate glasses have revealed that the structure of alkali metal borate glasses is dependent not only upon the content of the alkali metal ion but also upon the difference in the alkali metal and borate ions.

Iron ions have strong bearing on electrical, optical and magnetic properties of glasses [3-5]. 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 [6-14]. 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 and mobility of the modifier cation. 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. 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.

In the present paper, the influence of increasing concentration of Fe$_2$O$_3$ on dielectric properties of K$_2$O-BaO-B$_2$O$_3$ and the effect of modifier oxides (CaO, SrO and BaO) on Na$_2$O-B$_2$O$_3$-Fe$_2$O$_3$ glass systems have been investigated from a systematic study on dielectric constant $\varepsilon'$, loss tan$\delta$ and ac conductivity $\sigma_{ac}$ over a moderately wide range of frequency and temperature. Spectroscopic properties (viz., IR and ESR spectra) are also included.

This chapter is divided into two sections. In section I, we discussed the influence of iron ions on spectroscopic and dielectric properties of K$_2$O-BaO-B$_2$O$_3$ glasses. Section II explore the effect of alkaline earth oxides on spectroscopic and dielectric properties of RO-Na$_2$O-B$_2$O$_3$-Fe$_2$O$_3$ glasses (R=Ca, Sr, Ba).

**Section-I**

For the present investigation particular composition is chosen: 10K$_2$O-20BaO-(70-x)B$_2$O$_3$-xFe$_2$O$_3$ with $0 \leq x \leq 1$ in steps of 0.2. The details of compositions for the glasses along with the labels are given as below:

- $F_0$: 10K$_2$O-20BaO-70B$_2$O$_3$
- $F_2$: 10K$_2$O-20BaO-(69.8)B$_2$O$_3$-0.2Fe$_2$O$_3$
- $F_4$: 10K$_2$O-20BaO-(69.6)B$_2$O$_3$-0.4Fe$_2$O$_3$
- $F_6$: 10K$_2$O-20BaO-(69.4)B$_2$O$_3$-0.6Fe$_2$O$_3$
- $F_8$: 10K$_2$O-20BaO-(69.2)B$_2$O$_3$-0.8Fe$_2$O$_3$
Section-II

This section deals with the glasses with composition 20RO-10Na2O-69B2O3-1Fe2O3 where R=Ca, Sr and Ba. The fabricated glasses along with details were labeled as follows:

CNBF: 20CaO-10Na2O-69B2O3-1Fe2O3
SNBF: 20SrO-10Na2O-69B2O3-1Fe2O3
BNBF: 20BaO-10Na2O-69B2O3-1Fe2O3 (all are in mol%)

The methods of synthesis of the glasses and the techniques involved for recording X-ray diffraction (XRD) pattern, optical absorption, FTIR, ESR, etc., and for measuring dielectric properties are same as that mentioned in previous chapters.

3.2 Brief review of the previous work on iron ions doped glasses

Veerabhadra Rao et al. [15] have studied dielectric relaxation and a.c. conduction phenomena of PbO-PbF2-B2O3 glasses doped with Fe2O3; the analysis shows that iron ions exist mainly in Fe3+ state, occupy tetrahedral positions and at higher concentrations iron ions exist mainly in divalent state. Baiocchi et al. [16] 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 Fe3+ ions is more common than the six fold in silicate glasses. Fe2O3-induced crystallization and the physical properties of lead arsenate glass
system have studied by Nagarjuna et al. [17] and they analyzed the optical absorption studies together with ESR and magnetic susceptibility measurements indicated the dominant presence of iron ions in the trivalent state when the concentration of nucleating agent Fe$_2$O$_3$ is less than 0.3 mol%.

The environment of Fe$^{3+}$ ion and its influence on dielectric and spectroscopic properties of PbO-Nb$_2$O$_5$-P$_2$O$_5$ glasses have reported by Krishna Mohan et al. [18]. The results of these studies have been analyzed in the light of different oxidation states of iron ions. Muralidhara et al. [19] have analyzed the EPR and optical absorption studies of Fe$^{3+}$ ions in sodium borophosphate glasses; the EPR spectra at different temperatures (123-295 K) have also been investigated. Sanjay et al. [20] have reported analysis of structural, optical and transport properties of semiconducting Fe$_2$O$_3$-PbO-B$_2$O$_3$ glasses and the dc conductivity of these samples was measured in the temperature range 473-623 K. Dielectric properties and physical features of phosphate glasses containing iron oxide have studied by Bergo et al. [21] and the dielectric constant of the glasses studied in this work was found to increase with the temperature in the range of 25-330 $^0$C.

The role of iron ions on transport properties of LiI-AgI-B$_2$O$_3$ glass system is studied by Srilatha et al. [22]. Horea et al. [23] have reported structural investigation of xFe$_2$O$_3$. (100-x) [P$_2$O$_5$.TeO$_2$] glass system by FTIR study and EPR spectroscopy. In these glasses the addition and the increasing of Fe$_2$O$_3$ content modify progressively the structure of the glass matrix. Srekanth Chakradhar et al. [24] have reported the interesting results on mixed alkali effect (MAE) in xLi$_2$O-
(30-x)Na$_2$O-69.5B$_2$O$_3$ (5≤x≤28) glasses containing Fe$_2$O$_3$ studied by electron paramagnetic resonance (EPR) and optical absorption techniques; the paramagnetic Curie temperature (θ$_p$) is negative for the investigated sample, which suggests that the iron ions are antiferromagnetically coupled by negative super exchange interactions at very low temperatures.

Effect of divalent metal oxides on absorption spectra of some sodium borate glasses containing mixed nickel and iron oxides have reported by El-Betal et al. [25]. Stefan and Simon [26] 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 [27] studied structural and physical properties of Fe$_2$O$_3$ doped lead vanadate glasses; they concluded that there is a strong role of iron both in the glass network and in the conduction mechanism of the glasses. Shiv prakash Singh et al. [28] have investigated the EPR, FTIR, optical absorption and photoluminescence properties of Fe$_2$O$_3$ and CeO$_2$ doped ZnO-Bi$_2$O$_3$-B$_2$O$_3$ glasses. From EPR and optical studies it is observed that iron ions are present in trivalent state with distorted octahedral symmetry. Dance et al. [29] have investigated ESR of Fe$^{3+}$ ions in fluoro aluminate glasses and attributed the single line centered at g=4.3 in the ESR spectrum to the presence of Fe$^{3+}$ ions in sites of fully rhombic symmetry. Sreekanth Chakradhar et al. [30] have investigated Fe$^{3+}$ ions in alkali lead tetra borate glasses on electron paramagnetic resonance and optical study. The electrochemical behaviour of Fe$^{2+}$/Fe$^{3+}$ redox couple in sodium disilicate glasses
has been studied by Mariac et al. [31]; from the results they have concluded that Fe$^{3+}$ acts both as network former and network modifier while Fe$^{2+}$ acts as network modifier.

Though a considerable amount of literature is available on the glasses doped with Fe$_2$O$_3$, sustained studies particularly on dielectric and spectroscopic properties of K$_2$O-BaO-B$_2$O$_3$ glass systems alloyed with Fe$_2$O$_3$ are not available.

**Section-I: Spectroscopic properties and dielectric dispersion of K$_2$O-BaO-B$_2$O$_3$ glasses doped with Fe$_2$O$_3$**

### 3.3 Characterization

#### 3.3.1 X-Ray diffraction

The X-ray diffraction pattern of the K$_2$O-BaO-B$_2$O$_3$ pure and Fe$_2$O$_3$ doped glasses are recorded in the range $10^\circ \leq 2\theta \leq 80^\circ$ is shown in Fig. 3.1. The absence of sharp peaks in the pattern indicates the amorphous nature of the samples.

![X-Ray diffraction patterns](image)

**Fig. 3.1** X-Ray diffraction patterns of K$_2$O-BaO-B$_2$O$_3$ glasses doped with different concentrations of Fe$_2$O$_3$. 


3.3.2 Physical parameters

The samples prepared were free from visible inhomogeneities, such as inclusions, cracks or bubbles. From the measured values of density $d$ and the average molecular weight $M$ of the samples, various other physical parameters such as iron ion concentration $N_i$, mean iron ion separation $r_i$ and polaron radius $r_p$ are calculated and presented in the Table 3.1.

**Table 3.1** Summary of data on various physical parameters of $K_2O$-$BaO$-$B_2O_3$: $Fe_2O_3$ glasses.

<table>
<thead>
<tr>
<th>Glass</th>
<th>Density $d$ (g/cm$^3$) $(±0.0001)$</th>
<th>Avg. mol. Wt. (M) gm/mol $(±0.001)$</th>
<th>iron ion concentration $N_i$ $(×10^{21}$ions/cm$^3$) $(±0.001)$</th>
<th>Inter-ionic distance of iron ions $r_i$(Å) $(±0.001)$</th>
<th>Polaron radius $r_p$(Å$^o$) $(±0.001)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_0$</td>
<td>2.1333</td>
<td>96.572</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$F_2$</td>
<td>2.1409</td>
<td>96.768</td>
<td>2.665</td>
<td>7.213</td>
<td>2.908</td>
</tr>
<tr>
<td>$F_4$</td>
<td>2.1485</td>
<td>96.963</td>
<td>5.338</td>
<td>5.723</td>
<td>2.307</td>
</tr>
<tr>
<td>$F_6$</td>
<td>2.1561</td>
<td>97.159</td>
<td>8.020</td>
<td>4.996</td>
<td>2.014</td>
</tr>
<tr>
<td>$F_8$</td>
<td>2.1637</td>
<td>97.355</td>
<td>10.709</td>
<td>4.536</td>
<td>1.829</td>
</tr>
<tr>
<td>$F_{10}$</td>
<td>2.1714</td>
<td>97.551</td>
<td>13.406</td>
<td>4.209</td>
<td>1.697</td>
</tr>
</tbody>
</table>
3.4 Results

3.4.1 FTIR

The infrared transmission spectra of pure K$_2$O-BaO-B$_2$O$_3$ glasses exhibit three groups of bands: (i) in the region 1300-1400 cm$^{-1}$, (ii) in the region 940-1050 cm$^{-1}$ and (iii) a band around 700 cm$^{-1}$ (Fig. 3.2). With the introduction of Fe$_2$O$_3$ (0.4 mol %) into the glass network, the intensity of second group of bands (bands due to BO$_4$ units) [30] is observed to decrease with a shifting of meta-center towards slightly higher wave number, beyond this concentration it is found to increase. For further increase of Fe$_2$O$_3$ the intensity of this band is continued to decrease where as that of the first group of bands (bands due to the BO$_3$ structural units) is also observed to decrease. The data on various band positions of the spectra are presented in Table 3.2.

![Fig. 3.2 IR Spectra of K$_2$O-BaO-B$_2$O$_3$ glasses doped with different concentrations of Fe$_2$O$_3$.](image-url)
Table 3.2 IR spectral band positions of K$_2$O-BaO-B$_2$O$_3$: Fe$_2$O$_3$ glasses with probable error of ±0.1 cm$^{-1}$.

<table>
<thead>
<tr>
<th>Glass</th>
<th>BO$_3$ units (cm$^{-1}$)</th>
<th>BO$_4$ units (cm$^{-1}$)</th>
<th>B-O-B units (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F$_0$</td>
<td>1371</td>
<td>947</td>
<td>696</td>
</tr>
<tr>
<td>F$_2$</td>
<td>1385</td>
<td>1020</td>
<td>696</td>
</tr>
<tr>
<td>F$_4$</td>
<td>1373</td>
<td>1022</td>
<td>694</td>
</tr>
<tr>
<td>F$_6$</td>
<td>1356</td>
<td>1018</td>
<td>690</td>
</tr>
<tr>
<td>F$_8$</td>
<td>1386</td>
<td>1008</td>
<td>694</td>
</tr>
<tr>
<td>F$_{10}$</td>
<td>1373</td>
<td>1006</td>
<td>692</td>
</tr>
</tbody>
</table>

Fig. 3.3 ESR spectra of K$_2$O-BaO-B$_2$O$_3$ glasses doped with different concentrations of Fe$_2$O$_3$. 
3.4.2 ESR spectra

The ESR spectra of K$_2$O-BaO-B$_2$O$_3$: Fe$_2$O$_3$ glasses recorded at room temperature are shown in Fig. 3.3. The intense line centered at about $g = 4.25$ could clearly be seen in the spectra of these glasses, a weak resonance line at $g = 2.01$ is observed and also a resonance at $g = 6.2$ is observed as a shoulder of the resonance centered at $g = 4.25$. The intensity of this signal is, however, observed to increase gradually with increase in the concentration of Fe$_2$O$_3$ in the glass matrix up to 0.8 mol%.

3.4.3 Dielectric properties

The dielectric constant $\varepsilon'$ and loss tan$\delta$ of K$_2$O-BaO-B$_2$O$_3$ (F$_0$) glass at 10 kHz and room temperature (30 °C) are measured to be 7.77 and 0.0218, respectively; and are found to increase with the decrease in frequency. The values of dielectric constant $\varepsilon'$ and loss tan$\delta$ are found to decrease gradually with increase in the concentration of Fe$_2$O$_3$ up to 0.8 mol% in the glass network at any frequency and decrease considerably with increase in frequency. Fig. 3.4 and its inset show the variation of dielectric constant and loss respectively as a function of frequency at room temperature for K$_2$O-BaO-B$_2$O$_3$ glasses doped with different concentrations of Fe$_2$O$_3$.

In Fig. 3.5 the variation of dielectric constant at different frequencies, with temperature for the concentration 0.2 mol% Fe$_2$O$_3$ is shown. A comparison plot of variation of dielectric constant with temperature at 100 kHz for the glasses
containing different concentrations of Fe$_2$O$_3$ is shown in Fig. 3.6. With the increase in the concentration of Fe$_2$O$_3$ the dielectric constant is observed to decrease at any given temperature similar to that at room temperature up to 0.8 mol% of Fe$_2$O$_3$ and beyond that it is found to increase.

**Fig. 3.4** Variation of dielectric constant with frequency at room temperature for K$_2$O-BaO-B$_2$O$_3$ glasses doped with different concentrations of Fe$_2$O$_3$ and inset shows variation of dielectric loss with frequency at room temperature for K$_2$O-BaO-B$_2$O$_3$ glasses doped with different concentrations of Fe$_2$O$_3$.

**Fig. 3.5** Variation of dielectric constant with temperature for glass F$_2$ at different Frequencies.
**Fig. 3.6** A comparison plot of variation of dielectric constant with temperature at 100 KHz for K₂O-BaO-B₂O₃: Fe₂O₃.

**Fig. 3.7** Variation of dielectric loss with temperature for glass F₄ at different frequencies.
The variation of loss $\tan \delta$ with temperature at different frequencies for the glass $F_4$ is shown in Fig. 3.7 and it is found to exhibit a considerable increase at high temperatures especially at lower frequencies. Fig. 3.8 shows the variation of dielectric loss with temperature for all the glasses at a frequency of 1 kHz. The loss curves of pure and $Fe_2O_3$ doped $K_2O-BaO-B_2O_3$ glasses have exhibited distinct maxima; with increasing frequency the temperature maximum shifts towards higher temperature and with increasing temperature the frequency maximum shifts towards higher frequency, indicating the dielectric relaxation character. The comparison of dielectric loss variation with temperature at a particular frequency for different glasses indicates a gradual decrease of relaxation intensity with increase in the concentration of $Fe_2O_3$. Using the standard relation:
\[ f = f_0 \exp \left( -\frac{W_d}{KT} \right) \]  

(3.1)

(where \( f \) is the relaxation frequency which is equal to the reciprocal of the relaxation time \( \tau \)), the effective activation energy \( W_d \), for the dipoles is calculated for different glasses and shown in Table 3.3.

**Table 3.3** Summary of the data on dielectric loss of K\(_2\)O-BaO-B\(_2\)O\(_3\): Fe\(_2\)O\(_3\) glasses.

<table>
<thead>
<tr>
<th>Glass</th>
<th>Loss ((\tan\delta)) (±0.0001)</th>
<th>Temperature region of relaxation (°C) (±1°C)</th>
<th>Activation energy for dipoles (eV) (±0.01)</th>
<th>Spreading factor (\beta) (±0.01)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(F_0)</td>
<td>0.0359</td>
<td>60-80</td>
<td>2.51</td>
<td>0.55</td>
</tr>
<tr>
<td>(F_2)</td>
<td>0.0351</td>
<td>70-90</td>
<td>2.65</td>
<td>0.51</td>
</tr>
<tr>
<td>(F_4)</td>
<td>0.0327</td>
<td>82-100</td>
<td>2.80</td>
<td>0.48</td>
</tr>
<tr>
<td>(F_6)</td>
<td>0.0211</td>
<td>90-110</td>
<td>2.95</td>
<td>0.44</td>
</tr>
<tr>
<td>(F_8)</td>
<td>0.0155</td>
<td>100-120</td>
<td>3.10</td>
<td>0.41</td>
</tr>
<tr>
<td>(F_{10})</td>
<td>0.0248</td>
<td>90-110</td>
<td>2.85</td>
<td>0.46</td>
</tr>
</tbody>
</table>

The activation energy is found to increase with increase in the concentration of Fe\(_2\)O\(_3\) in the glass matrix.

The a.c. conductivity \(\sigma_{ac}\) for different frequencies is calculated at temperatures using the following equation:

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

(3.2)

where \(\varepsilon_0\) is the vacuum dielectric constant.

The plots of log \(\sigma\) against \(1/T\) are shown in Fig. 3.9 for sample \(F_6\) for different frequencies. Fig. 3.10 shows the plot of \(\sigma_{ac}\) against \(1/T\) for all samples at
10 kHz frequency. The variation of $\sigma_{ac}$ vs concentration of Fe$_2$O$_3$ is shown in inset (a) and inset (b) of Fig. 3.10 gives the variation of conductivity with activation energy. From these plots, the activation energy for conduction, in the high temperature region over which a near linear dependence of $\log \sigma$ with $1/T$ could be observed, is evaluated and presented in Table 3.4; the activation energy is found to increase with increase in the concentration of Fe$_2$O$_3$ up to 0.8 mol%. Further the variation of $\sigma_{ac}$ with the concentration (up to 0.8 mol %) of Fe$_2$O$_3$ shows a decreasing trend as shown in Fig. 3.10.

**Table 3.4** Summary of data on ac conductivity $\sigma_{ac}$ for K$_2$O-BaO-B$_2$O$_3$:Fe$_2$O$_3$ glasses.

<table>
<thead>
<tr>
<th>Glass</th>
<th>$\sigma_{ac}$ (X10$^{-8}$) (Ω-cm)$^{-1}$ (±0.01)</th>
<th>N(E$_F$) in (10$^{20}$, eV$^{-1}$/cm$^3$)</th>
<th>Activation energy for conduction (eV) (±0.01)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F$_0$</td>
<td>10.60</td>
<td>-</td>
<td>0.15</td>
</tr>
<tr>
<td>F$_2$</td>
<td>7.47</td>
<td>5.58</td>
<td>5.67</td>
</tr>
<tr>
<td>F$_4$</td>
<td>5.72</td>
<td>4.88</td>
<td>4.96</td>
</tr>
<tr>
<td>F$_6$</td>
<td>1.74</td>
<td>2.69</td>
<td>2.74</td>
</tr>
<tr>
<td>F$_8$</td>
<td>0.56</td>
<td>1.52</td>
<td>1.55</td>
</tr>
<tr>
<td>F$_{10}$</td>
<td>3.42</td>
<td>3.77</td>
<td>3.84</td>
</tr>
</tbody>
</table>
Fig. 3.9 Variation of $\sigma_{ac}$ with $1/T$ for glass F$_6$ at different frequencies.

Fig. 3.10 A comparison plot of variation of a.c. conductivity with $1/T$ at 10 KHz for K$_2$O-BaO-B$_2$O$_3$: Fe$_2$O$_3$ glasses.
Inset (a) gives the variation of a.c. conductivity with the concentration of Fe$_2$O$_3$ measured at 10 KHz at 200 °C.
Inset (b) gives the variation of conductivity with the activation energy.
**Fig. 3.11** A Pseudo Cole-Cole plot for glass F₆ drawn at 10 KHz.

### 3.5 Discussion

#### 3.5.1 FTIR

It is well known that the effect of introduction of alkali oxides like K₂O into B₂O₃ glass network is the conversion of sp² planar BO₃ units into more stable sp³ tetrahedral BO₄ units and may also create non-bridging oxygens. Each BO₄ unit is linked to two such other units and one oxygen from each unit with a metal ion and the structure leads to the formation of long tetrahedron chains. The evidence for the presence of BO₃ and BO₄ structural units can be seen from the IR spectra of these glasses. 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 (Ba²⁺ ions) take the interstitial positions.
With the increase of Fe\textsubscript{2}O\textsubscript{3} content in the glass network, the intensity of second group of bands (bands due to BO\textsubscript{4} units) is observed to decrease up to maximum concentration with a shifting of meta center towards slightly higher wave number up to 0.4 mol %, beyond this concentration the meta center is found to shift towards slightly lower wave number. The intensity of first group of bands (bands due to the BO\textsubscript{3} structural units) is also observed to decrease until the last concentration but it is noticed almost the reverse trend in the shift of meta center compared to that of BO\textsubscript{4} structural units. This observation clearly suggests, there is an increase in the rigidity of the glass network with increasing concentration of Fe\textsubscript{2}O\textsubscript{3} up to 0.8 mol% in the glass matrix.

3.5.2 ESR spectra

The ESR spectra of Fe\textsubscript{2}O\textsubscript{3} doped glasses exhibit an intense sharp resonance signal at \( g = 4.25 \pm 0.05 \), a moderately intense signal at \( g = 2.01 \pm 0.05 \) and a shoulder in the region of \( g = 6.2 \pm 0.5 \) \cite{24,30,32}. A trivalent iron ion Fe\textsuperscript{3+} has electronic configuration 3d\textsuperscript{5} corresponding to half filled d shell and is particularly most stable. Since the iron ions in Fe\textsuperscript{3+} state belonging to d\textsuperscript{5} configuration with 6S as ground state in the free ion and there is no spin orbit interaction \cite{30}. The \( g \) value is expected to lie very near the free ion value of 2.0023. However, the \( g \) value very much greater than 2.0023 often occurs; in particular an isotropic \( g \) value of 4.02 occurs and these large values arise when certain symmetry elements are present in the Hamiltonian.
When Fe$^{3+}$ impurity complexes are present in crystal field with large axial component, the free ion ground state i.e., 6S splits into three Kramer doublets $|\pm 5/2>$, $|\pm 3/2>$ and $|\pm 1/2>$ with separation usually greater than the micro wave quantum. Normally the selection rules permit ESR transitions in the $|\pm 1/2>$ doublet with $g$ approximately 2.0 and 6.0 [32].

In large number of glasses and other Fe$^{3+}$ containing materials a symmetric and isotropic line at $g$ approximately 4.0-4.2 is observed. Castner et.al. explained it as arising from the middle Kramer doublet containing admixture of different $|\pm m_j>$ states, which are caused by the presence of lower symmetry term i.e., E $(S_x^2-S_y^2)$ in the Hamiltonian. The ESR spectra of Fe$^{3+}$ ions in various glasses have been extensively studied [24,30,32]. Usually the two resonance signals occurring at $g=4.2$ and 2.0 have been reported. In some cases the resonance near $g=6.0$ is also observed as a shoulder of the resonance near $g = 4.2$ [30]. So the resonance at $g = 4.2$ and 2.0 have been interpreted in different ways. Some researchers suggested the value of $g$ in glasses containing Fe$^{3+}$ ions is related to the coordination. The absorption at $g = 4.2$ and 2.0 arise from Fe$^{3+}$ ion in tetrahedral and octahedral coordination respectively [30]. In the present ESR spectra the intensity of the resonance line at $g = 4.25$ is found to increase with increase of concentration up to 0.8 mol%, beyond that it is observed to decrease. The ESR spectral study indicates the presence of iron ions predominantly in Fe$^{3+}$ state which participates in the substitutional position and make the glass network more
rigid up to 0.8 mol%, beyond this the presence of some of the Fe$^{3+}$ ions are being converted into Fe$^{2+}$ ions, as a result the intensity of line is found to decrease.

### 3.5.3 Dielectric properties

The dielectric constant of a material is due to electronic, ionic, dipolar and space charge polarizations. Out of these, the space charge contribution will depend on the purity and the perfection of the glasses. Its influence is in general negligible at very low temperatures and noticeable in the low frequency region. The dipolar effects can sometimes be seen in the glasses even up to $10^6$ Hz. Recollecting the data the slight increase in the dielectric constant and loss at room temperature, particularly at low frequencies for K$_2$O-BaO-B$_2$O$_3$: Fe$_2$O$_3$ glasses may be ascribed to the defects produced in the glass network which contribute to the space charge polarization. The defects thus produced create easy pathways for the migration of charges that would build up space charge polarization leading to the increase in the dielectric parameters as observed [32,33].

With the gradual increase in the content of Fe$_2$O$_3$ up to 0.8 mol% in the glass matrix, the values $\varepsilon'$, $\tan\delta$ and $\sigma_{ac}$ are found to decrease at any frequency and temperature and beyond that concentration these parameters are found to increase while the value of activation energy for a.c. conduction is observed to follow the reverse trend. This is because of a gradual increase in the concentration of iron ions that exist in Fe$^{3+}$ state, that take part network forming positions. As a result
there will be a decrease in the space charge polarization leading to a decrease in the values of dielectric parameters, as observed.

Yet, another evidence for the presence of iron ions in Fe\(^{2+}\) state in higher concentrations in the glass F\(_2\) can be established from the data on dielectric loss; in general, the dielectric relaxation effects are observed only when the metal ions present, are in the divalent state [32-34]. The divalent ions of iron together with a pair of any cationic vacancies may form dipoles and such dipoles are responsible for the observed dielectric relaxation effects in the pure and Fe\(_2\)O\(_3\) doped K\(_2\)O-BaO-B\(_2\)O\(_3\) glasses. Hence, the divalent ions of barium together with a pair of any cationic vacancies may also form dipoles and such dipoles are responsible for the observed dielectric relaxation effects.

To know whether there is single relaxation time or spreading of relaxation times in K\(_2\)O-BaO-B\(_2\)O\(_3\): Fe\(_2\)O\(_3\) glasses, we have adopted a pseudo Cole-Cole plot method (instead of conventional Cole-Cole plot between \(\varepsilon'(\omega)\) and \(\varepsilon''(\omega)\) at a fixed temperature) suggested by Sixou [35] in which \(\varepsilon'(T)\) versus \(\varepsilon''(T)\) is plotted at a fixed frequency. As mentioned before, we have observed decrease in \((\tan\delta)_{\text{max}}\) with increase in Fe\(_2\)O\(_3\) concentration for the present glasses. Further, the nature of variation of \(\varepsilon'(T)\) and \(\tan\delta\) with temperature for these glasses indicates that the Cole-Davidson Eq [35].:

\[
\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{(1 + i\omega\tau)^\beta}
\]  
(3.3)
can safely be applied to these glasses. Separating real and imaginary terms of Eq.(3.3) and rewriting with explicit temperature dependence of terms:

\[
\varepsilon'(\omega, T) = \varepsilon_\infty + (\varepsilon_s - \varepsilon_\infty)[\cos\phi(T)]^\beta \cos\beta\phi(T)
\]  

(3.4)

and

\[
\varepsilon''(\omega, T) = (\varepsilon_s - \varepsilon_\infty)[\cos\phi(T)]^\beta \sin\beta\phi(T)
\]  

(3.5)

where \( \phi(T) = \tan^{-1}(\omega\tau) = \tan^{-1}(\omega A_0 e^{W_d/\kappa T}) \) (3.6)

In Eq. (3.6) \( A_0 \) is a constant and \( W_d \) is the activation energy for the dipoles. The plot between \( \varepsilon'(T) \) and \( \varepsilon''(T) \) given by Eqs. (3.4) and (3.5) at a fixed frequency is conventionally called as pseudo Cole-Cole plot, which cuts \( \varepsilon' \) axis at \( \varepsilon_s \) and \( \varepsilon_\infty \). Here, \( \varepsilon_s \) is known as high temperature dielectric constant (in contrast to the low frequency dielectric constant in the conventional Cole-Cole plot) and similarly \( \varepsilon_\infty \) is the low temperature dielectric constant. The plot cuts \( \varepsilon' \) axis (as per Sixou) at low temperature side at an angle of \( \beta (\pi/2) \), where \( \beta \) is the spreading factor for relaxation times. For \( K_2O-BaO-B_2O_3 \) glass containing 0.6 mol % of \( Fe_2O_3 \) (glass \( F_6 \)), the pseudo Cole-Cole plot at 10 kHz is shown in Fig. 3.11. From this plot, the value of \( \beta \) is estimated to be 0.44. Such plots have also been drawn for all other glasses and the value of \( \beta \) is estimated in a similar way and the values are found to be \( \beta = 0.55( F_0 ), 0.51( F_2 ), 0.48( F_4 ), 0.44( F_6 ), 0.41( F_8 ), 0.46( F_{10} ). \) The close look on these values shows that value of \( \beta \) to decrease with increase in the concentration of \( Fe_2O_3 \) from 0.2 to 0.8 mol %. The spreading of relaxation times in
these glasses may be understood due to the participation of Fe$^{2+}$ ions also along with barium ions in dipolar relaxation effects.

Among various mechanisms of conduction in the amorphous materials (such as band conduction, conduction in extended states, conduction in localized states near the band edge and conduction in localized states near the Fermi level), the conduction in the localized states near the Fermi level occurs when a conductivity is nearly temperature independent and varies linearly with frequency. The conduction in present $\text{K}_2\text{O-BaO-B}_2\text{O}_3$: Fe$\text{2O}_3$ glasses in the low temperature region (up to nearly 330 K) can safely be attributed to take place by this mechanism. The value of $N(E_F)$, i.e., the density of energy states near Fermi level, for a frequency of $10^5$ Hz and at 330 K is evaluated on the basis of quantum mechanical tunneling model using the equation:

$$\sigma(\omega) = \eta e^2 K T [N(E_F)]^2 \omega^5 \alpha^4 [ln(\nu_{ph}/\omega)]^4$$

(3.7)

With the usual meaning of the symbols (with the value of $\eta = \pi/3$ (Austin and Mott) [33], $=3.66\pi^2/6$ (Butcher and Hyden) [33], $=\pi^3/96$ (Pollak) [33] and the procedure reported in earlier papers [20,34-37]. The value of $N(E_F)$ is observed to decrease with the increase in the concentration of Fe$\text{2O}_3$. Further more, the range of $N(E_F)$ values obtained $\sim 10^{20}$ eV$^{-1}$/cm$^3$; such values of $N(E_F)$ suggest the localized states near the Fermi level.
3.6 Conclusions

From the analysis of dielectric studies coupled with spectroscopic properties of present glass system it has been observed that when iron present in the lower concentration up to 0.8 mol % the iron ions exist in Fe\textsuperscript{3+} state that take modifier as well as former positions and it is also supported by ESR spectra in terms of variation of intensity of the resonance peak and beyond this concentration part of the iron ions exist in Fe\textsuperscript{2+} state that take network modifier positions and weakens structure of the glass system.
Section-II Influence of alkaline earth oxides (R = Ca, Sr and Ba) on spectroscopic and dielectric studies of iron doped RO-Na2O-B2O3 glasses

3.7 Characterization

3.7.1 X-Ray diffraction

The X-ray diffraction pattern of the BNBF glass is presented in Fig. 3.12. The absence of sharp Bragg’s peaks in the pattern indicates the amorphous nature of the samples.

**Fig. 3.12** XRD pattern of the 20BaO-10Na2O-69B2O3-1Fe2O3 glass.

3.7.2 Physical parameters

The samples prepared were free from visible in homogeneities such as inclusions, cracks or bubbles. From the measured values of density \( \rho \) and the
average molecular weight $M$ of the samples, various physical parameters such as iron ion concentration $N_i$, mean iron ion separation $r_i$ and polaron radius $r_p$ are calculated and presented in Table 3.5 along with the refractive index ($\mu$) values of the present samples. The measured density of CNBF glass is found to be 2.7089 g/cm$^3$ and is gradually increased by the substitution of CaO with SrO and BaO. A similar trend in refractive index and molar volume is also observed as given in Table 3.5. This result is 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 [38]. From the Table 3.5 it is clear that as CaO is substituted by SrO and BaO in the investigated glass samples an increase in the glass density is seen followed by an increase in the molar volumes which suggest that the glass network become less compact.

**Table 3.5** The density $\rho$, average molecular weight $M$, molar volume $V_m$, Fe$^{3+}$ ion concentration $N_i$, mean Fe$^{3+}$ ion separation $R_i$, polaron radius $R_p$ and refractive index $\mu$ of the glasses 20RO-10Na$_2$O-69B$_2$O$_3$-1Fe$_2$O$_3$ [ where $R = \text{Ca, Sr and Ba} ]$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\rho$ (g/cm$^3$)</th>
<th>$M$ (g/mol)</th>
<th>$V_m$ (cm$^3$/mol)</th>
<th>$N_i \times 10^{21}$ (ions/cm$^3$)</th>
<th>$R_i$ (Å)</th>
<th>$R_p$ (Å)</th>
<th>$\mu$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNBF</td>
<td>2.7089</td>
<td>67.0468</td>
<td>24.7506</td>
<td>24.335</td>
<td>3.451</td>
<td>1.391</td>
<td>1.651</td>
</tr>
<tr>
<td>SNBF</td>
<td>2.9789</td>
<td>76.5552</td>
<td>25.6992</td>
<td>23.437</td>
<td>3.494</td>
<td>1.408</td>
<td>1.656</td>
</tr>
<tr>
<td>BNBF</td>
<td>3.1829</td>
<td>86.4966</td>
<td>27.1754</td>
<td>22.164</td>
<td>3.560</td>
<td>1.435</td>
<td>1.658</td>
</tr>
</tbody>
</table>
3.8 Results
3.8.1 Electron Spin Resonance

The ESR spectra of present samples recorded at room temperature are shown in Fig. 3.13. The intense line centered at about \( g = 4.28 \) could clearly be seen in the spectra of these glasses, a weak resonance line at \( g = 2.04 \) is observed and a shoulder of the resonance centered at \( g = 8.03 \) is also observed. Interestingly, by the substitution of CaO with SrO in CNBF glass sample the intensity of the signals at \( g = 4.28 \) and 2.04 are slightly increased and then decreased with further substitution of BaO as shown in the figure.

![ESR spectra](image)

**Fig. 3.13** ESR spectra of 20RO-10Na\(_2\)O-69B\(_2\)O\(_3\)-1Fe\(_2\)O\(_3\) glass matrices [where R=Ca, Sr and Ba ].
3.8.2 Optical Absorption

The optical absorption spectrum of RNBF glasses doped with fixed (1 mol %) concentration of Fe$_2$O$_3$, at room temperature in the wavelength region 400-1400 nm is shown in Fig. 3.14 and its inset shows the absorption spectra observed in the region 400 to 500 nm. The absorption spectrum of CNBF glass has exhibited a band around 448 nm and is slightly red shifted to 452 nm and broadened with the substitution of SrO. Further substitution of SrO with BaO is interestingly shifted the band position to 449 nm and a new broad band around 1000 nm is also observed in BNBF glass sample.

The short wavelength absorption edge (SWAE) provides very useful information on the band structure around the energy gap. As shown in Fig. 3.15 the fundamental (SWAE) or cut-off wavelength $\lambda_c$, which shows the rapid rise in the absorption coefficient, of CNBF sample is observed at 369 nm and is blue shifted to 366 nm with the substitution of SrO and then red shifted to 370 nm with further substitution of BaO in the glass matrix. Fig. 3.16 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 and Davis [39]. As mentioned in Table 3.6 all the $E_g$ values are measured by extrapolating the linear region of the graph to meet X-axis i.e, $(\alpha h\nu)^{1/2} = 0$. Among all the investigated samples the $E_g$ value is maximum for SNBF (3.307 eV) and is minimum for BNBF (3.283 eV).
**Fig. 3.14** Optical absorption spectra of RNBF glasses in the wavelength range 400-1400 nm. Inset shows the absorption spectra of the samples in the region (400-500 nm).

**Fig. 3.15** Short wave length absorption spectra of RNBF glasses.
Fig. 3.16 Urbach plots for optical gap of prepared glasses.

Fig. 3.17 $\ln(\alpha)$ versus $h\nu$ (photon energy) plots of RNBF glasses.
A very useful parameter in determining defect states known as Urbach energy is obtained from absorption coefficient $\alpha(\nu)$ values in Urbach’s exponential tail region lying between $10^2$ and $10^4$ cm$^{-1}$ [40] are given by Eq 3.8.

$$\alpha(\nu) = C \exp \left( \frac{h\nu}{\Delta E} \right)$$

(3.8)

Where $C$ is a constant and $\Delta E$ is the Urbach’s energy interpreted as the energy gap between localized tail states in the forbidden region. $\Delta E$ values are determined by taking the reciprocals of the slopes of the linear portion of the $\ln \alpha(\nu)$ vs. $h\nu$ plots as shown in Fig 3.17. These values are included in Table 3.6. From the Table it is clear that the $\Delta E$ value is minimum (0.261 eV) for the SNBF glass and maximum (0.291) for the BNBF glass samples.

**Table 3.6** Cut off wavelength ($\lambda_c$), absorption band positions, optical band gap ($E_g$), Urbach energy ($\Delta E$) and theoretical optical basicity ($\Lambda_{th}$) of the glasses 20RO-10Na$_2$O-69B$_2$O$_3$-1Fe$_2$O$_3$ [ where R = Ca, Sr and Ba ].

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\lambda_c$ (nm)</th>
<th>Band position (nm) $\pm$0.1</th>
<th>Band position (nm) $\pm$0.1</th>
<th>$E_g$ (eV) $\pm$0.001</th>
<th>$\Delta E$ (eV) $\pm$0.001</th>
<th>$\Lambda_{th}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNBF</td>
<td>369</td>
<td>448</td>
<td>--</td>
<td>3.293</td>
<td>0.265</td>
<td>0.489</td>
</tr>
<tr>
<td>SNBF</td>
<td>366</td>
<td>449</td>
<td>--</td>
<td>3.307</td>
<td>0.261</td>
<td>0.497</td>
</tr>
<tr>
<td>BNBF</td>
<td>370</td>
<td>452</td>
<td>1000</td>
<td>3.283</td>
<td>0.291</td>
<td>0.509</td>
</tr>
</tbody>
</table>

**3.8.3 Theoretical Optical basicity ($\Lambda_{th}$)**

Theoretical optical basicity values of all glasses are calculated [41] using the equation (3.9) and are presented in Table 3.6.
Here ‘n’ is the number of cations present, $Z_i$ is the oxidation number of the $i^{th}$ cation, $r_i$ is the ratio of the number of $i^{th}$ cation to the number of oxides present and $\gamma_i$ is the basicity moderating parameter of the $i^{th}$ cation. Using the following equation (3.10) the ‘$\gamma_i$’ values are calculated.

$$\gamma_i = 1.36(x_i - 0.26)$$

where ‘$x_i$’ is Pauling electro negativity of the cation. It is observed that by the substitution of CaO with SrO and BaO in the glass network the value of optical basicity is increased.

### 3.8.4 FTIR

Fig 3.18 represents the IR transmission spectra of as prepared RNBF glasses. The obtained band positions and their corresponding assignments are presented in Table 3.7. From the figure the observed broad bands are due to the convolution of individual bands with each other. In CNBF glass matrix the principle bands are observed at 1378, 1020, 696 and 468 cm$^{-1}$ with shoulders around 1252 and a small feeble band is also observed at 766 cm$^{-1}$. By the substitution of CaO with SrO and BaO the centers of the bands around 1378, 696 and 468 are slightly blue shifted to 1387, 704 and 471 cm$^{-1}$ while the bands around 1252 and 1020 cm$^{-1}$ are red shifted to 1234 and 991 cm$^{-1}$ respectively (for BNBF glass sample). Interestingly a new band is found at 1513 cm$^{-1}$ in BNBF glass matrix.
Fig. 3.18 FTIR spectra of 20RO-10Na$_2$O-69B$_2$O$_3$-1Fe$_2$O$_3$ glasses [where R=Ca, Sr and Ba].
Table 3.7 Assignment of vibrational modes in the FTIR spectra (with a probable resolution of ±0.5 cm\(^{-1}\)) of 20RO-10Na\(_2\)O-69B\(_2\)O\(_3\)-1Fe\(_2\)O\(_3\) [ where R = Ca, Sr and Ba ].

<table>
<thead>
<tr>
<th>CNBF</th>
<th>SNBF</th>
<th>BNBF</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>468</td>
<td>470</td>
<td>471</td>
<td>A doubly degenerate vibrating band due to O-B-O bond bending vibrations and Fe-O bonds stretching vibrations of FeO(_6) units.</td>
</tr>
<tr>
<td>696</td>
<td>696</td>
<td>704</td>
<td>B-O-B bending vibrations and specific vibrations of Fe-O bonds in FeO(_4) structural units</td>
</tr>
<tr>
<td>766</td>
<td>765</td>
<td>--</td>
<td>O(_3)B-O-BO(_4) bonds bending vibrations.</td>
</tr>
<tr>
<td>1020</td>
<td>999</td>
<td>991</td>
<td>Stretching vibrations of B-O bonds in BO(_4) units from tri, tetra and penta borate groups.</td>
</tr>
<tr>
<td>1252</td>
<td>1245</td>
<td>1234</td>
<td>B-O(_{\text{sym}}) stretch in BO(_3) units from pyro and ortho borate groups</td>
</tr>
<tr>
<td>1378</td>
<td>1384</td>
<td>1387</td>
<td>B-O(_{\text{sym}}) stretch in BO(_3) units from varied types of borate groups</td>
</tr>
<tr>
<td>--</td>
<td>--</td>
<td>1213</td>
<td>B-O(^{-}) stretch in BO(_2)O(^{-}) units from varied types of borate groups</td>
</tr>
</tbody>
</table>

3.8.5 Dielectric Studies

The dielectric constant \(\varepsilon'\) and loss tan\(\delta\) of CaO-Na\(_2\)O-B\(_2\)O\(_3\)-Fe\(_2\)O\(_3\) glass at 10 KHz and room temperature (30\(^\circ\)C) are measured to be 9.78 and 0.01121, respectively; and are found to increase with the decrease in frequency. The temperature dependence of \(\varepsilon'\) of the glasses with different modifier oxides at 1KHz is shown in Fig 3.19 and inset shows the variation of dielectric constant with temperature at different frequencies of SNBF glass network. The values of \(\varepsilon'\) are found to exhibit a considerable increase at higher temperatures especially at
lower frequencies; the rate of increase of ε' with temperature is found to be the highest for the BNBF glass and it is minimum for SNBF glass.

![Comparison plot of variation of dielectric constant with temperature at 1KHz for RO-Na₂O-B₂O₃: Fe₂O₃ glasses [where R=Ca, Sr and Ba]. Inset of the figure shows the variation of dielectric constant at different frequencies for glass SNBF.](image)

**Fig. 3.19** Comparison plot of variation of dielectric constant with temperature at 1KHz for RO-Na₂O-B₂O₃: Fe₂O₃ glasses [where R=Ca, Sr and Ba]. Inset of the figure shows the variation of dielectric constant at different frequencies for glass SNBF.

The temperature dependence of tanδ of all the glasses measured at a frequency of 10 KHz is presented in Fig 3.20. The inset of the figure shows the variation of tanδ for BNBF at different frequencies. These curves have exhibited distinct maxima; with increase in frequency the peak maximum shifts towards higher temperature indicating the dielectric relaxation character of dielectric losses of these glasses. The relaxation intensity is found to be maximum for the BNBF glass and minimum for SNBF glass. From the figures, the effective
The activation energy for dipoles ($W_d$) is calculated for all glass matrices and presented in Table 3.8; the activation energy is found to be the lowest for the BNBF glass and highest for the SNBF glass.

**Table 3.8** Summary of the data on dielectric loss of 20RO-10Na$_2$O-69B$_2$O$_3$-1Fe$_2$O$_3$ [where R = Ca, Sr and Ba].

<table>
<thead>
<tr>
<th>Glass</th>
<th>$(\text{Tan} \delta)_{\text{Avg}}$</th>
<th>Temp. Region of relaxation (°C)</th>
<th>Activation energy for dipoles (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNBF</td>
<td>0.013</td>
<td>90-122</td>
<td>2.776</td>
</tr>
<tr>
<td>SNBF</td>
<td>0.008</td>
<td>110-135</td>
<td>2.836</td>
</tr>
<tr>
<td>BNBF</td>
<td>0.015</td>
<td>80-115</td>
<td>2.761</td>
</tr>
</tbody>
</table>

The ac conductivity $\sigma_{ac}$ is evaluated at different temperatures from the values of dielectric constant and loss $\text{Tan} \delta$ using the conventional equation and its variation with $1/T$ for all the glasses at 100 KHz is presented in Fig 3.21. $\sigma_{ac}$ is found to be the highest for the glass BNBF at any temperature. The variation of ac conductivity with temperature is found to exhibit a plateau up to 110 °C and thereafter (beyond the relaxation region) it is increased rapidly exhibiting the highest rate of increase for the glass BaO. From these plots, the activation energy for the conduction, in the high temperature region over which a near linear dependence of log $\sigma_{ac}$ with $1/T$ could be observed, is evaluated and presented in the Table 3.9. The break down strength is maximum (8.75 kV/cm) for the SNBF glass matrix and is minimum (6.67 kV/cm) for the BNBF glass network, it is also included in Table 3.9.
**Fig. 3.20** Variation of dielectric loss with temperature of all glasses at a frequency 10 KHz. The inset of figure shows the variation of dielectric loss with temperature for sample BNBF.

**Table 3.9** Summary of data on ac conductivity $\sigma_{ac}$ for 20RO-10Na$_2$O-69B$_2$O$_3$-1Fe$_2$O$_3$ [where R = Ca, Sr and Ba].

<table>
<thead>
<tr>
<th>Glass</th>
<th>$\sigma_{ac}$ ($\times 10^{-11}$) ($\Omega$·cm)$^{-1}$</th>
<th>N ($E_F$) in ($10^{22}$ eV$^{-1}$/cm$^3$)</th>
<th>Activation energy for conduction (eV)</th>
<th>Breakdown strength (kV/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Austin and Mott</td>
<td>Butcher and Hyden</td>
<td>Pollak</td>
</tr>
<tr>
<td>CNBF</td>
<td>4.526</td>
<td>4.074</td>
<td>1.699</td>
<td>4.138</td>
</tr>
<tr>
<td>SNBF</td>
<td>2.324</td>
<td>2.642</td>
<td>1.102</td>
<td>2.683</td>
</tr>
<tr>
<td>BNBF</td>
<td>5.950</td>
<td>4.228</td>
<td>1.763</td>
<td>4.294</td>
</tr>
</tbody>
</table>
3.9 Discussion

3.9.1 Electron Spin Resonance

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 belongs to d$^5$ configuration with 6S as ground state in the free ion and there is no spin–orbit interaction [42]. 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 arise 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 [43]
\[ H = g \beta BS + D \left[ S_Z^2 - \frac{S(S+1)}{3} \right] + E(S_x^2 - S_y^2) \] (3.11)

Where \( S = 5/2 \). Here \( D \) and \( E \) are the axial and rhombic structure parameters, \( \lambda = \frac{E}{D} \) lies within the limits \( 0 < \lambda < 1/3 \) [44]. The EPR spectra of \( \text{Fe}^{3+} \) ions containing glasses are generally characterized by the appearance of resonance signals at \( g = 2.1 \), \( g = 4.2 \) and \( g = 8.0 \) with their relative intensities being strongly dependent on composition [45-48]. This feature at \( g = 4.2 \) is due to rhombic distortions of the crystal field around \( \text{Fe}^{3+} \) ions [48]. In a large number of glasses containing \( \text{Fe}^{3+} \) ions a symmetric and isotropic line at \( g \approx 4 \) to 4.2 is observed. Castner et al. [49] explained it as when \( \text{Fe}^{3+} \) ions are placed in a crystal field environment, the 6\( S \) 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 mainly consists of a broad resonance signal at \( g \approx 2.04 \), an intense resonance signals at \( g \approx 4.28 \) and a shoulder in the region of \( g \approx 8.03 \). The resonance at \( g \approx 4.28 \) is attributed to the isolated \( \text{Fe}^{3+} \) ions predominantly situated in rhombically distorted octahedral sites where as \( g \approx 8.03 \) resonance arises from axially distorted sites, respectively. The \( g \approx 2.04 \) resonance may be attributed to either \( \text{Fe}^{3+} \) 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 \( \text{Fe}_2\text{O}_3 \) is fixed in the present glass compositions the increase in signal intensity and area of the resonance signals around \( g \approx 2.04 \) and \( g \approx 4.28 \) in SNBF glass matrix indicates the
existence of higher concentration of Fe\textsuperscript{3+} ions in SNBF glass matrix than the remaining glass matrices. The reason might be as follows:

Whenever modifier oxides in the glass matrix were changed they alter the glass-forming ability associates with the cation compatibilities due to various levels of their ionic radii and polarizabilities, consequently reduction of Fe\textsuperscript{3+} cations to Fe\textsuperscript{2+} ions (Fe\textsuperscript{3+} + e\textsuperscript{-} → Fe\textsuperscript{2+}) occurs during melting and annealing processes since it takes place only with $E^0 = 0.77$ eV [50].

### 3.9.2 Optical Absorption

It is known, from the famous Tanabe-Sugano diagram of d\textsuperscript{5} ions, Fe\textsuperscript{3+} ions never show any spin-allowed transitions and generally give 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\textsuperscript{3+} ions with distorted octahedral symmetry [30]. In all the present studied glasses the band around 450 nm may be due to the later transition i.e., $^6A_1g(S)\rightarrow^4E_g(G)$. Moreover, an absorption band around 1000 nm in BNBF glass is attributed to $^5T_{2g}\rightarrow^5E_g$ transition of Fe\textsuperscript{2+} (d\textsuperscript{6}) ions [34]. The formation of this band is clearly indicates the formation and/or increase of Fe\textsuperscript{2+} ions concentration through the reduction of Fe\textsuperscript{3+} ions, which also supports the decrease in ESR signal intensity around $g\approx 4.2$ in BNBF glass matrix. The more understanding in this concern is augmented by collecting the calculated $N_i$ values of Fe\textsuperscript{3+} ions from measured densities of the present glasses. From Table 3.5, $N_i$ values of Fe\textsuperscript{3+} ions are gradually decreased with the substitution of BaO though
Fe$_2$O$_3$ concentration is fixed in the composition. These results suggest that the reduction of Fe$^{3+}$ into Fe$^{2+}$ is favorable in BNBF glass matrix. The fluctuation of absorption band around 450 nm with fixed concentration of iron indicates that iron ions were affected due to presence of different modifier oxides in the glass matrix. Such fluctuations may be due to the variation of energy separation between the $^6$A$_{1g}$($S$) and $^4$E$_g$($G$) energy levels [51]. The fluctuations in the band position are consequences by variations either in Fe-O bond length or in radial position of electron cloud or in both of them.

The maximum band gap in SNBF glass matrix is explained by considering the large area of ESR signal and optical band at 452 nm corresponding to Fe$^{3+}$ ions. The presence of a large number of Fe$^{3+}$ ions takes place in network forming positions in the glass matrix and consequently reduces the non bridging oxygens (NBOs). The minimum $E_g$ value in BNBF glass matrix suggests that the formation of a large number of non bridging oxygens (NBOs) occurs by the substitution of CaO with BaO in the glass network, which predictably affects the structural properties. The addition of BaO to the B$_2$O$_3$ matrix undertakes web incorporations in the form of $BaO_n$ polyhedron groups. The negative charge on the polyhedron pushes transition metals to form the bond within the network. Thus the concentration of bridging oxygens (BO) is decreased. Such effect is very strong in BNBF due to the higher deformability of the larger radius of Ba-ions. The decrease of optical band gap in the BNBF glass matrix is also explained on the basis of ratios of Fe$^{3+}$/Fe$^{2+}$ and/or Fe$^{3+}$/ΣFe which are controlled by the glass-
modifying admixtures of the glass composition, which generally affect the level of NBO. Several researchers [52,53] observed that NBO content in the melt increases with decrease of Fe$^{3+}$/Fe$^{2+}$ ratio. In compliance with a decrease of the ESR signal corresponding to Fe$^{3+}$ ions and an increase of absorption band corresponding to Fe$^{2+}$ at 1000 nm, the decrease of optical band gap is ascribed to the increase of NBO due to decrease of Fe$^{3+}$/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 [40].

The observed minimum Urbach energy for SNBF indicates the least width of the tails among investigated samples. The increase in $\Delta E$ value with the substitution of BaO is due to formation of defects like wrong bonds and fluctuations in bond angle distortions [40]. The additional factor contributing to edge broadening is static disorder which increases the density of localized states $N(E_F)$ of these defects.

3.9.3 Theoretical Optical basicity ($\Lambda_{th}$)

From Table 3.6, 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. 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 [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.

3.9.4 FTIR

It is widely accepted that 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 (RO) into glass network transfers the BO$_4$ tetrahedral into BO$_3$, by forming a RO$_n$ polyhedron when it is surrounded by several BO$_4$ tetrahedrons [57]. 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 [58]. The bands at 766 and 696 cm$^{-1}$ are attributed to O$_3$B-O-BO$_4$ and B-O-B bending vibrations respectively and the broad ness of later band is due to specific vibrations of Fe-O bonds in FeO$_4$ units. A feeble band around 468 cm$^{-1}$ is ascribed to degenerate vibrational bands of O-B-O bending vibrations and Fe-O bonds of FeO$_6$ units. With the replacement of CaO by SrO the area of the band around 1020 cm$^{-1}$ is observed to increase and is clearly indicating that the conversion of some
BO₃ units into BO₄ units occurred. Moreover the intensity of the vibrational band at 468 cm⁻¹ corresponding to FeO₆ units is drastically decreased. In reminiscence with the increase in ESR signal intensity and optical band gap values; the observed decrease in FeO₆ units in the SNBF glass matrix indicates the increase in FeO₄ units. Interestingly, with further substitution of BaO the band intensity corresponding to BO₃ and FeO₆ units is increased and a new band at 1513 cm⁻¹ indicates the formation of BO₂O⁻ units which consists of NBOs. In compliance with the structural changes inferred from IR studies, the observed decrease in band gap and increase in ΔE [Table 3.6] induced by the substitution of BaO in the glass network might be explained by the increase of BO₃ and FeO₆ structural units along with the increase of NBOs (with increase of B-O⁻ bonds).

### 3.9.5 Dielectric Studies

The dielectric constant of a substance is due to electronic, ionic, dipolar and space charge polarizations. Among these, space charge polarization depends on the purity and the perfection of the glasses. Its influence is in general negligible at very low temperatures and noticeable in the low frequency region. The dipolar effects can some times be seen in the glasses even up to 10⁶ Hz. Recollecting the data the slight increase in the dielectric constant and loss at room temperature, particularly at low frequencies for RNBF glasses may be ascribed to the defects produced in the glass network which contribute to the space charge polarization. The defects thus produced create easy path ways for
the migration of charges that would build up space charge polarization leading to
the increase in the dielectric parameters as observed [34,59].

The values of dielectric constant $\varepsilon'$, loss tan$\delta$ and ac conductivity $\sigma_{ac}$ are
found to decrease with the substitution of SrO and then increased with BaO as
modifier oxide at any frequency and temperature. The activation energy for ac
conduction is observed to follow the reverse trend. This is because of a gradual
increase in the concentration of iron ions that exist in Fe$^{3+}$ state, that take part
network forming positions FeO$_4$ units in the SNBF glass matrix. As a result there
will be a decrease in the space charge polarization leading to a decrease in the
values of dielectric parameters, as observed.

However the BNBF glass network is confirmed the existence of the
presence of iron ions in Fe$^{2+}$ state, which is established from the absorption band
at 1000 nm in optical absorption data; in general, the dielectric relaxation effects
are observed only when the metal ions present in the divalent state [34,59]. The
divalent ions of iron together with a pair of any cationic vacancies may form
dipoles and such dipoles are responsible for higher values of the observed
dielectric relaxation effects in the glasses.

Among various mechanisms of conduction in the amorphous materials
(such as band conduction, conduction in extended states, conduction in localized
states near the band edge and conduction in localized states near the Fermi
level), the conduction in the localized states near the Fermi level occurs when ac
conductivity is nearly temperature independent and varies linearly with
frequency. The conduction in present glasses especially in the low temperature region (up to nearly 330 K) can safely be attributed to take place by this mechanism. The value of $N(E_F)$, i.e., the density of energy states near Fermi level, for a frequency of $10^5$ Hz and at 330 K is evaluated on the basis of quantum mechanical tunneling model using the equation:

$$\sigma\omega = \eta e^2 KT[N(E_F)]^2\alpha^{-5}\omega[\ln(\nu_{ph}/\omega)]^4$$

(3.12)

With the usual meaning of the symbols [with the value of $\eta = \pi/3$ (Austin and Mott), $= 3.66\pi^2/6$ (Butcher and Hyden), $= \pi^4/96$ (Pollak)] [59] and the procedures reported earlier [34-37]. The value of $N(E_F)$ is observed to be maximum for BNBF glass and minimum for SNBF glass matrix, it is also supported by optical band gap and Urbach energy ($\Delta E$) values. Furthermore, the range of $N(E_F)$ values obtained $\sim 10^{22}$ eV$^{-1}$/cm$^3$; such values of $N(E_F)$ suggest the localized states near the Fermi level.

3.10 Conclusions

The following conclusions were drawn from the analysis of the results on spectroscopic studies coupled with dielectric properties of RO-Na$_2$O-B$_2$O$_3$:Fe$_2$O$_3$ of glasses:

- The increase in ESR signal intensity and optical band gap and decrease in dielectric parameters for SNBF glass matrix when compared to the other glasses confirm that a high concentration of iron ions exists in Fe$^{3+}$ state in the glass with network forming positions as FeO$_4$ units. Therefore SNBF
glass showed high rigidity which is also supported by high value of breakdown strength.

- The presence of optical absorption band at 1000 nm corresponding to Fe$^{2+}$ ions and decrease in ESR signal intensity of Fe$^{3+}$ ions in BNBF glass network indicate that the reduction of Fe$^{3+}$ ions into Fe$^{2+}$ state occurs with Ba$^{2+}$ ions modified due to its higher polarizability in the glass network.

- The decrease in optical band gap and increase of dielectric parameters in the BNBF glass matrix is supported by the increase in FeO$_6$ and BO$_3$ units along with NBOs from FTIR studies. It caused the less rigidity and high conductivity of BNBF glass network.
References


