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

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Alkali borate glasses doped with different concentrations of ferric oxide in the range 0-1 mol % in steps of 0.2 mol % have been prepared. The dielectric properties, especially dielectric constant $\varepsilon'$, loss tan$\delta$, a c conductivity $\sigma_{ac}$ over a wide range frequency (1-100 kHz) and temperature (30-300°C), ESR and IR spectra of Fe$_2$O$_3$ containing K$_2$O-BaO-B$_2$O$_3$ glasses have been studied. The dielectric study reveals that the glasses have high insulating strength when Fe$_2$O$_3$ concentration is 0.8 mol % in the glass matrix. The results have been analyzed in the light of different oxidation states of iron ions with the help of IR and ESR spectra data. The analysis indicates that when the concentration of iron ions is up to 0.8 mol %, these ions exist in Fe$^{3+}$ state that takes modifier as well as network former position, beyond this concentration some of the iron ions switch over from Fe$^{3+}$ to Fe$^{2+}$ state that takes network modifier positions and weakens the insulating strength of the glass.

Keywords: Glasses, Dielectric properties, X-ray diffraction, ESR spectra, IR spectra

1 Introduction

Alkali/alkaline earth oxy borate glasses are well known due to their applications in phosphors, solar energy converters and several 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$_3$ glass system has been investigated from a systematic study on dielectric constant $\varepsilon'$, loss tan$\delta$ and a c conductivity $\sigma_{ac}$ over a moderately wide range of frequency and temperature. Spectroscopic properties (viz., IR and ESR spectra) are also studied.

2 Experimental Details

With in the glass-forming region of doped K$_2$O-BaO-B$_2$O$_3$ glass system, the composition 10 K$_2$O-20 BaO- (70-x) B$_2$O$_3$-x Fe$_2$O$_3$ with the values x ranging from 0 to 1 mol % in steps of 0.2 mol % is chosen for the present study. Basing on the values of x the samples are labeled as F$_0$ (pure), F$_2$ (0.2 mol %), F$_4$ (0.4 mol %), F$_6$ (0.6 mol %), F$_8$ (0.8 mol %) and F$_{10}$ (1 mol %). The glasses used for the present study are prepared by the melting and quenching techniques. The starting materials used for the preparation of the present glasses were analytical grade reagents (99.9% pure) of K$_2$O, H$_3$BO$_3$, BaO, and Fe$_2$O$_3$. The
compounds of required compositions were thoroughly mixed in an agate mortar and melted in a platinum crucible at about 940°C for a 1/2 h till a bubble free liquid was formed. The furnace used was a PID temperature controlled furnace. The resultant melt was poured on a rectangular brass mould (containing smooth polished inner surface) held at room temperature. The samples were subsequently annealed at 200°C in another furnace. The glasses were then ground and optically polished. The approximate final dimensions of the glasses used for studying the electrical properties are 1 cm × 1 cm × 0.2 cm. For dielectric measurements thin coating of silver paint was applied on either side of the glasses, to serve as electrodes.

The density \( d \) of the glasses was determined by the standard principle of Archimedes using o-xylene (99.99% pure) as the buoyant liquid. Using density and average molecular weight other physical parameters such as iron ion concentration \( N_i \), the polaron radius \( r_p \), inter-ionic distance \( r_i \) of these glasses are evaluated. The dielectric measurements in the present investigation were taken on L F Impedance analyzer in the frequency range \( 10^2-10^5 \) Hz and temperature range 30-300°C. The accuracy in measurement of dielectric constant and dielectric loss is \( \pm 0.001 \) and \( 0.0001 \), respectively. The amorphous state of the prepared glasses was verified by X-ray diffraction spectra recorded on SEIFFERT Diffractometer Model SODEBYE FLUX 202 fitted with copper target and nickel filter operated at 40 kV, 30 mA. The X-ray diffraction pattern of the \( \text{K}_2\text{O-BaO-B}_2\text{O}_3 \) pure and \( \text{Fe}_2\text{O}_3 \) doped glasses were recorded in the range \( 10^2 \leq 2\theta \leq 80^\circ \). The absence of sharp peaks in the pattern indicates the amorphous nature of the samples (Fig. 1). The infrared transmission spectra of pure \( \text{K}_2\text{O-BaO-B}_2\text{O}_3 \) 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. 2). With the introduction of \( \text{Fe}_2\text{O}_3 \) (0.4 mol %) into the glass network, the intensity of second

<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 ) ((10^2\text{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) ((±0.001))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( F_0 )</td>
<td>2.1333</td>
<td>96.572</td>
<td>—</td>
<td>—</td>
<td>2.908</td>
</tr>
<tr>
<td>( F_2 )</td>
<td>2.1409</td>
<td>96.768</td>
<td>2.665</td>
<td>7.213</td>
<td>2.014</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>

The X-ray diffraction pattern of the \( \text{K}_2\text{O-BaO-B}_2\text{O}_3 \)

3 Results and Discussion

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 Table 1.
group of bands (bands due to BO\textsubscript{4} units\textsuperscript{23}) 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\textsubscript{2}O\textsubscript{3} the intensity of this band is continued to decrease where as that of the first group of bands (bands due to the BO\textsubscript{3} structural units) is also observed to decrease. The data on various band positions of the spectra are presented in Table 2.

The ESR spectra of K\textsubscript{2}O-BaO-B\textsubscript{2}O\textsubscript{3}: Fe\textsubscript{2}O\textsubscript{3} glasses recorded at room temperature are shown in Fig. 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\textsubscript{2}O\textsubscript{3} in the glass matrix upto 0.8 mol%.

The dielectric constant $\varepsilon'$ and loss tan\(\delta\) of K\textsubscript{2}O-BaO-B\textsubscript{2}O\textsubscript{3} (F\textsubscript{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\textsubscript{2}O\textsubscript{3} upto 0.8 mol% in the glass network at any frequency, and decrease considerably with increase in frequency. Figure 4 and its inset show the variation of dielectric constant and loss respectively as a function of frequency at room temperature for K\textsubscript{2}O-BaO-B\textsubscript{2}O\textsubscript{3} glasses doped with different concentrations of Fe\textsubscript{2}O\textsubscript{3}.

In Fig. 5 the variation of dielectric constant at different frequencies, with temperature for the concentration 0.2 mol % Fe\textsubscript{2}O\textsubscript{3} is shown. A comparison plot of variation of dielectric constant with temperature at 100 kHz for the glasses containing different concentrations of Fe\textsubscript{2}O\textsubscript{3} is shown in Fig. 6. With the increase in the concentration of Fe\textsubscript{2}O\textsubscript{3} the dielectric constant is observed to decrease at any given temperature similar to that at room temperature upto 0.8 mol % of Fe\textsubscript{2}O\textsubscript{3} and beyond that it is found to increase.

### Table 2 — IR spectral band positions of K\textsubscript{2}O-BaO-B\textsubscript{2}O\textsubscript{3}: Fe\textsubscript{2}O\textsubscript{3} glasses with probable error of ±0.1 cm\textsuperscript{-1}

<table>
<thead>
<tr>
<th>Glass</th>
<th>BO\textsubscript{3} units (cm\textsuperscript{-1})</th>
<th>BO\textsubscript{4} units (cm\textsuperscript{-1})</th>
<th>B-O-B units (cm\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>F\textsubscript{0}</td>
<td>1371</td>
<td>947</td>
<td>696</td>
</tr>
<tr>
<td>F\textsubscript{2}</td>
<td>1385</td>
<td>1020</td>
<td>696</td>
</tr>
<tr>
<td>F\textsubscript{4}</td>
<td>1373</td>
<td>1022</td>
<td>694</td>
</tr>
<tr>
<td>F\textsubscript{6}</td>
<td>1356</td>
<td>1018</td>
<td>690</td>
</tr>
<tr>
<td>F\textsubscript{8}</td>
<td>1386</td>
<td>1008</td>
<td>694</td>
</tr>
<tr>
<td>F\textsubscript{10}</td>
<td>1373</td>
<td>1006</td>
<td>692</td>
</tr>
</tbody>
</table>

Fig. 3 — ESR spectra of K\textsubscript{2}O-BaO-B\textsubscript{2}O\textsubscript{3} glasses doped with different concentrations of Fe\textsubscript{2}O\textsubscript{3}.

Fig. 4 — Variation of dielectric constant with frequency at room temperature for K\textsubscript{2}O-BaO-B\textsubscript{2}O\textsubscript{3} glasses doped with different concentrations of Fe\textsubscript{2}O\textsubscript{3}.

Fig. 5 — Variation of dielectric constant with temperature for glass F\textsubscript{2} at different frequencies.
The variation of loss tanδ with temperature at different frequencies for the glass $F_4$ is shown in Fig. 7; and it is found to exhibit a considerable increase at high temperatures especially at lower frequencies. Figure 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 $\text{Fe}_2\text{O}_3$ doped $\text{K}_2\text{O}-\text{BaO}-\text{B}_2\text{O}_3$ 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 $\text{Fe}_2\text{O}_3$. Using the standard relation:

$$f = f_0 \exp \left(-\frac{W_d}{K T}\right) \quad \ldots (1)$$

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. The activation energy is found to increase with increase in the concentration of $\text{Fe}_2\text{O}_3$ in the glass matrix.

The ac conductivity $\sigma_{ac}$ for different frequencies is calculated at different temperatures using the following equation:

$$\sigma_{ac}(\omega) = \omega \epsilon_0 \epsilon \tan \delta \quad \ldots (2)$$

where $\epsilon_0$ is the vacuum dielectric constant.

The plots of log$\sigma$ against $1/T$ are shown in Fig. 9 for sample $F_6$ for different frequencies. Figure 10 shows the plot of $\sigma_{ac}$ against $1/T$ for all samples at 10 kHz frequency. The variation of $\sigma_{ac}$ versus concentration of $\text{Fe}_2\text{O}_3$ is shown in inset (a) and inset (b) of Fig. 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 4. The activation energy is found to increase with increase in the concentration of $\text{Fe}_2\text{O}_3$ upto 0.8 mol %. Further the variation of $\sigma_{ac}$ with the

<table>
<thead>
<tr>
<th>Glass</th>
<th>Loss (tanδ) $(\pm0.0001)$</th>
<th>Temperature region of relaxation $(^\circ\text{C})$ $(\pm1^\circ\text{C})$</th>
<th>Activation energy for dipoles (ev) $(\pm0.01)$</th>
<th>Spreading factor $\beta$ $(\pm0.01)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_0$</td>
<td>0.0359</td>
<td>60-80 $(\pm1^\circ\text{C})$</td>
<td>2.51 $(\pm0.01)$</td>
<td>0.55 $(\pm0.01)$</td>
</tr>
<tr>
<td>$F_2$</td>
<td>0.0351</td>
<td>70-90 $(\pm1^\circ\text{C})$</td>
<td>2.65 $(\pm0.01)$</td>
<td>0.51 $(\pm0.01)$</td>
</tr>
<tr>
<td>$F_4$</td>
<td>0.0327</td>
<td>82-100 $(\pm1^\circ\text{C})$</td>
<td>2.80 $(\pm0.01)$</td>
<td>0.48 $(\pm0.01)$</td>
</tr>
<tr>
<td>$F_6$</td>
<td>0.0211</td>
<td>90-110 $(\pm1^\circ\text{C})$</td>
<td>2.95 $(\pm0.01)$</td>
<td>0.44 $(\pm0.01)$</td>
</tr>
<tr>
<td>$F_8$</td>
<td>0.0155</td>
<td>100-120 $(\pm1^\circ\text{C})$</td>
<td>3.10 $(\pm0.01)$</td>
<td>0.41 $(\pm0.01)$</td>
</tr>
<tr>
<td>$F_{10}$</td>
<td>0.0248</td>
<td>90-110 $(\pm1^\circ\text{C})$</td>
<td>2.85 $(\pm0.01)$</td>
<td>0.46 $(\pm0.01)$</td>
</tr>
</tbody>
</table>
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Concentration (upto 0.8 mol %) of Fe$_2$O$_3$ shows a decreasing trend as shown in Fig. 10.

It is well known that the effect of introduction of alkali oxides like K$_2$O into B$_2$O$_3$ glass network is the conversion of sp$^2$ planar BO$_3$ units into more stable sp$^3$ tetrahedral BO$_4$ units and may also create non-bridging oxygens. Each BO$_4$ 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 BO$_3$ and BO$_4$ 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 (Ba$^{2+}$ ions) take the interstitial positions.

Table 4 — Summary of data on a.c. conductivity $\sigma_{ac}$ for K$_2$O-BaO-B$_2$O$_3$:Fe$_2$O$_3$ glasses

<table>
<thead>
<tr>
<th>Glass</th>
<th>$\sigma_{ac}$ ($\times 10^{-8}$) $(\Omega \cdot cm)^{-1}$</th>
<th>$N(E_F)$ in $10^{20}$ eV$^{-1}$cm$^{-3}$</th>
<th>Activation energy for conduction (eV) $\pm 0.01$</th>
</tr>
</thead>
<tbody>
<tr>
<td>F$_0$</td>
<td>10.60 ± 0.15</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>F$_2$</td>
<td>7.47</td>
<td>5.58</td>
<td>2.33</td>
</tr>
<tr>
<td>F$_4$</td>
<td>5.72</td>
<td>4.88</td>
<td>2.04</td>
</tr>
<tr>
<td>F$_6$</td>
<td>1.74</td>
<td>2.69</td>
<td>1.12</td>
</tr>
<tr>
<td>F$_8$</td>
<td>0.56</td>
<td>1.52</td>
<td>0.635</td>
</tr>
<tr>
<td>F$_{10}$</td>
<td>3.42</td>
<td>3.77</td>
<td>1.58</td>
</tr>
</tbody>
</table>

With the increase of Fe$_2$O$_3$ content in the glass network, the intensity of second group of bands (bands due to BO$_4$ units) is observed to decrease upto maximum concentration with a shifting of meta-center towards slightly higher wave number upto 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$_3$ 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$_4$ structural units. This observation clearly suggests, there is an increase in the rigidity of the glass network with increasing concentration of Fe$_2$O$_3$ up to 0.8 mol% in the glass matrix.

The ESR spectra of Fe$_2$O$_3$ 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 $g = 6.2 \pm 0.5$ (Refs. 15-17). A trivalent iron ion Fe$^{3+}$ has electronic configuration 3$d^5$ corresponding to half filled $d$ shell and is particularly most stable. Since the iron ions in Fe$^{3+}$ state belonging to $d^5$ configuration with 6S as ground state in the free ion and there is no spin orbit interaction. 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 (Ref. 17).
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., $E (S^x, S^y)$ in the Hamiltonian. The ESR spectra of Fe$^{3+}$ ions in various glasses have been extensively studied\(^\text{15-17}\). 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 $g = 4.2$ (Ref. 15). So the resonance at $g = 4.2$ and 2.0 have been interpreted in different ways. Some researchers suggested that 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\(^\text{15}\). 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.

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 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 path ways for the migration of charges that would build up space charge polarization leading to the increase in the dielectric parameters as observed\(^\text{17,18}\).

With the gradual increase in the content of Fe$_2$O$_3$ upto 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 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 Fe$_2$O$_3$ 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\(^\text{17-19}\). 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 frequency) suggested by Sixou\(^\text{20}\) 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 equation\(^\text{20}\):

$$\varepsilon'(\omega) = \varepsilon_\infty + \frac{\varepsilon_1 - \varepsilon_\infty}{(1 + i\omega\tau)^s}$$  \hspace{1cm} ... (3)

can safely be applied to these glasses. Separating real and imaginary terms of Eq. (3) and rewriting with explicit temperature dependence of terms:

$$\varepsilon'(\omega, T) = \varepsilon_\infty + (\varepsilon_1 - \varepsilon_\infty)[\cos \varphi(T)]^0 \cos \varphi(T)$$  \hspace{1cm} ... (4)

and

$$\varepsilon''(\omega, T) = (\varepsilon_1 - \varepsilon_\infty)[\cos \varphi(T)]^0 \sin \varphi(T)$$  \hspace{1cm} ... (5)

where

$$\varphi(T) = \tan^{-1}(\omega \tau) = \tan^{-1}(\omega A \mu e^{\omega_0/KT})$$  \hspace{1cm} ... (6)
The plot cuts which cuts
conventionally called as pseudo Cole-Cole plot,
energy for the dipoles. The plot between
In Eq. (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 (4) and (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
the low frequency dielectric constant in the conventional
Cole-Cole plot and similarly \( \varepsilon_\infty \) is the high 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\(_2\)O-BaO-B\(_2\)O\(_3\) glass containing 0.6 mol \% of Fe\(_2\)O\(_3\) (glass \( F_6 \)), the pseudo Cole-Cole plot at 10 kHz is shown in Fig. 11. From this plot, the value \( \beta \) 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, 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 (\( F_8 \)) and 0.46 (\( F_{10} \)). The close look on these values shows that value of \( \beta \) decreases with increase in the concentration of Fe\(_2\)O\(_3\) 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 K\(_2\)O-BaO-B\(_2\)O\(_3\); Fe\(_2\)O\(_3\) 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:

\[
\sigma \omega = \eta e^2 kT \left[ N(E_F) \right]^2 \alpha^{-5} \omega \ln(\nu_{ph}/\omega)^{1/4}
\]

With the usual meaning of the symbols (with the value of \( \eta = \pi 3 \) (Austin and Mott\(^{18} \)), \( = 3.66 \pi^2/6 \) (Butcher and Hyden\(^{18} \)), \( = \pi^4/96 \) (Pollak\(^{18} \)) and the procedures reported earlier\(^{19,22} \). The value of \( N(E_F) \) is observed to decrease with the increase in the concentration of Fe\(_2\)O\(_3\). 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.

4 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\(^{3+}\) 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\(^{2+}\) state that take network modifier positions and weakens structure of the glass system.

References