Na$_2$SO$_4$–BaO–P$_2$O$_5$ glasses doped with different concentrations of Fe$_2$O$_3$ (ranging from 0.5 to 2.0 mol%) were prepared. The valance states of iron ions and their coordination in the glass network have been investigated using optical absorption, ESR, IR and Raman spectroscopy. The analysis of the spectroscopic results has indicated that the iron ions exist in both Fe$^{3+}$ (occupy octahedral and tetrahedral positions) and Fe$^{2+}$ (occupy octahedral positions) local coordination sites. Moreover, the redox ratio is observed to be the highest in the glasses doped with 1.5 mol% of Fe$_2$O$_3$. Electrical and dielectric spectral features have been studied over a wide frequency range ($10^2$ – $10^6$ Hz) and within the temperature range from 303-523 K. The ac and dc conductivities have exhibited maximal effect, whereas the activation energy for the conductivity demonstrated minimal magnitude at 1.5 mol% of Fe$_2$O$_3$. In the low temperature region, the ac conductivity is nearly temperature independent and is varied linearly with frequency. The analysis of the dc conductivity has indicated that at $T > \theta_D/2$, the small polaron hopping model is appropriate and the conductivity is adiabatic in nature. These results additionally confirm that there is a mixed conductivity (both ionic and electronic originated) in these glasses. The relaxation effects have been analyzed quantitatively using traditional Cole-Cole plots and spreading of relaxation times has been established.
Spectroscopic and electrical properties of Fe$_2$O$_3$ doped Na$_2$SO$_4$–BaO–P$_2$O$_5$ glass system

3.1 Introduction

Alkali sulphate mixed phosphate glasses are considered as appropriate materials for the immobilization of radioactive waste [1]. These glasses exhibit unique electrolytic properties that make them suitable for several solid-state electrochemical devices such as high temperature solid-state sodium–sulphur batteries, high density micro-batteries, sensors, smart card and medical appliances etc [2, 3]. A material to be used as solid electrolyte should exhibit high electrical conductivity, purely ionic, compatible with the electrode materials and should be thermally and chemically stable. In sulpho-phosphate glasses, SO$_4^{2-}$ ions largely dissolve in the phosphate glass matrix. However, these ions and metaphosphate ions appear to be weakly interacting and resulting in a small dynamic concentration of dithiophosphate (DTP) units. Such weak and variable interaction between these two ions is expected to influence the electrical properties to a large extent.

Usually electrical conductivity of alkali phosphate glasses is inhibited due to their relatively poor chemical stability. The addition of transition metal ions like iron to these glasses is expected to improve their electrical properties. Regardless of the original oxidation state of the iron in the starting glass batch, the final glass contains Fe$^{3+}$ (in both tetrahedral and octahedral environments)
and Fe$^{2+}$ ions in octahedral environment [4, 5]. Few researchers have also reported that even Fe$^{2+}$ ions do occupy tetrahedral positions in the glass network [6]. Both Fe$^{3+}$ and Fe$^{2+}$ ions are well known paramagnetic ions. Fe$^{2+}$ ions exhibit large magnetic anisotropy due to its strong spin–orbit originated spin polarization of the 3d Fe orbital, where as such anisotropy energy of Fe$^{3+}$ ions is small since its orbital angular momentum is zero. The concentration of Fe$^{2+}$ (or Fe$^{3+}$) which will have a strong bearing on electrical properties of these glasses depends primarily upon the melting temperature, other constituents of the glass and to some extent on the melting time.

In the present study, we have investigated the influence of Fe$_2$O$_3$ on electrical properties of Na$_2$SO$_4$–BaO–P$_2$O$_5$ glasses. The studies cover electrical conductivity and dielectric dispersion (dielectric constant $\varepsilon'$ and loss tan $\delta$) over a wide frequency range from 0.01 Hz to 1 MHz and in temperature range from 303 to 523 K. To have some pre-structural understanding for explaining the conduction phenomenon, we have also undertaken optical absorption, ESR, IR and Raman spectral studies on these glasses.
3.2 Brief Review of the previous work on Fe$_2$O$_3$ glass systems

Ardelean et al. [7] have studied the magnetic susceptibility of xFe$_2$O$_3$-(100 - x)[3B$_2$O$_3$- BaO] glasses with 0 < x < 50 mol%. For x < 10 mol% they have shown that these glasses to obey Curie law and iron ions exist only in Fe$^{3+}$ state, but for higher concentrations, the magnetic susceptibility of these glasses is described by Curie-Weiss law and iron ions are found to exist in both Fe$^{3+}$ and Fe$^{2+}$ valence states that participate in antiferromagnetic interactions. El-Samanoudy et al. [8] have studied optical absorption and infrared spectra of Fe$_2$O$_3$ containing TeO$_2$-GeO$_2$ 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. [9] have investigated the local structure around iron ions in the Bi$_2$O$_3$-Fe$_2$O$_3$ glasses by means of ESR studies. They have ascribed the ESR lines centered at $g = 4.3$ and $g = 2.0$ to isolated Fe$^{3+}$ in the orthorhombic crystal field and Fe$^{3+}$-O-Fe$^{3+}$ spin pair respectively. The electrochemical behaviour of Fe$^{2+}$/Fe$^{3+}$ redox couple in sodium disilicate glasses has been studied by Maric et al. [10]; from the results they have concluded that Fe$^{3+}$ acts both as network former and network modifier while Fe$^{2+}$ acts as network modifier. Sanad et al. [11] have reported structural and magnetic properties of Fe$_2$O$_3$ contained in CaO-P$_2$O$_5$ glasses. They have concluded that iron exists in both Fe$^{2+}$ and Fe$^{3+}$ 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 FeO$_6$ to FeO$_4$.

Chaudhuri et al. [12] have reported the frequency dependent ac conductivity of amorphous Fe$_2$O$_3$-Bi$_2$O$_3$ glasses in the frequency range $10^2$-$10^5$ Hz and in the temperature range of 77 to 450 K. They have analyzed the experimental data based on various theoretical models and showed that the correlated barrier hoping model as the most appropriate. Dance et al. [13] have investigated ESR of Fe$^{3+}$ ions in fluoroaluminate 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. Baiocchi et al. [14] 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 et al. [15] have reported EPR of Fe$^{3+}$ ions doped in bismuth borate glasses and the studies indicate various sites for Fe$^{3+}$ ions in environments characterized by different crystalline field intensities. Mandal and Hazra [16] 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. Karabulut et al. [17]
have studied the Mossbauer and IR investigations of iron ultraphosphate glasses. Milankovic et al [18, 19] have reported the spectroscopic and electrical investigations on iron phosphate glasses. Murawski et al [20] have investigated the electronic conductivity of Na₂O-FeO-P₂O₅ glasses. Karabulut et al [21] have carried out a study on the investigation of the local iron environment in iron phosphate glasses. Reis et al [22] have studied the structural features of lead iron phosphate glasses. Santic et al. [23] have investigated the dc electrical conductivity of iron phosphate glasses. Resi et al. [24] have reported the chemical durability and structure of zinc-iron phosphate glasses. Hafid et al [25] have carried out a study on the thermal and infrared characterization of new barium-iron-metaphosphate glasses. Romero-Perez et al. [26] have investigated the magnetic properties of glasses with high iron oxide content. Desoky et al. [27] have studied the conductivity and dielectric behaviour of iron sodium phosphate glasses. Concas et. al [28] have reported the Mossbauer spectroscopic investigation of some iron-containing sodium phosphate glasses, Ray et al. [29] have carried out a study on the effect of melting temperature and time on iron valency and crystallization of iron phosphate glasses.

Despite of the fact that a number of recent investigations are available on the environment of iron ions in a variety of inorganic glass systems [30-33], no dedicated studies are available on the role of iron ions on dielectric properties of Na₂SO₄–BaO–P₂O₅ glasses.
3.3 Characterization

Within the glass forming region of Na$_2$SO$_4$–BaO–P$_2$O$_5$ system, the following composition in mol% were chosen for the present study:

BF$_5$: 19.5Na$_2$SO$_4$–20BaO–60P$_2$O$_5$:0.5Fe$_2$O$_3$

BF$_{10}$: 19.0Na$_2$SO$_4$–20BaO–60P$_2$O$_5$:1.0Fe$_2$O$_3$

BF$_{15}$: 18.5Na$_2$SO$_4$–20BaO–60P$_2$O$_5$:1.5Fe$_2$O$_3$

BF$_{20}$: 18.0Na$_2$SO$_4$–20BaO–60P$_2$O$_5$:2.0Fe$_2$O$_3$

3.3.1 Physical parameters

From the measured values of the density $d$ and average molecular weight $\bar{M}$ of the samples, various other physical parameters such as iron ion concentration $N_i$, mean iron ion separation, $R_i$, polaron radius, $R_p$, are calculated and presented in Table 3.1.

Table 3.1 Physical parameters of Na$_2$SO$_4$–BaO–P$_2$O$_5$: Fe$_2$O$_3$ glasses.

<table>
<thead>
<tr>
<th>Glass</th>
<th>$d$ (g/cm$^3$)</th>
<th>$N_i$ (10$^{20}$ ions/cm$^3$)</th>
<th>$R_i$ (Å)</th>
<th>$R_p$ (Å)</th>
<th>$F_i$ (10$^{15}$ cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BF$_5$</td>
<td>2.844</td>
<td>0.593</td>
<td>25.63</td>
<td>10.33</td>
<td>0.281</td>
</tr>
<tr>
<td>BF$_{10}$</td>
<td>2.849</td>
<td>1.188</td>
<td>20.33</td>
<td>8.195</td>
<td>0.446</td>
</tr>
<tr>
<td>BF$_{15}$</td>
<td>2.851</td>
<td>1.781</td>
<td>17.77</td>
<td>7.160</td>
<td>0.585</td>
</tr>
<tr>
<td>BF$_{20}$</td>
<td>2.878</td>
<td>2.397</td>
<td>16.09</td>
<td>6.486</td>
<td>0.713</td>
</tr>
</tbody>
</table>
3.3.2 Differential scanning calorimetric (DSC) studies

In Fig. 3.1 DSC scans for Na$_2$SO$_4$–BaO–P$_2$O$_5$ glasses doped with different Fe$_2$O$_3$ contents are presented. All the traces exhibited typical glass transition with the inflection point in the temperature region 620–650 K due to glass transition followed by an exothermic peak in the region 890–910 K due to crystallization ($T_C$). It is interesting that the glass transitions temperature ($T_g$) as well as ($T_C$–$T_g$) parameter, a parameter proportional to the resistance of the glass against crystallization, are observed to decrease with the content of Fe$_2$O$_3$ in the glass matrix (inset (a) of Fig. 3.1). Thermograms of all these samples have also exhibited another endothermic peak at about 1200 K due to melting. TG trace for one of the glasses (BF$_{20}$) along with corresponding DSC trace is shown as inset (b) of Fig. 3.1. The analysis up to 1100 K exhibits virtually no change in the mass of the samples. The TG traces of all other glasses have exhibited similar behaviour.
Fig. 3.1 DSC traces of Na$_2$SO$_4$-BaO-P$_2$O$_5$: Fe$_2$O$_3$ glasses. Inset (a) represents the variation of $T_g$ and $T_c$-$T_g$ with the concentration of Fe$_2$O$_3$. Inset (b) shows the TG trace along with DSC curve for the glass BF$_{20}$. 
3.4 Results

3.4.1 Optical absorption spectra

Fig. 3.2 depicts optical absorption spectra of Na$_2$SO$_4$–BaO–P$_2$O$_5$ glasses doped with different concentrations Fe$_2$O$_3$ recorded at room temperature in the wavelength region 300–1050 nm. The absorption edge observed at 334 nm for the glass sample BF$_5$ exhibited red spectral shift with increase in the content of Fe$_2$O$_3$ up to 1.5 mol%. From the observed spectral dependences of the observed absorption edges, we have evaluated the optical band gaps ($E_o$) of these samples by applying of Tauc plots (Fig. 3.3)) between $(\alpha \omega)^{1/2}$ and $\omega$ as per the equation.

$$\alpha(\omega)\omega=c(h\omega-E_o)^2$$  \hspace{1cm} (3.1)

From the extrapolation of the linear part of the curves, the values of optical band gap ($E_o$) were determined and its variation with the concentration of Fe$_2$O$_3$ are presented as the inset of Fig. 3.1. The value of $E_o$ has exhibited minimal effect at 1.5 mol% of Fe$_2$O$_3$.

Additionally, the UV-VIS spectrum of glass BF$_5$ exhibited three distinct kinks at the edge (350 nm to 375 nm) and two well resolved bands at 394 nm and 412 nm. With increasing Fe$_2$O$_3$ content up to 1.5 mol% the half width and intensities of all these bands decrease with simultaneous spectrally blue shift of the spectral peak positions.
Fig. 3.2 Optical absorption spectra of Na$_2$SO$_4$-BaO-P$_2$O$_5$ glasses doped with different concentrations of Fe$_2$O$_3$.
Fig. 3.3 Tauc plots of Na$_2$SO$_4$–BaO–P$_2$O$_5$: Fe$_2$O$_3$ glasses. Inset shows the variation of optical band gap with the concentration of Fe$_2$O$_3$. 
Additionally the spectra of all the glasses exhibited a significant band in the NIR region at wavelength about 1000 nm whose intensity is increased with the content of Fe₂O₃ up to 1.5 mol%. However, when the concentration of Fe₂O₃ is raised from 1.5 to 2.0 mol%, a reversal trend in the intensity of these bands is established. The summary of the data on optical absorption spectra of these glasses is furnished in Table 3.2.

Table 3.2 Principal optical absorption spectra of Na₂SO₄–BaO–P₂O₅: Fe₂O₃ glasses

<table>
<thead>
<tr>
<th>Glass</th>
<th>Cut-off wavelength (nm)</th>
<th>Band positions (nm)</th>
<th>⁶A₁g (S) →⁴Eg (D)</th>
<th>⁴T₂g (D)</th>
<th>⁴T₁g (P)</th>
<th>⁴A₁g (G)</th>
<th>⁴Eg (G)</th>
<th>⁵T₂g →⁵Eg</th>
<th>Optical band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BF₅</td>
<td>334</td>
<td>358 364 372 394 420</td>
<td>1003</td>
<td>3.68</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BF₁₀</td>
<td>340</td>
<td>357 363 371 393 412</td>
<td>1005</td>
<td>3.63</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BF₁₅</td>
<td>347</td>
<td>356 362 369 392 407</td>
<td>1016</td>
<td>3.55</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BF₂₀</td>
<td>342</td>
<td>359 365 373 396 414</td>
<td>1006</td>
<td>3.59</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
3.4.2 ESR spectra

X-band ESR spectra of Na$_2$SO$_4$–BaO–P$_2$O$_5$: Fe$_2$O$_3$ glasses recorded at ambient temperature are shown in Fig. 3.4. The spectra exhibited an intense spectral line situated at about $g \approx 2.012$ (signal - 1) and a weak signal at about $g \approx 4.471$ (signal - 2). A slight variation in the $g$ parameters of the signals with the content of Fe$_2$O$_3$ is clearly observed (Table 3.3). Further, the intensity of both the signals is observed to be the lowest for the glass BF$_{15}$.

Table 3.3 ESR spectra of Na$_2$SO$_4$–BaO–P$_2$O$_5$: Fe$_2$O$_3$ glasses.

<table>
<thead>
<tr>
<th>Glass</th>
<th>$g$ – factors</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Signal-1</td>
<td>Signal-2</td>
<td></td>
</tr>
<tr>
<td>BF$_5$</td>
<td>2.012</td>
<td>4.470</td>
<td></td>
</tr>
<tr>
<td>BF$_{10}$</td>
<td>2.016</td>
<td>4.470</td>
<td></td>
</tr>
<tr>
<td>BF$_{15}$</td>
<td>2.022</td>
<td>4.475</td>
<td></td>
</tr>
<tr>
<td>BF$_{20}$</td>
<td>2.019</td>
<td>4.471</td>
<td></td>
</tr>
</tbody>
</table>

3.4.3 Infrared spectra

The infrared transmission spectra (Fig. 3.5) of Na$_2$SO$_4$–BaO–P$_2$O$_5$ glasses exhibited vibrational bands at about $\approx 1400$ cm$^{-1}$ (due to P=O stretching vibrations), 1280 cm$^{-1}$ (due to anti–symmetrical vibrations of PO$_2^-$ groups), 1080 cm$^{-1}$ (vibrational mode of PO$_3$ units), 1030 cm$^{-1}$ (a normal vibrational mode in PO$_4^{3-}$ group originating from $\nu_3$ – symmetric stretching), 900 cm$^{-1}$ (due to P–O–P
Fig. 3.4 ESR spectra of Fe$_2$O$_3$ doped Na$_2$SO$_4$-BaO-P$_2$O$_5$ glasses recorded at room temperature. Inset in BF$_{20}$ represents the variation of the intensity signal-1 with the concentration of Fe$_2$O$_3$. 
Fig. 3.5 Infrared transmission spectra of Na$_2$SO$_4$–BaO–P$_2$O$_5$: Fe$_2$O$_3$ glasses.
asymmetric stretching vibrations, this region may also consist of bands due to pyrophosphate groups viz., $\text{P}_2\text{O}_7^{4-}$ and another band at 780 cm$^{-1}$ due to P–O–P symmetric stretching vibrations. It should be emphasized that the spectral band positions of various phosphate structural groups observed for the studied samples are well sufficiently well agreed with the results presented in the ref. [34-36].

With the gradual introduction of Fe$_2$O$_3$ into the glass network, a steady decrease in the intensity of symmetrical vibrational bands of phosphate groups was accompanied by a blue spectral. Moreover, the bands due to asymmetrical vibrations are observed to grow at the expense of symmetrical bands with a red spectral shift. Additionally, the spectra of these glasses have exhibited an intense $\nu_1$- FeO$_6$ octahedral originated band and a weak kink caused by $\nu_3$- FeO$_6$ vibrations at about 570 and 420 cm$^{-1}$ frequencies, respectively [37, 38]. With the increase of Fe$_2$O$_3$ content, the growth of octahedral bands (FeO$_6$) is clearly visualized. The spectra of these glasses have also exhibited a feeble kink situated at about 660 cm$^{-1}$ originated from vibrations of FeO$_4$ tetrahedra and (or) due to bending vibrations of SO$_4$ groups [39]. Various IR spectral band positions for the studied glasses are summarized in the Table 3.4.

3.4.4 Raman spectra

The Raman spectra of Fe$_2$O$_3$ doped Na$_2$SO$_4$–BaO–P$_2$O$_5$ glasses exhibited several symmetrical and asymmetrical vibrational bands due to prevailingly covalence P–O, PO$_2$, PO$_3$ and PO$_4$ groups (Fig. 3.6). The details of various band positions are given in Table 3.4.
Table 3.4 Data on infrared spectra of Na$_2$SO$_4$–BaO–P$_2$O$_5$: Fe$_2$O$_3$ glasses recorded at room temperature (assignment of band positions in cm$^{-1}$)

<table>
<thead>
<tr>
<th>Assignment</th>
<th>BF$_5$</th>
<th>BF$_{10}$</th>
<th>BF$_{15}$</th>
<th>BF$_{20}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P=O stretching</td>
<td>1398</td>
<td>1397</td>
<td>1396</td>
<td>1394</td>
</tr>
<tr>
<td>PO$_2^-$ asym. groups</td>
<td>1286</td>
<td>1284</td>
<td>1276</td>
<td>1280</td>
</tr>
<tr>
<td>Asym. stretching of SO$_4$ groups</td>
<td>1151</td>
<td>1146</td>
<td>1163</td>
<td>1156</td>
</tr>
<tr>
<td>PO$_3$ groups</td>
<td>1079</td>
<td>1080</td>
<td>1084</td>
<td>1085</td>
</tr>
<tr>
<td>PO$_4^{3-}$ sym.</td>
<td>1026</td>
<td>1035</td>
<td>1037</td>
<td>1040</td>
</tr>
<tr>
<td>P-O-P asym. stretching</td>
<td>910</td>
<td>902</td>
<td>891</td>
<td>898</td>
</tr>
<tr>
<td>P-O-P sym. stretching</td>
<td>770</td>
<td>774</td>
<td>783</td>
<td>779</td>
</tr>
<tr>
<td>FeO$_4$ tetrahedra/ Bending of SO$_4$</td>
<td>653</td>
<td>661</td>
<td>667</td>
<td>663</td>
</tr>
<tr>
<td>$\nu_1$-FeO$_6$ octahedra</td>
<td>579</td>
<td>577</td>
<td>564</td>
<td>572</td>
</tr>
<tr>
<td>$\nu_3$-FeO$_6$ octahedra</td>
<td>428</td>
<td>420</td>
<td>415</td>
<td>419</td>
</tr>
</tbody>
</table>

It is interesting that the bands due to all the four modes (viz., $\nu_1$, $\nu_2$, $\nu_3$ and $\nu_4$) of vibrations of SO$_4$ groups [40] have also been observed in these spectra. Some of these bands are overlapped with those of phosphate groups demonstrating possible inter-cluster covalence-ionic interactions between sulphate and phosphate groups. Additionally, a band due to Fe-O vibrations [41] is also situated at about 530 cm$^{-1}$. With the gradually increasing Fe$_2$O$_3$, the asymmetrical bands are enhanced at the expense of symmetrical bands.
Fig. 3.6 Raman spectra of Na$_2$SO$_4$–BaO–P$_2$O$_5$:Fe$_2$O$_3$ glasses.
A gradual increase of P–O symmetric stretch intensities (presumably due to non-bridging oxygens) located at about 1000 cm$^{-1}$ could clearly be observed with increase of Fe$_2$O$_3$ content up to 1.5 mol%. The pertinent data related to Raman spectral band positions are presented in Table 3.5.

Table 3.5 Summary of Raman positions for Na$_2$SO$_4$–BaO–P$_2$O$_5$: Fe$_2$O$_3$ glasses (assignment of band positions in cm$^{-1}$)

<table>
<thead>
<tr>
<th>Assignment</th>
<th>BF$_5$</th>
<th>BF$_{10}$</th>
<th>BF$_{15}$</th>
<th>BF$_{20}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bending and torsional vibrations of PO$_4$ units</td>
<td>395</td>
<td>390</td>
<td>384</td>
<td>404</td>
</tr>
<tr>
<td>Sym. O-S-O bending modes $\nu_2$ – SO$_4$</td>
<td>465</td>
<td>468</td>
<td>475</td>
<td>471</td>
</tr>
<tr>
<td>Fe-O</td>
<td>530</td>
<td>534</td>
<td>537</td>
<td>540</td>
</tr>
<tr>
<td>Bending mode related to the chain motion and chain conformation of phosphate groups</td>
<td>561</td>
<td>564</td>
<td>575</td>
<td>569</td>
</tr>
<tr>
<td>Asym. O–S–O bend modes $\nu_4$ – SO$_4$</td>
<td>695</td>
<td>692</td>
<td>684</td>
<td>689</td>
</tr>
<tr>
<td>$\nu_s$ – POP</td>
<td>753</td>
<td>756</td>
<td>760</td>
<td>758</td>
</tr>
<tr>
<td>(PO$<em>4$)$</em>{asym}$ stretch ($Q^0$)</td>
<td>914</td>
<td>911</td>
<td>907</td>
<td>909</td>
</tr>
<tr>
<td>Sym. S–O stretch. $\nu_1$ – SO$_4$ / P-O$^-$ stretch ($Q^0$) (NBO)</td>
<td>1001</td>
<td>1003</td>
<td>1006</td>
<td>1009</td>
</tr>
<tr>
<td>(PO$<em>3$)$</em>{sym}$ stretch ($Q^1$)</td>
<td>1049</td>
<td>1051</td>
<td>1056</td>
<td>1053</td>
</tr>
<tr>
<td>(PO$<em>2$)$</em>{sym}$ stretch ($Q^2$)</td>
<td>1113</td>
<td>1116</td>
<td>1119</td>
<td>1117</td>
</tr>
<tr>
<td>Asym. Stretch. S-O $\nu_3$ – SO$_4$ / Strained</td>
<td>1175</td>
<td>1170</td>
<td>1165</td>
<td>1169</td>
</tr>
<tr>
<td>(PO$<em>2$)$</em>{sym}$ stretch ($Q^1$)</td>
<td>1273</td>
<td>1271</td>
<td>1265</td>
<td>1268</td>
</tr>
<tr>
<td>(P = O)$_{sym}$ stretch</td>
<td>1330</td>
<td>1333</td>
<td>1338</td>
<td>1335</td>
</tr>
</tbody>
</table>
3.4.5 Dielectric properties

The variation of dielectric constant $\varepsilon'(\omega)$ dispersion for the glass sample (BF$_5$) versus temperature at different frequencies is shown in Fig. 3.7 (a). At the same time the dielectric constant dispersion at various temperatures for the same glass is presented in Fig. 3.7(b). At higher frequency, $\varepsilon'(\omega)$ approaches to achieve a constant value, $\varepsilon'_\infty(\omega)$. The variation of dielectric constant with temperature and frequency for all the other glasses have demonstrated similar behaviour. In the inset of Fig. 3.7(a), variation of dielectric constant (measured at 423 K and 1.02 kHz) versus Fe$_2$O$_3$ content is presented. The variation exhibited maximal effect at 1.5 mol% of Fe$_2$O$_3$.

The dielectric loss, tan $\delta$ dispersions at different temperature and vice versa - at fixed temperature and different frequencies for the glass BF$_{15}$ are presented in Figs. 3.8 (a) and (b), respectively. The loss dispersion curves have exhibited distinct maxima: with increasing temperature, the frequency maximum is shifted towards higher frequencies and with increasing frequency the temperature maximum shifted towards higher temperatures. These observations indicate the dielectric relaxation character of dielectric loss peak for these glasses [42, 43]. The origin of such variations of the dielectric loss dispersion versus temperature is found to be similar for all the other samples in this study.
Fig. 3.7(a) Variation of dielectric constant $\varepsilon'(\omega)$ with temperature for the glass sample (BF$_3$) at different frequencies. Inset represents the variation of dielectric constant with the concentration of Fe$_2$O$_3$ measured at 423 K and 1.02 kHz.
Fig. 3.7(b) Variation of dielectric constant $\varepsilon'(\omega)$ with frequency for the glass sample BF$_3$ at different temperatures
We have compared the loss plots with the temperature at different frequencies for all the glasses. Breadth and the intensity, \((\text{Tan } \delta)_{\text{avg.max.}}\), of the dielectric relaxation peaks have increased with the content of Fe\(_2\)O\(_3\) up to 1.5 mol\%, in the glass network, the frequency region of relaxation is shifted towards the lower temperature (Table 3.6). Following the Boltzmann relation, \(f = f_0 \exp \left(-\frac{W_d}{k_B T}\right)\), \((f_0\) is a constant, \(k_B\) is the Boltzmann constant, \(T\), is absolute temperature and, \(f\), is relaxation frequency), the effective activation energy, \(W_d\), for the dipoles is evaluated for all the glasses by drawing and extrapolating the plots of \(\log f\) vs \(1/T\). The value of \(W_d\), is found to be the lowest for the glass BF\(_{15}\) (Table 3.6).

Table 3.6 Data on dielectric loss of Na\(_2\)SO\(_4\)–BaO–P\(_2\)O\(_5\): Fe\(_2\)O\(_3\) glasses

<table>
<thead>
<tr>
<th>Glass</th>
<th>((\text{Tan} \delta)_{\text{max. avg.}})</th>
<th>A.E. for dipoles (W_d) (eV) ((\pm 0.01))</th>
<th>Relaxation time (\tau) ((\mu)s)</th>
<th>Spreading factor (\alpha) (rads)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BF(_5)</td>
<td>131</td>
<td>1.22</td>
<td>86</td>
<td>0.16</td>
</tr>
<tr>
<td>BF(_{10})</td>
<td>149</td>
<td>1.06</td>
<td>78</td>
<td>0.18</td>
</tr>
<tr>
<td>BF(_{15})</td>
<td>163</td>
<td>0.98</td>
<td>67</td>
<td>0.21</td>
</tr>
<tr>
<td>BF(_{20})</td>
<td>142</td>
<td>1.05</td>
<td>80</td>
<td>0.17</td>
</tr>
</tbody>
</table>

For understanding the thermally stimulated mobility of the conducting ions we have plotted the impedance spectra for the studied glasses. Fig. 3.9 represents these spectra for the glass BF\(_{10}\) at four different temperatures,
Fig. 3.8(a) Variation of dielectric loss with frequency at different temperature for the glass BF$_{15}$
Fig. 3.8(b) Variation of dielectric loss with temperature at different frequencies for the glass BF$_{15}$. 
Fig. 3.9 Impedance spectra for the glass BF$_{10}$ drawn at four different temperatures.
whereas Fig. 3.10 represents the same for all the glasses at two different temperatures viz., 513 and 523 K. The spectra of all the glasses exhibited semicircles followed by inclined spur at higher temperatures. With increasing Fe$_2$O$_3$ content up to 1.5 mol%, the low-frequency linear spur also increases.

In Fig. 3.11(a) isotherms of ac conductivity dispersion are plotted for BF$_2$O$_3$ glass, whereas in Fig. 3.11(b) ac conductivity is presented as a function of inverse temperature at different frequencies for the same glass is reported. The frequency dependence of ac conductivity at a given temperature exhibited a universal feature [44] where at low frequency region the conductivity is independent on frequency and corresponds to the dc conductivity, $\sigma_{dc}$ of glass. At the same time at higher frequency there is observed dispersion in power law fashion. It should be noted that the dispersion starts at a higher frequency with increasing temperature. However, at low temperature and frequency the leveling-off of the conductivity is not sufficiently distinct. The dependence of ac conductivity with the content of Fe$_2$O$_3$ at any given frequency and temperature exhibited an increasing trend up to 1.5 mol% and for further increase of the dopant concentration, a considerable decrease is visualized (inset (a) of 3.11(b)).
Fig. 3.10 Impedance spectra for Na$_2$SO$_4$–BaO–P$_2$O$_5$ glasses doped with different concentrations of Fe$_2$O$_3$ drawn at 513 and 523 K.
Fig. 3.11(a) Variation of ac conductivity with frequency for the glass BF$_{20}$ at different temperatures.
Fig. 3.11(b) Variation of ac conductivity with 1/T for the glass BF$_{20}$ at different frequencies. Inset (a): variation of $\sigma_{ac}$ (measured at 523 K) and activation energy with the concentration of Fe$_2$O$_3$. Inset (b): variation of $\sigma_{ac}$ with the activation energy in the high temperature region.
From the plots of \( \log \sigma_{ac} \) vs \( 1/T \), we have evaluated the activation energy, \( W_{ac} \), for the conduction in the high temperature region over which a near linear dependence of \( \log \sigma_{ac} \) with \( 1/T \) could be observed; the activation energy is found to decrease with the concentration of Fe\(_2\)O\(_3\) up to 1.5 mol% (inset (a) of 3.11(b)).

The values of dc resistance, \( R \), for all the glasses is obtained following fitting analysis. Using this resistance and the sample dimensions, we have evaluated dc electrical conductivity for the titled glasses. The temperature dependence of dc conductivity for these glasses is presented as an Arrhenius plot in Fig. 3.12. Similar to ac conductivity the dc conductivity also exhibited maximal effect at 1.5 mol% of Fe\(_2\)O\(_3\) (inset (a) of Fig. 3.12). The activation energy, \( W_{dc} \), for each glass was determined from the slope of \( \log \sigma_{dc} \) vs \( 1/T \) plots.

The variation of, \( W_{dc} \), with the content of Fe\(_2\)O\(_3\) exhibited minimal effect at 1.5 mol% of Fe\(_2\)O\(_3\) (inset (a) of Fig. 3.12). Other pertinent data related to dc conductivity are furnished in Table 3.7. It may be noted here that log \((\sigma_{dc}T)\) vs \( 1/T \) plots are also being used instead of log \( \sigma_{dc} \) vs \( 1/T \) plots for the conductivity of ionic solids. However, for the present studied glasses both the plots are essentially same (inset (c) of Fig. 3.12). Since both the plots are almost parallel, the activation energy evaluated from both the plots is nearly the same.
Table 3.7 Summary of data on dc conductivity studies of Na$_2$SO$_4$–BaO–P$_2$O$_5$: Fe$_2$O$_3$ glasses.

<table>
<thead>
<tr>
<th>Glass</th>
<th>$W_{dc}$ (eV)</th>
<th>$W_H$ (eV)</th>
<th>J (eV)</th>
<th>$\sigma_0$ (x 10$^2$, Ω-cm)$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BF$_5$</td>
<td>1.063</td>
<td>0.635</td>
<td>0.042</td>
<td>5.69</td>
</tr>
<tr>
<td>BF$_{10}$</td>
<td>1.058</td>
<td>0.630</td>
<td>0.055</td>
<td>6.13</td>
</tr>
<tr>
<td>BF$_{15}$</td>
<td>1.056</td>
<td>0.632</td>
<td>0.063</td>
<td>9.03</td>
</tr>
<tr>
<td>BF$_{20}$</td>
<td>1.081</td>
<td>0.645</td>
<td>0.070</td>
<td>3.92</td>
</tr>
</tbody>
</table>

To avoid an influence of electrode polarization effects for the better understanding of electrical relaxation behavior in ion conducting materials like the titled glasses, we have evaluated real and imaginary electric moduli, $M'(\omega)$ and $M''(\omega)$ dispersion, from real and imaginary parts of complex dielectric constant, $\varepsilon^*$, using the expressions:

$M^* = 1/\varepsilon^*(\omega) = M'(\omega) + i M''(\omega),$  \hspace{1cm} (3.2)

here $M'(\omega) = \frac{\varepsilon'(\omega)}{(\varepsilon'(\omega))^2 + (\varepsilon''(\omega))^2}$  \hspace{1cm} (3.3)

and $M''(\omega) = \frac{\varepsilon''(\omega)}{(\varepsilon'(\omega))^2 + (\varepsilon''(\omega))^2}$  \hspace{1cm} (3.4)

at different temperatures for all these samples. And their dependence with the frequency for one of the glasses (viz., BF$_{20}$) is presented in Figs. 3.13 (a) and (b), respectively. These figures clearly exhibited the relaxation feature for dielectric properties of the studied glasses.
Fig. 3.12 Variation of $\sigma_{dc}$ with $1/T$ for Na$_2$SO$_4$–BaO–P$_2$O$_5$ glasses doped with different concentrations of Fe$_2$O$_3$. Insets (a) shows the variation of $\sigma_{dc}$ with the concentration of Fe$_2$O$_3$ at different temperatures (b) shows the variation of $\sigma_{dc}$ (at 393 K) with the activation energy and (c) represents the variation of $\sigma_{dc}$ and $\sigma_{dc}T$ with $1/T$ for the glass BF$_5$. 
It should be noted that the $M'(\omega)$ increases with increasing temperature and at sufficiently high temperature reaches a plateau which corresponds to the limiting value of $M_\infty$. The maximum in the $M''(\omega)$ peak is shifted to higher frequency with increasing temperature. The plots of electric moduli versus frequency for other glasses resemble the same. The frequency region under the peak maximum of $M''(\omega)$ determines the range in which charge carriers are mobile on long distances. At frequency above peak maximum $M''(\omega)$, the carriers are spatially confined to potential wells, being mobile on short distances and making only localized motion within the wells.

In Fig. 3.14, the variation of $M'(\omega)$ and $M''(\omega)$ with frequency at 523 K for the glass BF$_5$ is presented. The point of intersection of two curves at $(M'')_{\text{max}}$, represents characteristic frequency which is equal to the relaxation frequency described by $\omega_{\text{max}} = 1/\tau_M$, where $\tau_M$ describes the relaxation time for the dipoles. The relaxation times, $\tau_M$, evaluated for all glasses in the similar way at 523 K and are presented in Table 3.6. The value of $\tau_M$ is found to be the lowest for the BF$_{15}$ glass (Table 3.6).
Fig. 3.13(a) The frequency dependence of $M'$ at different temperatures for BF$_{20}$ glass.
Fig. 3.13(b) The frequency dependence of $M''$ at different temperatures for BF$_{20}$ glass
Fig. 3.14 Frequency dependence of the real and imaginary part of electrical moduli, $M'$ and $M''$ for the glass sample BF$_5$ measured at 523 K
3.5 Discussion

Among various constituents of Na$_2$SO$_4$–BaO–P$_2$O$_5$:Fe$_2$O$_3$ glass system P$_2$O$_5$ is a strong glass forming oxide, participates in the glass network with PO$_4$ structural clusters. Normally, the structure of the simple phosphate glasses is dependent on O/P ratios and the fraction of Q phosphate tetrahedra. For single P$_2$O$_5$ glass O/P = 2.5 and the glass network is build up of Q$^3$ tetrahedra with the bridging oxygens and with the fourth oxygen, is doubly bonded to the phosphorus atom. With the addition of modifiers like iron oxide an ultraphosphate network consisting of Q$^2$ and Q$^3$ tetrahedra may form with O/P < 3.0 [45]. The PO$_4$ tetrahedra are linked together with covalent bonding in chains or rings by bridging oxygens. Neighbouring phosphate chains are linked together by cross-bonding between the metal cation and two non-bridging oxygen atoms of each PO$_4$ tetrahedron [46]. The presence of such PO$_4$ units in the titled glass samples is evident from the performed IR and Raman spectral studies.

The addition of Na$_2$SO$_4$ results in gradual depolymerization of the phosphate chains and formation of short phosphate units. The sulphate units will remain by and large as terminal groups [47]. However, the formation of dithiophosphate (DTP) units (due to the weak interaction between pyrophosphates and sulphahate ions) is possible as mentioned before [48]. The interaction of Na$_2$SO$_4$ and P$_2$O$_5$ is possible only if the phosphate network
contains \([\text{POO}_{2/2}\text{O}]\) (phosphate tetrahedra with one bridging oxygen) and
\([\text{POO}_{1/2}\text{O}_2]^{2-}\) (phosphate tetrahedra with two bridging oxygens) structural
groups [49]. The two bridging oxygen phosphate groups in the presence of the
modifier oxides \(\text{BaO}\), can be written as
\[
2 \,[\text{POO}_{3/2}]^0 + \text{BaO} \rightarrow 2 \,[\text{POO}_{2/2}\text{O}]^- + \text{Ba}^{2+}.
\]
Similarly, the phosphate group with one bridging oxygen can be written as
\[
2 \,[\text{POO}_{2/2}\text{O}]^- + \text{BaO} \rightarrow 2 \,[\text{POO}_{1/2}\text{O}_2]^{2-} + \text{Ba}^{2+}.
\]
\(\text{BaO}\) is a well-known modifier and may enter the glass network by
transforming two \(\text{Q}^3\) tetrahedra (viz., \(\text{PO}_4\) tetrahedra with three bridging
oxygens and one terminal de-bonded oxygen) into two \(\text{Q}^2\) tetrahedra (viz., \(\text{PO}_4\)
tetrahedra with two bridging oxygens and two terminal de-bonded oxygen) and
thus a \(\text{BaO}\) polyhedron is formed when it is surrounded by such two \(\text{Q}^2\) and
several \(\text{Q}^3\) tetrahedra. This structure behaves like a structurally defected in the
network of \(\text{P}_2\text{O}_5\) [50].

Iron ions may exist both in \(\text{Fe}^{2+}\) and \(\text{Fe}^{3+}\) states in these glasses. The speciation
of iron is controlled by the reversible reaction:
\[
4\text{Fe}^{3+} + 2\text{O}^2- \rightleftharpoons 4\text{Fe}^{2+} + 2\text{O}_2.
\]
\(\text{Fe}^{3+}\) ions are expected to occupy both tetrahedral and octahedral local site
positions in the glass network. Both of these \(\text{Fe}^{3+}\) sites can be considered as
substitutional and subjected to strong interaction between its external orbitals
and the p-orbitals of the neighbouring oxygens [51-54] and form the linkages
of the type P–O–Fe. 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 [54]) and act as modifiers similar to Na$^+$ and Ba$^{2+}$ ions.

Iron in the oxidation state +3 is reported to occur predominantly in fourth-fold coordination, i.e., as FeO$_4$ than the six fold coordination as reported in many other glass systems [55-58]. These tetrahedra have a negative charge and hence require cations like Na$^+$ ions, for charge compensation. In numerous studies on the thermodynamics of the Fe$^{2+}$/Fe$^{3+}$ equilibrium and on the diffusivity of iron, it was shown that normally decrease of alkali ion content (Na$^+$) - leads to a shift in the redox ratio Fe$^{2+}$/Fe$^{3+}$ towards higher values [55].

The density of the studied glasses is increased considerably with the content of Fe$_2$O$_3$. The increase of structural compactness, the modification of the geometrical configuration of the glassy network, changes in the coordination of the glass forming ions and the fluctuations in the dimensions of the interstitial holes, are crucial factors responsible for such an increase. Concerning DSC studies, the variations of $T_g$ and $T_C-T_g$ with the concentration of Fe$_2$O$_3$ exhibited a dip at $x = 1.5$ mol%. This behaviour suggests a high degree of disorder in the network of glass BF$_{15}$, owing to the presence of larger concentrations of Fe$^{2+}$ ions which may act as modifiers.
In octahedral symmetry, the ground state of Fe\(^{3+}\) ion is spherically non-degenerate \(6\,^A_{1g}\) state. In a cubic crystalline field of low and moderate strengths, the five localized d electrons of Fe\(^{3+}\) are distributed among \(t_{2g}\) and \(e_g\) orbitals, with three in the former and two in the latter states. Therefore, the ground state configuration is normally written as \((t_{2g})^3(e_g)^2\). This configuration gives rise to \(6\,^A_{1g}, 4\,^A_{1g}, 4\,^E_g, 4\,^T_{1g}, 4\,^T_{2g}, 4\,^A_{2g}\) electronic states and a number of doublet states. \(6\,^A_{1g}\) lies at the lowest according to Hund’s rule. The observed optical absorption bands are originated from the ground state \(6\,^A_{1g}\) to some quartet states and these are both spin and parity forbidden. Using Tanabe-Sugano energy level diagram for \(d^5\) configuration, the bands observed at about 353 nm, 365 nm, 371 nm, 394 nm and 413 nm wavelengths are assigned to \(6\,^A_{1g}\) (S) \(\rightarrow 4\,^E_g\) (D), \(4\,^T_{2g}\) (D), \(4\,^T_{1g}\) (P), \(4\,^A_{1g}\) (G)\(+\) \(4\,^E_g\) (G) and \(4\,^T_{1g}\) (G) octahedral transitions of Fe\(^{3+}\) ions, respectively [59-61]. So all the excited states preset spin quartet states and no spin allowed transitions would occur for Fe\(^{3+}\) ions. Hence, Fe\(^{3+}\) ions are characterized by weak bands, which arise due to the spin forbidden transitions. However, the transition \(6\,^A_{1g}\) (S) \(\rightarrow 4\,^T_{1g}\) (G) involves a transformation of configuration from \((t_{2g})^3(e_g)^2\) to \((t_{2g})^4(e_g)^1\) and is therefore expected to be relatively broader as observed [62, 63]. The broad peak observed at around 1000 nm is due to \(5\,^T_{2g}\) \(\rightarrow 5\,^E_g\) intra-octahedral transition of Fe\(^{2+}\) ions [64]. The successive growth of this Fe\(^{2+}\) band with increasing content of Fe\(_2\)O\(_3\) up to 1.5 mol% suggests an increase in the redox ratio Fe\(^{2+}\)/Fe\(^{3+}\) ratio in the glass matrix.
The reversal trend is observed beyond this concentration of FeO$_3$ indicates that the concentration of trivalent iron ions that participate in the glass network forming with FeO$_4$ structural units is dominating with respect to divalent ions.

The validity of the quadratic relation (Eq. 3.1) related to optical band gap points out that the band gap is caused by amorphous optical absorption edge. This confirms a fact that the disordered amorphous glass materials are formed prevailingly by direct transitions between the valence band and the conduction bands and the absence of the indirect inter-band transitions like in the case of the crystals (i.e. the transitions in the different points of the Brillouin zone). Minor deviations observed from this dependence are understood due to trapping of some disordered states within the energy gap.

The value of optical band gap ($E_o$) decreases with increasing FeO$_3$ content in the glass network up to 1.5 mol% (Table 3.3). The divalent ions, similar to sodium ions, depolymerize the glass network by creating more bonding defects and non-bridging oxygens (NBO). The increase in the concentration of Fe$^{2+}$ (O$_h$) ions in the glass network, an increase in the formation of donor centers is expected and subsequently, the excited states of localized electrons originally trapped on Fe$^{2+}$ sites begin to overlap by energy with the empty 3d Fe states on the neighboring Fe$^{3+}$ sites. As a result, the impurity or polaron band becomes more extended into the main band gap. This new polaronic development might have shifted the absorption edge to the
lower energy, which leads up to a significant decrement in the band gap as the concentration of Fe$_2$O$_3$ is increased up to 1.5 mol%.

The optical activation energy associated with $^6A_{1g}(S) \rightarrow ^4T_{1g}(G)$ octahedral band of Fe$^{3+}$ ions is increased from 2.95 eV (glass BF$_5$) to 3.04 eV (glass BF$_{15}$), whereas the energy of Fe$^{2+}$ ion transition band is decreased from 1.24 eV to 1.22 eV. This is clearly a characteristic feature for inter-valence transfer or a polaronic type of absorption. It means that the associated electrons are trapped at shallow sites within the main band gap and as a consequence possess smaller effective wave-function radii. This kind of situation is only possible if the local potential fluctuation may be neglected with respect to transfer integral, $j$. A small overlap between electronic wave functions (corresponding to adjacent sites) due to strong local disorder is contributive to polaron formation. So within a framework of polaronic model, the electron delivered by the impurity atom at the Fe$^{3+}$ site converts this one into a lower valence state Fe$^{2+}$. Afterwards the trapped electron at this Fe$^{2+}$ site is transferred to the neighboring new Fe$^{3+}$ site by absorbing a photon quantum. Thus the optical absorption in the glass samples is dominated by polaronic transfer between the Fe$^{2+}$ and Fe$^{3+}$ species [65, 66].

In the ESR spectra, the spectral line centered at $g \approx 4.471$ is identified as being due to the isolated Fe$^{3+}$ ions in the low symmetry orthorhombic crystal field sites of either tetrahedral or octahedral coordination. The signal at $g \approx$
2.012 is due to the isolated Fe$^{3+}$ in slightly distorted structural units in samples with a low Fe$_2$O$_3$ content and due to Fe$^{3+}$–O–Fe$^{3+}$ cluster formations in the samples containing higher content of Fe$_2$O$_3$ [67]. The 6S ground state of Fe$^{3+}$ (d$^5$)-free ion is expected to split into three Kramers doublets $|\pm 5/2\rangle$, $|\pm 3/2\rangle$ and $|\pm 1/2\rangle$ with separation normally greater than the microwave quantum. The weak symmetric and isotropic line is observed at $g \approx 4.471$ in the studied glasses and is caused by the middle Kramers doublets containing an admixture of different $j$ $|\pm m_j\rangle$ which are identified as being due to the low symmetry term $E(S_x^2 - S_y^2)$ in the Hamiltonian. Whereas the signal at $g \approx 2.012$ is due to ESR transitions in the $|\pm 1/2\rangle$ doublet [68]. The intensity ($\Im$) of the ESR signal is evaluated using $\Im \approx I (\Delta B)^2$, where $I$ is the peak-to-peak height and $\Delta B$ is the square of width of the signal [69]. The dependence of this factor, for $g_{\text{eff}} \approx 2.012$ (signal-1) resonance versus Fe$_2$O$_3$ is shown as an inset of Fig. 3.4. This variation demonstrates a decrease of $\Im$ with increasing Fe$_2$O$_3$ up to 1.5 mol%.

There are two main types of interactions between paramagnetic ions that have been recognized: dipole–dipole interaction and exchange interaction contributing to the line broadening of the ESR signal. The former shifts the resonance field of any given ion by an amount representing the average magnetic fields (both static and dynamic) that it experiences due to all the other magnetic ions in the solid. This one determines inhomogeneous
broadening and often results in a Gaussian line shape. Exchange interactions result from what may be viewed as mutual spin flipping, which under some circumstances can tend to average out the local dipolar fields, leading to line narrowing. In the simplest theoretical treatment, “the phenomenon of exchange narrowing depends on the property that the isotropic exchange interaction does not contribute to the second moment when we have a system of identical ions [70]. The second mechanism which causes narrowing of the signal is supposed to dominate in the samples containing higher content of Fe₂O₃. However, in the present case, the narrowing process seems to be influenced by other broadening processes such as increase in network disordering and interaction between multivalent iron ions (viz., Fe²⁺ and Fe³⁺). The final line width depends on the relative strengths of the two mechanisms influencing the line width. The decrease in the line width of the signal-1 with Fe₂O₃ content up to 1.5 mol% shows the dominance of the exchange mechanisms which in turn indicates a gradual increase in Fe²⁺ ion concentration. The decrease in g ≈ 4.471 line intensity reflects a reduction in the number of Fe³⁺ ions in octahedral (tetrahedral) environment in the vitreous matrix and also reflects changes in the matrix structure when the concentration of iron ions is increased.

Further, the effective value of g obtained from ESR spectra shows a gradual increase from the glass BF₅ to BF₁₅ (Table 3.3). This is partially ascribable to the contribution of orbital angular momentum to the magnetic
moment of Fe$^{3+}$ ions. The fraction of the magnetic moment due to the orbital angular momentum $I_o$(orb) to that due to spin angular momentum, $I_s$(spin) may be expressed as follows [71]:

$$\frac{I_s}{I_o} = (g/2)-1.$$  \hspace{1cm} (3.5)

Such an interesting feature may be understood in terms of the effect of $P^{5+}$ ions. The spin-orbit interaction of the 3p orbital of $P^{5+}$ ion is relatively high and this interaction has an influence on the valence state of Fe$^{3+}$ ion through the charge transfer to 2p O orbitals. This interaction leads to an appearance of the orbital angular momentum which contributes to magnetic moment of Fe$^{3+}$ ion. The strong dipolar interaction, which is more predominant in the glass containing 1.5 mol% of Fe$_2$O$_3$, causes a localized magnetic field at the site of Fe$^{3+}$ ion and increases the effective g value as observed.

The IR and Raman spectra indicate that the bands originated by asymmetric vibrations of phosphate groups, sulphate groups and FeO$_6$ lead to growth of corresponding symmetrical vibrational bands with increase in the content of Fe$_2$O$_3$ up to 1.5 mol%. Such variations suggest an increase in the degree of disorder in the glass network owing to increasing presence of divalent iron ions that acts as modifiers. Thus the results of IR and the Raman spectral studies point out that, the depolymerization of the network of BF$_{15}$ glass is the highest among all the studied glasses.
Thus in a nutshell the measurements on optical absorption, ESR spectra clearly suggest, whereas IR and Raman support, the viewpoint that the redox ratio of iron ions increases with the content of Fe$_2$O$_3$ up to 1.5 mol% and decreases form the glass BF$_{15}$ to BF$_{20}$.

Recollecting the data on dielectric properties of Na$_2$SO$_4$–BaO–P$_2$O$_5$:Fe$_2$O$_3$ glasses, at higher frequency, the $\varepsilon'(\omega)$ approaches a constant value, $\varepsilon'_{\infty}(\omega)$, which results from rapid polarization processes occurring in the glasses under applied field [42, 72]. With decreasing frequency, $\varepsilon'(\omega)$ increases and reaches a low-frequency plateau, $\varepsilon'_s(\omega)$, usually associated with the polarization effects of the long range hoping of mobile ions (in this case defects created by Fe$^{2+}$ modifier ions such as [SO$_4$]$^{2-}$, [POO$_{1/2}$O$_2$]$^{2-}$, [POO$_{0/2}$O$_3$]$^{3-}$, Na$^+$ and (NaSO$_4$)$^-$/free ions) with respect to the immobile glass matrix.

The bulk polarization of the glass sample results from the presence of metallic electrodes, which avoid transfer of the charge species into the external circuit. Consequently, charge species are accumulated near the electrodes causing large space neare-surface charge polarization of the glass. The observed increase in, $\varepsilon'(\omega)$, at higher temperatures and at lower frequency can be caused by this polarization. The behavior of dielectric permittivity with frequency is related to the application of the field which favours electron hopping between two different sites in the glasses. This also leads to an
increase of the electronic component in dielectric constant dispersion. At higher frequency, the charge carriers will no longer be able to rotate sufficiently rapidly, so their oscillation will begin to lay behind this field leading to a decrease of dielectric permittivity, $\varepsilon'(\omega)$.

With the increase of Fe$_2$O$_3$ up to 1.5 mol% in the glass network, permittivity, $\varepsilon'(\omega)$, increases at any frequency and temperature. This observation supports an increase in the space charge polarization owing to the largest degree of disorder in the network of BF$_{15}$ glass [73, 74]. From the optical absorption and ESR studies it is evident that the glass BF$_{15}$ contains the largest concentration of Fe$^{2+}$ ions. The Fe$^{2+}$ ions similar to Ba$^{2+}$ and Na$^+$ ions, act as modifiers and create dangling bonds and non bridging oxygen ions by disrupting P–O–P, P–O–S, and P–O–Fe linkages. Such produced defects create easy pathways for the migration of charge carriers that would enhance the space charge polarization and facilitate to an increase $\varepsilon'(\omega)$ with the increase of Fe$_2$O$_3$ content up to 1.5 mol% [75-77].

The temperature features dielectric loss and $\varepsilon''$ dispersion indicate that there is a spreading of relaxation times. For understanding the dependence of this spreading with the concentration of Fe$_2$O$_3$, we have plotted Cole–Cole diagrams for $\varepsilon''(\omega) - \varepsilon'(\omega)$ at a fixed temperature. Fig. 3.15 shows the plot for the glass BF$_{15}$ at 453 K. The diagram shows that the dielectric relaxation in these glasses is a Debye-type like relaxation with a certain set of relaxation
times $\tau$. The points of intersection of the circular arc with the $X$-axis correspond to the low frequency and high frequency dielectric constants ($\varepsilon'_{\omega}$) and $\varepsilon'_{\infty}(\omega)$, respectively. Similar plots have also been drawn for other glasses. The parameter $\alpha$ is known as spreading factor, evaluated from these plots and characterizes the distribution function of relaxation time, $\tau$. The value of, $\alpha$, increases with the increase in the concentration of Fe$_2$O$_3$ up to 1.5 mol% (Table 3.6).

If it is assumed that the electrical field in these glasses is a Lorenz field, the connection between the number, $N$, of the dipoles per unit volume, the dipole moment, $\mu$, and the low and high frequency dielectric constants, $\varepsilon'_{\omega}(\omega)$ and $\varepsilon'_{\infty}(\omega)$, can be presented according to Classius–Mosetti Debye relation with modification of Bottcher and Bordewijk [42]:
Fig. 3.15 Cole-Cole plot (\(\log \varepsilon''(\omega) \) vs \(\log \varepsilon'(\omega)\)) drawn at 453 K for the glass BF\(_{15}\). Inset represents the variation of the quantity, \(4\pi N\mu^2/9k_B\), with the concentration of Fe\(_2\)O\(_3\).
Due to the fact in the present glasses, ions and dipoles can be approximately regarded as mere points and the concentration of dipoles is not abnormally high, one need not doubt the applicability of the Eq. (3.6), for these glasses. After rearranging the terms, Eq. (3.6) modified to:

\[
\frac{\epsilon'_s - 1}{\epsilon'_s + 2} - \frac{\epsilon'_\infty - 1}{\epsilon'_\infty + 2} = \frac{4\pi N\mu^2}{27k_B T}
\]  

(3.6)

The quantity, \(N\mu^2\), in the right hand side of Eq. (3.7) represents the strength of dipoles. Substituting the values of, \(\epsilon'_s(\omega)\) and \(\epsilon'_\infty(\omega)\), the quantity, \(4\pi N\mu^2/9k_B\) is evaluated at 453 K for different concentrations of Fe\(_2\)O\(_3\) and its dependence with the concentration of Fe\(_2\)O\(_3\) is presented in Fig. 3.15 for the titled glasses. The curve demonstrates an enhancement up to 1.5 mol% for Fe\(_2\)O\(_3\). Such behaviour obviously indicates an increase in the degree of spreading of relaxation times with several types of dipoles up to this concentration and a decrease in spreading beyond this concentration. Such spreading is possibly due to the coupling of individual relaxation processes, one site needing to relax before the other can do so. Even if each relaxation site has the same value of \(\tau\) the coupling between them ensures that the time domain is effectively stretched leading to the spreading of relaxation times as observed \([42, 78, 79]\). The possible contributors to the dipolar effects in
addition to the octahedral complexes of Fe$^{2+}$ ions are the complexes of Ba$^{2+}$ ions [80]. The decrease of activation energy for dipoles and also the relaxation time with increase in the content of Fe$_2$O$_3$ up to 1.5 mol % (Table 3.6), suggests the highest degree of freedom for dipoles to orient in the field direction in the network of BF$_{15}$ glass.

The impedance spectra are usually typical for glasses with two types of electrical conduction. In the spectra, semicircle arc corresponds to the bulk conduction, whereas the linear spur appeared in the low frequency side is due to the electrode polarization. The gradual increase of this spur with the increase of temperature suggests the thermally stimulated mobility of conducting ions. With increasing Fe$_2$O$_3$ content up to 1.5 mol% the spur increases gradually (Fig. 3.10). When Fe$_2$O$_3$ content is raised from 1.5 to 2.0 mol%, the spur is decreased indicating that even at high temperature, 523 K, the contribution of ionic mobility is too low for the formation of electrode spike in this glass. Such variations of the spur with the concentration of Fe$_2$O$_3$ in the impedance spectra indicate that conduction in the titled glasses undergoes a transition from predominantly ionic to electronic transport mechanism.

When a plot is made between log $\sigma_{ac}$ (or $\sigma_{dc}$) vs activation energy for conduction, a near-linear relationship is observed (inset (b) of Fig. 3.11(b)). This observation suggests that the conductivity enhancement is directly related to the thermally stimulated mobility of the charge carriers at higher
temperatures. As mentioned earlier, the glasses under study show mixed, ionic and polaronic, conductivity. Generally, electronic conduction is due to the polaron hopping between Fe\(^{2+}\) and Fe\(^{3+}\) ions whereas ionic conduction is predominately due to migration of Na\(^+\) ions. For the studied glasses, the ac conductivity increases with increasing content of Fe\(_2\)O\(_3\) up to 1.5 mol\%. The possible explanation for such a behavior is that with the gradual increase of Fe\(_2\)O\(_3\) content up to 1.5 mol\%, there is a growing presence of Fe\(^{2+}\) ions in the glass network. This is in accordance with the optical absorption, IR, Raman, ESR studies. These divalent iron ions act as modifiers and enhance the concentration of dangling bonds. This in turn causes a decrease in the electrostatic binding energy and the strain energy for the easy passage of sodium ions, which consequently leads to a substantial decrement in the jump distance for such ions. Such behavior is in good accordance with the observed decrease in activation energy for conduction. Therefore, the decrease in activation energy and increase in the conductivity with increasing Fe\(_2\)O\(_3\) content is obviously caused by decreasing degree of augmented cross-links in the glass network. In glasses containing Fe\(_2\)O\(_3\) greater than 1.5 mol\%, the concentration of Fe\(^{3+}\) ions that participate in the glass network forming with FeO\(_4\) structural exceeds that of Fe\(^{2+}\) ions. The decrease in the conductivity can, therefore, be interpreted in terms of transition of the mixed conduction with higher ionic contribution to the predominant electronic conduction.
The frequency response of real part of a.c conductivity is usually described by power law dependence with $s$ as exponent:

$$\sigma(\omega) = \sigma_{dc} [1 + (\omega/\omega_c)^s], \quad 0 \leq s < 1$$

(3.8)

$\omega_c$ is the characteristic macroscopic relaxation frequency.

When the mean square displacement of ions is small then, the ion transport is characterized by the non–random forward–backward hopping process, under these conditions Eq. (3.8) modifies to

$$\sigma(\omega) \propto \omega^s$$

(3.9)

The variation of the exponent (obtained by plotting $\log \sigma(\omega)$ vs $\omega$) is found to be the highest for the glass BF$_{15}$ (Table 3.7) suggesting that dimensionality of conducting space is the highest for this glass [81-83].

The a.c conductivity in the low temperature region (near plateau region) can be understood following the quantum mechanical tunneling model. Based on Austin and Mott’s model (quantum mechanical tunneling model) [84], the density of defect energy states near the Fermi level, $N(E_F)$, at nearly temperature independent region of the conductivity (low temperature) is evaluated using

$$\sigma(\omega) = (\pi/3)e^2k_BT \left[ N(E_F) \right]^2 \alpha'^{-5} \omega \left( \ln(v_o/\omega) \right)^4$$

(3.10)

In Eq. (3.10) $\alpha'$ is the electronic wave function decay constant, $v_0 (~5\times10^{12} \text{ Hz})$ is the phonon frequency. The value of $N(E_F)$ was calculated at a frequency of $1.02 \text{ kHz}$, $T = 363 \text{ K}$, taking $\alpha = 0.52 \text{ (Å)}^{-1}$ (obtained by plotting $\log \sigma_{ac}$
against $R_i$), using Eq. (3.4) and the values obtained are presented in Table 3.7. The value of $N(E_F)$ is found to be the highest for the glass BF$_{15}$. This result supports the viewpoint that the glass BF$_{15}$ contains the highest concentration of defect energy states.

For explaining the dc conductivity dispersion versus temperature different models were proposed. Some of the principal models are, (this model is based on single optical phonon approach in strong electron lattice coupling [85]), Schnakenberg’s model (according to this model as the temperature is lowered, the multi-phonon process is replaced by a single optical phonon process and, at the lowest temperatures, the polarons hop with one or more acoustic phonons). Normally this model is applicable for the temperatures $T < \theta_D/2$ [86]) and variable range hopping (VRH) model (this model works for the low temperatures $T < \theta_D/4$. according to this model, $\log \sigma \propto T^{-1/4}$ [87]). The critical examination of the obtained dc conductivity data for the present studied glasses indicates that, the applicability of last two models is quite unlikely.

According to small polaron hoping model [85],

$$\sigma_{dc} = \sigma_0 \exp(-W_{dc}/kT) \quad (3.11)$$

Where $\sigma_0 = \nu_o N_i e^2 R^2 C/k_B T (1-C) \exp(-2\alpha R_i) \quad (3.12)$

In Eq. (3.12), $N_i$ is the concentration of ions that contribute to the conductivity, $\nu_o$ is the phonon frequency ($= \theta_D k_B/h$); $C$ is the mole fraction of the sites occupied by conducting ions and $\alpha$ is the electron wave function decay
constant $R_i$, is the mean separation between iron ions. The term $\exp(-\alpha R_i)$ represents electron overlap integral. The graph obtained in Fig. 3.12 indicates Eq. (3.11) is perfectly suitable for the studied glasses. The increase of the dc conductivity, $\sigma_{dc}$, and decrease in activation energy, $W_{dc}$, up to 1.5 mol% of Fe$_2$O$_3$ inset (a) of Fig. 3.12, indicate the gradual increase of the ionic component of conductivity. In the region $x = 1.5$ to $2.0$ mol%, the polarons involved in the process of transfer from Fe$^{2+}$ to Fe$^{3+}$ are attracted by the oppositely charged Na$^+$ ions. This cation–polaron pair moves together as a neutral entity. As expected, the migration of this pair is not associated with any net displacement of the charge and hence there is a decrement of conductivity in this region.

To explore the origin of the hopping conduction in Na$_2$SO$_4$–BaO–P$_2$O$_5$: Fe$_2$O$_3$ glasses, a graph between log $\sigma_{dc}$ at 453 K and the activation energy, $W_{dc}$, is plotted as the inset (b) of Fig. 3.12 The graph obtained is a straight line. From the slope of this curve, the value of $1/k_B T$ is obtained and the temperature $T$ is estimated. The value of $T$ is found to be 468 K which is very close to the actual temperature. This suggests that the hopping is adiabatic.

Additionally in the interpretation of the origin, the hopping conduction was investigated. It is well known that the activation energy, $W_{dc}$, for the dc conductivity is expressed as [84]:

$$W_{dc} = W_{H^+} + \frac{1}{2} W_D \quad \text{for} \quad T > \theta_D/2$$  \hspace{1cm} (3.13)
\( W_{dc} = W_D \) for \( T < \theta_D / 4 \)

where \( W_H \) is the polaron hopping energy; \( W_D \) is the disorder energy and \( \theta_D \) is the Debye temperature. The polaron hopping energy is evaluated using the equation:

\[
W_H = W_p/2 = \frac{e^2}{4\varepsilon_p} \left( \frac{1}{R_p} - \frac{1}{R_i} \right)
\]

(3.14)

here, \( W_p \), is the polaron binding energy, \( R_p \) is the polaron radius and \( \varepsilon_p \) is effective dielectric constant. The calculated values for \( W_H \) (Table 3.8), decrease with increasing concentration of \( \text{Fe}_2\text{O}_3 \) in the glass network.

Table 3.8 Summary of the data related to ac conductivity of \( \text{Na}_2\text{SO}_4-\text{BaO-P}_2\text{O}_5: \text{Fe}_2\text{O}_3 \) glasses.

<table>
<thead>
<tr>
<th>Glass</th>
<th>A.E. for ac conduction (( W_{ac} ) (eV) (( \pm 0.001 ))</th>
<th>Exponents (at 483 K)</th>
<th>( N(E_F) ) (x ( 10^{21} ), eV(^{-1}) /cm(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>BF(_5)</td>
<td>0.85</td>
<td>0.72</td>
<td>1.20</td>
</tr>
<tr>
<td>BF(_{10})</td>
<td>0.743</td>
<td>0.81</td>
<td>1.34</td>
</tr>
<tr>
<td>BF(_{15})</td>
<td>0.66</td>
<td>0.92</td>
<td>1.54</td>
</tr>
<tr>
<td>BF(_{20})</td>
<td>0.71</td>
<td>0.85</td>
<td>1.06</td>
</tr>
</tbody>
</table>

In small polaron hopping model, SPH, the polaron bandwidth, \( J \), for adiabatic process is given by:

\[
J > \left( 2k_B T W_H/\pi \right)^{1/4} \left( h\nu_0 / \pi \right)^{1/2}
\]

(3.15)
The polaron bandwidths calculated from the relation $J = J_0 \exp(-\alpha R)$, where $J_0 = W_{H_{\text{min}}}/4$ [88] are presented in Table 3.8. It should be noted that the $J$ for all glasses satisfies the Eq. (3.15) and hence the conduction can be as assumed to be an adiabatic. This means that there appears a non–compatibility between the hopping rate of polaron and phonon frequency. According to a more general polaron hopping model, where $W_D > 0$, the optical multi-phonon determines the dc conductivity at high temperatures, whereas at low temperatures, charge carrier transport is via an acoustical phonon–assisted hopping process [86].

3.6 Conclusions

$\text{Na}_2\text{SO}_4$–$\text{BaO}$–$\text{P}_2\text{O}_5$ glasses mixed with different concentrations of $\text{Fe}_2\text{O}_3$ (ranging from 0.5 to 2.0 mol%) were synthesized. A complex spectroscopic (optical absorption, ESR, IR and Raman) electrical and dielectric studies have been carried out. The thermal analysis of these samples has indicated that the glass containing 1.5 mol % possesses lower stability against devitrification. The optical absorption and ESR studies indicated that iron ions exist in $\text{Fe}^{2+}$ and $\text{Fe}^{3+}$ local states. The results of these studies have confirmed that with the increasing concentration of $\text{Fe}_2\text{O}_3$ up to 1.5 mol%, there is a gradual increase in the redox ratio. The IR and Raman spectral investigations have revealed higher degree of disorder in the network of $\text{BF}_{15}$ glass. This may be understood as caused by higher depolymerization of the glass network by the $\text{Fe}^{2+}$ ions presented in larger concentration in this glass matrix. The ac and dc
conductivities have exhibited maximal effect, whereas the activation energy for the conduction exhibited minimal effect at 1.5 mol\% of Fe$_2$O$_3$. This is understood as follows: the divalent iron ions that present in larger proportions act as modifiers and increase the concentration of dangling bonds. This leads to a decrement in the electrostatic binding energy and the strain energy facilitating for the easy passage of conducting ions which ultimately cause to a substantial decrement in the jump distance of these ions. The analysis of the results of dc conductivity has indicated that when T > $\theta_D$/2, the small polaron hopping model is appropriate and the conduction is adiabatic in nature. These results further indicated that there is a mixed conduction both ionic and electronic in these glasses. The ac conductivity in the low temperature region is explained based on quantum mechanical tunneling model.

The variations of dielectric constant, $\varepsilon' (\omega)$, and loss, tan $\delta$, with temperature have been analyzed on the basis of dielectric polarization. The frequency and temperature dependence of the electrical moduli as well as dielectric loss parameters have exhibited relaxation character. The relaxation effects have been analyzed quantitatively using Cole-Cole plots and spreading of relaxation times has been established.
References


