CHAPTER 3

Dielectric and spectroscopic properties of CuO doped multi–component Li$_2$O–PbO–B$_2$O$_3$–SiO$_2$–Bi$_2$O$_3$–Al$_2$O$_3$ glass system

Multi-component silicate glasses of the chemical composition 19.4Li$_2$O–20PbO–20B$_2$O$_3$–30SiO$_2$–(10-x) Bi$_2$O$_3$–0.6 CuO: x Al$_2$O$_3$ with x ranging from 0-5mol% have been synthesized. A variety of spectroscopic (optical absorption, IR, Raman and ESR) and dielectric properties (over a range of frequency and temperature) of these glasses have been investigated as a function of Al$_2$O$_3$ concentration. The results of optical absorption and ESR spectral studies have indicated that a part of copper ions do exist in Cu$^+$ state in addition to Cu$^{2+}$ state especially in the samples containing low concentration of Al$_2$O$_3$. The IR and Raman spectral studies have revealed that there is a decreasing degree of disorder in the glass network with increase in the concentration of Al$_2$O$_3$ upto 3.0 mol%. The values of dielectric parameters viz., dielectric constant, loss and ac conductivity at any frequency and temperature are observed to decrease as the concentration of Al$_2$O$_3$ is increased upto 3.0 mol%. Such changes have been attributed to increase of redox ratio or increasing proportions of Cu$^+$ ions that take part in the glass network with CuO$_4$ structural units. The quantitative analysis of the results of ac conductivity and dielectric properties have indicated a decrease in the insulating character of the glasses when the concentration of Al$_2$O$_3$ is raised beyond 3.0 mol% in the glass network. This has been attributed to adaption of aluminium ions from tetrahedral co-ordination to octahedral co-ordination and also due to declustering influence of copper ions by aluminium ions in the glass network.
3.1 Introduction

Lithium borosilicate glasses containing transition metal ions have been the subject of an increasing academic and technological interest. These glasses find a wide range of applications such as glass fibers, optical lenses, as electrodes, for radioactive waste immobilization, in hermetic sealing of metallic and ceramic materials and as glass planar optical waveguides fabricated by ion exchange [1–4]. The addition of heavy metal oxides like PbO and Bi₂O₃ makes these glasses more denser, increases the refractive index and makes the glasses to exhibit non-linear optical effects since these oxides posses high electrical polarizability. Bi ions normally exist in Bi³⁺ state; however these ions also subsist in Bi⁺, Bi⁴⁺ and Bi⁵⁺ states in different hosts according to their fabricating technique, environmental atmosphere, temperature and local structure [5]. Earlier, it was also reported that Bi⁵⁺ and Bi⁺ ions do exhibit NIR emission with meta center at about 1200 nm with higher life times in the glass matrices [6, 7]. In view of these factors, the addition of Bi₂O₃ widens the range of applications of these glasses in optical and optoelectronic devices such as ultrafast switches, infrared windows, optical isolators, thermal and mechanical sensors [8–10].

Al₂O₃ added silicate glasses are being widely used as low cost optical connectors, dielectric and sealant materials for solid oxide fuel cells, as laser ion hosts, seals and as in vivo radiation delivery vehicles because of their high mechanical strength, electrical resistance and chemical durability [11–14].
Further, it has been widely accepted that aluminum ions influence the optical characteristics of transition metal ions in the host material. Normally, the transition metal ions will be partitioned by $\text{Al}^{3+}$, forming $\text{Al}–\text{O}–\text{M}$ bonds rather than sitting together to form $\text{M}–\text{O}–\text{M}$ bonds. Subsequently, the spacing among transition metal ions is larger in the alumina–doped silica host rather than in the non–alumina–containing host. As a result there will be enormous changes in the optical and electrical characteristics of the glass material contains transition metal ions [15, 16].

Among various transition metal ions, copper ion is a very interesting ion to probe in the multi–component silicate glass systems. In the silicate glass matrices this ion is expected to exist as metallic Cu, cuprous ($\text{Cu}^+$), or cupric ($\text{Cu}^{2+}$) states as per the following redox reaction

$$4\text{Cu}^{2+} + 2\text{O}_2^- \leftrightarrow 4\text{Cu}^+ + \text{O}_2$$

and affects not only optical, chemical, electrical and mechanical properties but also the glass–forming ability of the system [17,18]. Glasses containing copper ions in different oxidation states are highly useful for consideration of the materials to use in electrical memory switching devices. There are also some reports suggesting that copper ions in some glass systems containing alkali ions like lithium do exist in $\text{Cu}^{3+}$ state and form Li–Cu–O layered structures and makes the glass useful for cathode material in advanced lithium ion batteries [19].
In this study we have synthesized multi-component Li$_2$O–PbO–B$_2$O$_3$–SiO$_2$–Bi$_2$O$_3$: CuO glasses with different contents of Al$_2$O$_3$ and investigated the influence of variation of Al$_2$O$_3$ concentration on spectroscopic characteristics (optical absorption and ESR spectra) of copper ions and dielectric properties of the bulk material. The IR and Raman spectral studies have also been taken under so as to have some pre–structural information of the glass system that may facilitate for understanding the electrical properties as well as optical properties of the titled glass system.

3.2 Brief review of previous work on the glasses contains aluminium and copper ions

Wang et al. [20] have studied broad band infrared luminescence in a novel Bi–doped P$_2$O$_5$–B$_2$O$_3$–Al$_2$O$_3$ glass. From this study they have suggested that the introduction of B$_2$O$_3$ makes the glass structure closer and broadens NIR emission derives from Bi$^0$: $^2$D$_{3/2}$→$^4$S$_{3/2}$ and Bi$^+$: $^3$P$_1$→$^3$P$_0$ transitions. Kaur et al. [21] have studied the effect of swift heavy ions on structural and optical properties of bismuth based alumino–borosilicate glasses. From this study, it is seen that irradiation causes significant changes in compaction of the glass network. Yasser et al. [22] have studied structural influence of PbO by means of FTIR and acoustics on calcium alumino– borosilicate glass system. The observed compositional dependence of the ultrasonic velocity and the elastic moduli was interpreted in terms of the effect of PbO on the coordination of the borate structural units with oxygens and the depolymerization of the silicate network.
*Petru et al.* [23] have reported influence of europium ions on structure and crystallization properties of bismuth–alumino–borate glasses and glass ceramics. This site differs from the first one in the population of one position. In the third case the bismuth atoms, as well as the boron and aluminum atoms, respectively, are strongly bonded to four oxygen atoms. As per their report bismuth and boron atoms have a trigonal pyramidal geometry. *Achim Wiedenroth* and *Christian Russel* have studied thermodynamics of the redox equilibrium Fe\(^{2+}/Fe^{3+}\) and the diffusivity of iron in 5Na\(_2\)O – 15MgO – x Al\(_2\)O\(_3\) . (80 – x)SiO\(_2\) (x = 0–20) melts [24]. A structural model is proposed which explains the effect of the alumina concentration on the thermodynamics of the Fe\(^{2+}/Fe^{3+}\)–equilibrium and on the diffusivity of iron. *Carl et al.* [25] investigated the effect of composition on UV–vis–NIR spectra of iron doped glasses in the systems Na\(_2\)O/MgO/SiO\(_2\) and Na\(_2\)O/MgO/Al\(_2\)O\(_3\)/SiO\(_2\). At [Al\(_2\)O\(_3\)] > [Na\(_2\)O], the UV–cut off is found to be strongly shifted to smaller wavenumbers and the NIR peak at around 10000 cm\(^{-1}\) was attributed to Fe\(^{2+}\) in six fold coordination gets narrower. Furthermore, the intensity of the NIR peak at 5500 cm\(^{-1}\) increases. This is explained by the incorporation of iron in the respective glass structures.

*Abdel Wahab* and *Manal Abdel–Baki* have studied the electrical conduction and dielectric properties of lithium aluminum silicate glasses doped with Cr\(^{3+}\) ions [26]. The results of the real dielectric constant (\(ε’\)), loss factor (\(ε''\)) and loss tangent (tan δ) together with the Cole–Cole diagrams and the optical
(\varepsilon_{\infty}) and static (\varepsilon_s) dielectric constants for the studied samples are given and discussed. Hughes et al. [27] have reported the spectroscopy of bismuth–doped lead–aluminum–germanate glass and yttrium–aluminum–silicate glass. In Bi:YAS the strength of the Bi absorption had a quadratic dependence on Bi$_2$O$_3$ content. Mansour has studied Semi–quantitative analysis for FTIR spectra of Al$_2$O$_3$–PbO–B$_2$O$_3$–SiO$_2$ glasses [28]. A series of glass of the molar formula xAl$_2$O$_3$–(50–x) PbO–25B$_2$O$_3$–25SiO$_2$ with x: 2.5–17.5 with step of 2.5 mol. % was prepared. The role of PbO in PbO–B$_2$O$_3$ glasses arises from the same origin in both PbO–B$_2$O$_3$–SiO$_2$ and Al$_2$O$_3$–PbO–B$_2$O$_3$–SiO$_2$ glasses. It could be concluded that the IR band located near 700 cm$^{-1}$ is mainly due to the vibrations of BO’s between trigonal boron atoms. Measurements of density indicate that each oxide would contribute in density with a specific factor while the molar volume is found to be nonlinear. Stefan et al. [29] have studied the effect of copper ions addition on structural and optical properties of zinc borate glasses. This leads to the major changes of structural and optical properties of the studied glasses as can be seen from the data obtained by FTIR and EPR spectroscopies. Song et al [30] have studied time resolved current spectra (TRCS) and dielectric properties of 50Li$_2$O–50B$_2$O$_3$–xCu$_2$O glass system. El–Zaiat et al. [31] have studied spectral dispersion of linear optical properties for Sm$_2$O$_3$ doped B$_2$O$_3$–PbO–Al$_2$O$_3$ glasses. The effects of introducing different Sm$_2$O$_3$ concentrations on the different dispersion parameters are investigated. Doping B$_2$O$_3$–PbO–Al$_2$O$_3$
glass with 0.5g of Sm$_2$O$_3$ produced the highest changes in values of atomic parameters related to dispersive parameters of Wemple–DiDomenico single oscillator model and one–term Sellmeier dispersion relations. Yoon et al. [32] have studied Phase formation in the Al$_2$O$_3$–, quartz–, and cordierite–zinc borosilicate glass composites. From these studies it could be concluded that zinc in the ZBS glass reacted with ceramics and zinc compounds such as zinc silicate and zinc aluminate were formed. Cheng et al. [33] have reported viscosity, fragility and structure of Na$_2$O–CaO–Al$_2$O$_3$–SiO$_2$ glasses of increasing Al/Si ratio. Their analysis indicated that the number of NBO reducing and a more polymerized structure with adding Al/Si ratios were found to be responsible for the increase of viscosity while the tetrahedral distortion, a decrease of Q$^3$/Q$^2$ in the Q$^n$ species, were reported to be responsible for the increase of fragility.

Fang Wu et al. [34] have investigated the crystallization behavior and properties of K$_2$O–CaO–Al$_2$O$_3$–SiO$_2$ glass–ceramics. Liu et al. [35] have studied Eu/Dy ions co–doped white light luminescence zinc–alumino borosilicate glasses for white LEDs. Furthermore, the reduction of Eu$^{3+}$ → Eu$^{2+}$ in air at high temperature was observed in the zinc–alumino borosilicate glasses. Yuan et al. [36] investigated the effects of CuO secondary phase on dielectric properties of CaCu$_3$Ti$_4$O$_{12}$ ceramics. The high sintering temperature of 1000 °C causes the CuO phase to separate out and aggregate at grain boundaries of the surface layer in the ceramic pellet. The presence of the CuO phase is found to increase the
average grain size and decreases the grain–boundary thickness that leads the enhancement of the dielectric constant. Song et al. [37] have studied the glass transition temperature \( T_g \), thermal coefficient of expansion (TCE), and root–mean square (rms) roughness of 0.005 wt% CuO doped Bi\(_2\)O\(_3\)–B\(_2\)O\(_3\)–BaO–ZnO glasses. From the observed range of these values results the authors have concluded that prepared glass is suitable for a transparent dielectric layer for PDP application. In spite of availability of a considerable amount of literature on Al\(_2\)O\(_3\) glasses, as such no detailed studies (especially the dielectric properties) on the influence of CuO on Li\(_2\)O–PbO–B\(_2\)O\(_3\)–SiO\(_2\)–Bi\(_2\)O\(_3\)–Al\(_2\)O\(_3\) glasses.

3.3 Characterization

The detailed compositions of the glasses used in the present study are as follows:

A0: 19.4Li\(_2\)O–20PbO–20B\(_2\)O\(_3\)–30SiO\(_2\)–10Bi\(_2\)O\(_3\)–0.6 CuO
A1: 19.4Li\(_2\)O–20PbO–20B\(_2\)O\(_3\)–30SiO\(_2\)–9Bi\(_2\)O\(_3\)–0.6CuO: 1Al\(_2\)O\(_3\)
A2: 19.4Li\(_2\)O–20PbO–20B\(_2\)O\(_3\)–30SiO\(_2\)–8Bi\(_2\)O\(_3\)–0.6CuO: 2Al\(_2\)O\(_3\)
A3: 19.4Li\(_2\)O–20PbO–20B\(_2\)O\(_3\)–30SiO\(_2\)–7Bi\(_2\)O\(_3\)–0.6CuO: 3Al\(_2\)O\(_3\)
A4: 19.4Li\(_2\)O–20PbO–20B\(_2\)O\(_3\)–30SiO\(_2\)–6Bi\(_2\)O\(_3\)–0.6CuO: 4Al\(_2\)O\(_3\)
A5: 19.4Li\(_2\)O–20PbO–20B\(_2\)O\(_3\)–30SiO\(_2\)–5Bi\(_2\)O\(_3\)–0.6CuO: 5Al\(_2\)O\(_3\)

3.3.1 Physical parameters

From the measured values of the density and average molecular weight \( \bar{M} \) of the samples, various other physical parameters such as copper ion concentration
$N_i$, mean copper ion separation $r_i$, polaron radius $r_p$ in Li$_2$O–PbO–B$_2$O$_3$–SiO$_2$–Bi$_2$O$_3$–CuO: Al$_2$O$_3$ glass samples have been evaluated and presented in Table 3.1.

3.3.2 X–ray diffraction

XRD patterns of some of the prepared samples are shown in Fig. 3.1; the pattern did not indicate any sharp Bragg peaks confirming the amorphous nature of samples.

Fig 3.1 XRD patterns of Li$_2$O–PbO–B$_2$O$_3$–SiO$_2$–Bi$_2$O$_3$–CuO glasses mixed with various concentrations of Al$_2$O$_3$. 
Table 3.1

Physical Parameters of Li$_2$O–PbO–B$_2$O$_3$–SiO$_2$–Bi$_2$O$_3$–CuO glasses mixed with various concentrations of Al$_2$O$_3$

<table>
<thead>
<tr>
<th>Sample</th>
<th>Conc. Al$_2$O$_3$ (mol%)</th>
<th>Avg.Mol. wt. $\frac{\mu}{M}$</th>
<th>Density $\rho$ (g/cm$^3$) (±0.001)</th>
<th>Molar Volume $V_m$ (cm$^3$) (±0.0001)</th>
<th>Conc. copper ions $N_i$ (x10$^{21}$ ions/cm$^3$) (±0.001)</th>
<th>Inter ionic distance of copper ions $R_i$ (Å) (±0.001)</th>
<th>Polaron radius $R_p$ (Å) (±0.001)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A0</td>
<td>0</td>
<td>129.37</td>
<td>4.445</td>
<td>0.43</td>
<td>12.42</td>
<td>4.34</td>
<td>1.74</td>
</tr>
<tr>
<td>A1</td>
<td>1</td>
<td>125.73</td>
<td>4.393</td>
<td>0.33</td>
<td>12.63</td>
<td>4.29</td>
<td>1.73</td>
</tr>
<tr>
<td>A2</td>
<td>2</td>
<td>122.09</td>
<td>4.297</td>
<td>0.41</td>
<td>12.72</td>
<td>4.28</td>
<td>1.72</td>
</tr>
<tr>
<td>A3</td>
<td>3</td>
<td>118.45</td>
<td>4.200</td>
<td>0.44</td>
<td>12.81</td>
<td>4.27</td>
<td>1.72</td>
</tr>
<tr>
<td>A4</td>
<td>4</td>
<td>114.81</td>
<td>4.208</td>
<td>0.43</td>
<td>13.25</td>
<td>4.23</td>
<td>1.70</td>
</tr>
<tr>
<td>A5</td>
<td>5</td>
<td>111.17</td>
<td>4.117</td>
<td>0.46</td>
<td>13.38</td>
<td>4.21</td>
<td>1.69</td>
</tr>
</tbody>
</table>
3.4 Results

3.4.1 Optical absorption

Fig. 3.2 represents the optical absorption spectra of Li$_2$O–PbO–B$_2$O$_3$–SiO$_2$–Bi$_2$O$_3$–CuO glasses mixed with different concentration of Al$_2$O$_3$ recorded at ambient temperature in the wavelength region 300–1200 nm. The cutoff wavelength observed at 362.5 nm for the glass A0 is found to decrease with increase in the concentration of Al$_2$O$_3$ up to 3.0 mol% and beyond this concentration the edge exhibited spectrally red shift. The absorption spectra further, exhibited broad absorption peak centered at 744 nm due to $^2$B$_{1g}$$\rightarrow$$^2$B$_{2g}$ octahedral transition of Cu$^{2+}$ ions; the intensity of this band is observed to decrease as the concentration of Al$_2$O$_3$ is increased up to 3.0 mol%. Additionally, another band at 364.5 nm identified as being due to charge transfer between the two oxidation states of copper ions viz., Cu$^+$→Cu$^{2+}$ is also located in the spectra of all these glasses.

From the observed absorption edges, we have evaluated the optical band gaps ($E_o$) of these glasses by drawing Tauc plots (Fig. 3.3) between $(\alpha\omega)^{1/2}$ and $\hbar\omega$ as per the following equation:

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

The values of optical band gap ($E_o$) evaluated from the extrapolation of these curves are presented in (Table 3.2); the value of $E_o$ with the concentration of
$\text{Al}_2\text{O}_3$ exhibited maximal effect at $x = 3.0 \text{ mol}\%$ and found to decrease for further increase of $\text{Al}_2\text{O}_3$ content (Table 3.2).

The coefficient of Urbach’s exponential tail region is given by

$$\alpha(\nu) = C \exp \left( \frac{\hbar \nu}{\Delta E} \right), \quad (3.2)$$

where $C$ is constant and $\Delta E$ is the Urbach’s energy interpreted as the energy required for optical transitions between localized tail states in the band gap [38].

The values of $\Delta E$ were calculated by taking reciprocals of the slopes of the linear portion of the $\ln \alpha(\nu)$ vs $\hbar \omega$ curves (Fig. 3.4) and are furnished in Table 3.2.;

![Optical absorption spectra](image)

**Fig. 3.2** Optical absorption spectra of $\text{Li}_2\text{O}–\text{PbO}–\text{B}_2\text{O}_3–\text{SiO}_2–\text{Bi}_2\text{O}_3–\text{CuO}$ glasses mixed with various concentrations of $\text{Al}_2\text{O}_3$. Inset shows the absorption band due to charge transfer between the two oxidation states of copper ions.
Fig. 3.3 Tauc plots of Li$_2$O–PbO–B$_2$O$_3$–SiO$_2$–Bi$_2$O$_3$–CuO glasses mixed with various concentrations of Al$_2$O$_3$. 
Fig. 3.4 $\ln \alpha$ vs. $h\omega$ (photon energy) of Li$_2$O–PbO–B$_2$O$_3$–SiO$_2$–Bi$_2$O$_3$–CuO glasses mixed with various concentrations of Al$_2$O$_3$.

Table 3.2

Cut–off wavelength ($\lambda_c$), Optical Bandgap ($E_o$) and Urbach Energy ($\Delta E$) of Li$_2$O–PbO–B$_2$O$_3$–SiO$_2$–Bi$_2$O$_3$–CuO glasses mixed with various concentrations of Al$_2$O$_3$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\lambda_c$ (nm) (±0.1)</th>
<th>Band Position $^2B_{1g} \rightarrow ^2B_{2g}$ (nm) (±0.1)</th>
<th>$E_o$ (eV) (±0.001)</th>
<th>$\Delta E$ (eV) (±0.001)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A0</td>
<td>362.5</td>
<td>755</td>
<td>3.394</td>
<td>0.206</td>
</tr>
<tr>
<td>A1</td>
<td>362.0</td>
<td>743</td>
<td>3.399</td>
<td>0.210</td>
</tr>
<tr>
<td>A2</td>
<td>360.5</td>
<td>736</td>
<td>3.404</td>
<td>0.208</td>
</tr>
<tr>
<td>A3</td>
<td>359.0</td>
<td>715</td>
<td>3.408</td>
<td>0.220</td>
</tr>
<tr>
<td>A4</td>
<td>362.5</td>
<td>759</td>
<td>3.394</td>
<td>0.215</td>
</tr>
<tr>
<td>A5</td>
<td>363.0</td>
<td>766</td>
<td>3.389</td>
<td>0.206</td>
</tr>
</tbody>
</table>
3.4.2 ESR Spectra

Fig. 3.5 represents the ESR spectra of titled glass samples recorded at ambient temperature. The spectra exhibited a pronounced resonance signal at about $g = 2.069$ (perpendicular component, $g_\perp$) and a shallow quadruplet at $g = 2.299$ (parallel component, $g_\parallel$). The line width of parallel and perpendicular hyperfine peaks is observed to decrease with the order of magnetic quantum number $m_l$. With the variation in concentration of $\text{Al}_2\text{O}_3$, slight variations in the $g$– tensors are observed (Table 3.3). A considerable decrease in the intensity of signal is also observed with increase in the concentration of $\text{Al}_2\text{O}_3$ up to 3.0 mol%.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$g_\parallel$ (±0.001)</th>
<th>$g_\perp$ (±0.001)</th>
<th>$\alpha^2$ (±0.01)</th>
<th>$\beta_1^2$ (±0.01)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A0</td>
<td>2.299</td>
<td>2.069</td>
<td>0.78</td>
<td>0.95</td>
</tr>
<tr>
<td>A1</td>
<td>2.407</td>
<td>2.065</td>
<td>0.75</td>
<td>0.93</td>
</tr>
<tr>
<td>A2</td>
<td>2.300</td>
<td>2.053</td>
<td>0.74</td>
<td>0.81</td>
</tr>
<tr>
<td>A3</td>
<td>2.291</td>
<td>2.043</td>
<td>0.73</td>
<td>0.80</td>
</tr>
<tr>
<td>A4</td>
<td>2.284</td>
<td>2.068</td>
<td>0.77</td>
<td>0.82</td>
</tr>
<tr>
<td>A5</td>
<td>2.277</td>
<td>2.077</td>
<td>0.79</td>
<td>0.86</td>
</tr>
</tbody>
</table>
Fig 3.5 EPR spectra of Li$_2$O–PbO–B$_2$O$_3$–SiO$_2$–Bi$_2$O$_3$–CuO glasses mixed with various concentrations of Al$_2$O$_3$. 
3.4.3 IR Spectra

The infrared transmission spectrum of Al$_2$O$_3$ free Li$_2$O–PbO–B$_2$O$_3$–SiO$_2$–Bi$_2$O$_3$–CuO glass (Fig. 3.6) exhibited vibrational bands at 1284 cm$^{-1}$ (identified as being due to BO$_3$ structural units), 1121 cm$^{-1}$ (due to BO$_4$ units), 1032 cm$^{-1}$ (due to Si–O–Si asymmetric bending vibrations), 849 cm$^{-1}$ (due to Si–O–Si symmetrical vibrations; in this region band due to AlO$_4$ vibrations is also possible), 697 cm$^{-1}$ (due to B–O–B bending vibrations), 475 cm$^{-1}$ (Si–O–Si rocking motion and this region may also consisting of vibrations due to PbO$_4$ and AlO$_6$ structural units) [39] and at 449 cm$^{-1}$ (due to vibrations Bi–O–Bi bonds of BiO$_6$ units[40]). With addition of Al$_2$O$_3$ in the glass sample up to 3.0 mol%, the intensity of all the symmetrical bands of silicate groups and also that of BO$_4$ units is observed to increase, whereas that of asymmetrical bands and also that of the band due to BiO$_6$ units and BO$_3$ units is observed to decrease. When the concentration of Al$_2$O$_3$ is raised beyond 3.0 mol%, the asymmetrical bands are observed to grow at the expense of symmetrical bands (Fig. 3.6) (Table 3.4).
Table 3.4

Assignment of FTIR bands (cm\(^{-1}\)) with a probable error of ± 0.1 cm\(^{-1}\) of Li\(_2\)O–PbO–B\(_2\)O\(_3\)–SiO\(_2\)–Bi\(_2\)O\(_3\)–CuO glasses mixed with various concentrations of Al\(_2\)O\(_3\).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Bi–O–Bi bonds/BiO(_6) units</th>
<th>Si–O–Si Rocking/Alo(_6)/PbO(_4) units</th>
<th>B–O–B bond</th>
<th>Si–O–Si Symmetrical/Alo(_4) units</th>
<th>Si–O–Si Assymtrical</th>
<th>BO(_4) units</th>
<th>BO(_3) units</th>
</tr>
</thead>
<tbody>
<tr>
<td>A0</td>
<td>449</td>
<td>475</td>
<td>697</td>
<td>849</td>
<td>1032</td>
<td>1121</td>
<td>1284</td>
</tr>
<tr>
<td>A1</td>
<td>443</td>
<td>475</td>
<td>685</td>
<td>842</td>
<td>1022</td>
<td>1119</td>
<td>1268</td>
</tr>
<tr>
<td>A2</td>
<td>443</td>
<td>488</td>
<td>677</td>
<td>840</td>
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<td>441</td>
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<td>685</td>
<td>838</td>
<td>1063</td>
<td>1121</td>
<td>1284</td>
</tr>
<tr>
<td>A4</td>
<td>449</td>
<td>480</td>
<td>677</td>
<td>843</td>
<td>1032</td>
<td>1125</td>
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<td>A5</td>
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<td>685</td>
<td>849</td>
<td>1014</td>
<td>1126</td>
<td>1284</td>
</tr>
</tbody>
</table>
Fig 3.6 FTIR patterns of Li$_2$O–PbO–B$_2$O$_3$–SiO$_2$–Bi$_2$O$_3$–CuO glasses mixed with various concentrations of Al$_2$O$_3$. 

- BO$_3$ units
- Si-O-Si Asymmetric
- Si-O-Si symmetric/AlO$_4$ units
- B-O-B Bending
- Bi-O bonds in BiO$_6$ units
- Si-O-Si rocking/AlO$_6$ units/PbO$_4$ units
- B-O-BO units from tri, tetra and penta borate groups
3.4.4 Raman spectra

The Raman spectra (Fig. 3.7) of CuO doped Li$_2$O–PbO–B$_2$O$_3$–SiO$_2$–Bi$_2$O$_3$–Al$_2$O$_3$ glasses have exhibited three prominent bands (Table 3.5) at about 1053, 810 and 478 cm$^{-1}$ assigned to symmetrical, asymmetrical and rocking vibrations motion of Si–O–Si structural units, respectively [41]. The spectra also exhibited a band at 1040 cm$^{-1}$, ascribed to diborate groups consisting of six membered rings containing two BO$_4$ tetrahedra and another band centered at 805 cm$^{-1}$ attributed to the boroxil ring oxygen breathing in which the boron coordinate atom is three [42, 43]. In this region Al–O stretching vibrations of Al tetrahedral coordination is also possible [44]. In the region of rocking vibrations of Si–O–Si structural units (at about 478 cm$^{-1}$) there is possibility for the presence of a band due to bridging oxygen breathing mode in (Si, Al) four membered rings [44]. A new band at about 544 cm$^{-1}$ identified due to Bi–O vibrations in BiO$_6$ units is also located in the spectra of these glasses [40]. In this region the vibrational band due to (Si, Al) three–membered rings was also reported [44]. The spectra also exhibited a weak kink at about 260 cm$^{-1}$ due to Bi–O breathing modes in BiO$_3$ pyramidal units [40]. As the concentration of Al$_2$O$_3$ is increased up to 3.0 mol% the intensity of SiO$_4$ symmetrical band and band due BO$_4$ structural units were found to be increasing. However, when the concentration of Al$_2$O$_3$ is raised beyond 3.0 mol% the intensity of all asymmetrical bands is found to be increasing in Table 3.5.
Table 3.5

Assignment of Raman bands (cm$^{-1}$) with a probable error of ± 0.1 cm$^{-1}$ of Li$_2$O–PbO–B$_2$O$_3$–SiO$_2$–Bi$_2$O$_3$–CuO glasses mixed with various concentrations of Al$_2$O$_3$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Breathing in BiO$_3$ pyramidal units</th>
<th>Si–O–Si Rocking/AIO$_6$/PbO$_4$ units</th>
<th>Bi–O vibration in distorted BiO$_6$ units/B–O–B bonding</th>
<th>Si–O–Si Symmetrical/AIO$_4$ units</th>
<th>Si–O–Si Asymmetrical units</th>
<th>BO$_4$ units</th>
<th>BO$_3$ units</th>
</tr>
</thead>
<tbody>
<tr>
<td>A0</td>
<td>284</td>
<td>452</td>
<td>590</td>
<td>841</td>
<td>1063</td>
<td>1196</td>
<td>1298</td>
</tr>
<tr>
<td>A1</td>
<td>284</td>
<td>433</td>
<td>579</td>
<td>852</td>
<td>1070</td>
<td>1212</td>
<td>1300</td>
</tr>
<tr>
<td>A2</td>
<td>280</td>
<td>426</td>
<td>579</td>
<td>852</td>
<td>1070</td>
<td>1212</td>
<td>1300</td>
</tr>
<tr>
<td>A3</td>
<td>275</td>
<td>433</td>
<td>579</td>
<td>840</td>
<td>1042</td>
<td>1215</td>
<td>1298</td>
</tr>
<tr>
<td>A4</td>
<td>284</td>
<td>429</td>
<td>580</td>
<td>811</td>
<td>1042</td>
<td>1218</td>
<td>1313</td>
</tr>
<tr>
<td>A5</td>
<td>283</td>
<td>433</td>
<td>585</td>
<td>772</td>
<td>1039</td>
<td>1212</td>
<td>1280</td>
</tr>
</tbody>
</table>
Fig 3.7 Raman spectra of Li$_2$O–PbO–B$_2$O$_3$–SiO$_2$–Bi$_2$O$_3$–CuO glasses mixed with various concentrations of Al$_2$O$_3$
3.4.5 Dielectrics

The temperature dependence of $\varepsilon'$ of the glasses containing different concentrations of $\text{Al}_2\text{O}_3$ measured at 1 kHz in the temperature range 30–300 °C is shown in Fig. 3.8 and the frequency dispersion with temperature of glass A5 is shown as the inset of same figure. The value of $\varepsilon'$ is increased with temperature at all frequencies; the rate of increase is, however, found to be the higher at lower frequencies. The variation of $\varepsilon'$ at any frequency and temperature with the content of $\text{Al}_2\text{O}_3$ exhibited minimal effect at 3.0 mol%.

A comparison plot of variation of dielectric loss tan $\delta$ with temperature measured at a frequency of 10 kHz for all glass samples is shown in Fig 3.9; the inset of this figure represents the temperature dependence of tan $\delta$ of A1 sample at different frequencies.

The temperature dependence of loss tan $\delta$ at different frequencies exhibits distinct maxima indicating dipolar relaxation character of dielectric loss in these glass samples. The comparison of dielectric loss variation with temperature for the glasses mixed with different concentration of $\text{Al}_2\text{O}_3$ indicated a gradual decrease in the broadness and $(\tan \delta)_{\text{max}}$ of relaxation curves with increase in the concentration of $\text{Al}_2\text{O}_3$ up to 3.0 mol% with a shift of the relaxation region towards higher temperature. Using the relation,

$$f = f_o \exp \left(-\frac{W_d}{kT}\right),$$  \hspace{1cm} (3.3)
the effective activation energy, $W_d$, for the dipoles is calculated and presented in Table 3.6. The activation energy is found to be the highest for glass A3.

**Fig. 3.8** Variation of dielectric constant $\varepsilon'$ with temperature at 1 kHz for different concentrations of $\text{Al}_2\text{O}_3$ in $\text{Li}_2\text{O–PbO–B}_2\text{O}_3–\text{SiO}_2–\text{Bi}_2\text{O}_3–\text{CuO}$ multi component glasses. Inset shows the variation of $\varepsilon'$ with temperature for different frequencies of A5 sample.
Fig. 3.9 Variation of dielectric loss $\tan \delta$ with temperature at 10 kHz for different concentrations of $\text{Al}_2\text{O}_3$ in $\text{Li}_2\text{O}–\text{PbO}–\text{B}_2\text{O}_3–\text{SiO}_2–\text{Bi}_2\text{O}_3–\text{CuO}$ multi component glasses. Inset shows the variation of $\tan \delta$ with temperature at different frequencies of A1 sample.
It may be noted here that we have measured both dielectric constant and loss at several frequencies in the range 1 kHz to 1 MHz. However, to avoid clumsiness only the data of some selected frequencies were presented.

Table 3.6
Summary of data on dielectric loss of Li$_2$O–PbO–B$_2$O$_3$–SiO$_2$–Bi$_2$O$_3$–CuO glasses mixed with various concentrations of Al$_2$O$_3$.

<table>
<thead>
<tr>
<th>Sample (±0.001)</th>
<th>(Tanδ)$_{max}$</th>
<th>Temp. region of relaxation (±1) °C</th>
<th>AE for dipoles (±0.01) eV</th>
<th>Spreading Factor β (rads)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A0</td>
<td>0.032</td>
<td>95–147</td>
<td>2.29</td>
<td>0.80</td>
</tr>
<tr>
<td>A1</td>
<td>0.031</td>
<td>105–153</td>
<td>2.41</td>
<td>0.72</td>
</tr>
<tr>
<td>A2</td>
<td>0.030</td>
<td>120–160</td>
<td>2.53</td>
<td>0.65</td>
</tr>
<tr>
<td>A3</td>
<td>0.029</td>
<td>130–165</td>
<td>2.66</td>
<td>0.58</td>
</tr>
<tr>
<td>A4</td>
<td>0.033</td>
<td>90–145</td>
<td>2.14</td>
<td>0.75</td>
</tr>
<tr>
<td>A5</td>
<td>0.034</td>
<td>80–140</td>
<td>2.06</td>
<td>0.87</td>
</tr>
</tbody>
</table>

The a.c conductivity $\sigma_{ac}$ for all the glasses is evaluated at different temperatures using the equation:

$$\sigma_{ac} = \omega \varepsilon' \varepsilon_0 \tan \delta,$$

(3.4)

(where $\varepsilon_0$ is the vacuum dielectric constant and $\omega$ is the frequency) and its variation with $1/T$ for all the glasses at 100 kHz is shown in the Fig. 3.10. From these plots, the activation energy for conduction in the higher temperature region over which a near linear dependence of $\log \sigma_{ac}$ with $1/T$ observed is calculated.
and presented in Table 3.7. The activation energy exhibited minimal effect at 3.0 mol% of Al$_2$O$_3$.

**Fig 3.10** Variation of $\sigma_{ac}$ with 1000/T at 100 kHz for different concentrations of Al$_2$O$_3$ in Li$_2$O–PbO–B$_2$O$_3$–SiO$_2$–Bi$_2$O$_3$–CuO glasses. Insets represent the variation of $\sigma_{ac}$ with (a) activation energy and (b) with the concentration of Al$_2$O$_3$. 
Table 3.7
Summary of the data on ac. conductivity of Li$_2$O–PbO–B$_2$O$_3$–SiO$_2$–Bi$_2$O$_3$–CuO glasses mixed with various concentrations of Al$_2$O$_3$.

<table>
<thead>
<tr>
<th>Glass</th>
<th>$\sigma_{ac}$ at 80 $^\circ$C ($10^{-6}$) (Ω⋅cm)$^{-1}$</th>
<th>N(E$_F$) ($10^{21}$, eV$^{-1}$/cm$^3$) (±0.01)</th>
<th>Exponent $S$</th>
<th>Activation energy for conduction (eV) (±0.01)</th>
<th>Breakdown strength (±0.01) kV/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>A0</td>
<td>5.57 (±0.01)</td>
<td>1.15 (±0.01)</td>
<td>0.87 (±0.01)</td>
<td>Austin</td>
<td>0.69 (±0.01)</td>
</tr>
<tr>
<td>A1</td>
<td>5.30 (±0.01)</td>
<td>1.12 (±0.01)</td>
<td>0.89 (±0.01)</td>
<td>0.76 (±0.01)</td>
<td>8.82 (±0.01)</td>
</tr>
<tr>
<td>A2</td>
<td>5.02 (±0.01)</td>
<td>1.08 (±0.01)</td>
<td>0.90 (±0.01)</td>
<td>0.86 (±0.01)</td>
<td>10.71 (±0.01)</td>
</tr>
<tr>
<td>A3</td>
<td>4.68 (±0.01)</td>
<td>1.05 (±0.01)</td>
<td>0.92 (±0.01)</td>
<td>0.96 (±0.01)</td>
<td>11.79 (±0.01)</td>
</tr>
<tr>
<td>A4</td>
<td>5.90 (±0.01)</td>
<td>1.18 (±0.01)</td>
<td>0.86 (±0.01)</td>
<td>0.65 (±0.01)</td>
<td>8.29 (±0.01)</td>
</tr>
<tr>
<td>A5</td>
<td>6.17 (±0.01)</td>
<td>1.21 (±0.01)</td>
<td>0.85 (±0.01)</td>
<td>0.55 (±0.01)</td>
<td>7.80 (±0.01)</td>
</tr>
</tbody>
</table>

3.5 Discussion

Among various constituents of Li$_2$O–PbO–B$_2$O$_3$–SiO$_2$–Bi$_2$O$_3$–CuO: Al$_2$O$_3$ glass system, SiO$_2$ participates in the glass network with tetrahedral [SiO$_{4/2}$]$^0$ units and all the four oxygens in SiO$_4$ tetrahedra are shared. With the entry of modifiers like Li$_2$O into Si–O–Si network, the structure gets depolymerised resulting the formation of meta, pyro and ortho–silicates in the order: [SiO$_{4/2}$]$^0$ (Q$^4$), [SiO$_{3/2}$O]$^-$(Q$^3$), [SiO$_{2/2}$O$_2$]$^{2-}$(Q$^2$), [SiO$_{1/2}$O$_3$]$^{3-}$(Q$^1$) and [SiO$_4$]$^{4-}$(Q$^0$) as per the following chemical equilibria [39]:

$$2[SiO_{4/2}]^0 + Li_2O \rightarrow [SiO_{3/2}O]^− + 2 Li^+$$

$$2 [SiO_{2/2}O_2]^{2−} + Li_2O \rightarrow 2 [SiO_{1/2}O_3]^{3−} + 2 Li^+$$
B₂O₃ is also a well–known strong glass former. When it is added to the silicate glasses, generally tetrahedral boron entities dominate in the silicate–rich domain and form B–O–Si bridges, whereas trigonal boron entities prevail in the borate–rich side.

Although Bi₂O₃ is a weak glass former, in the presence of glass formers like SiO₂ and B₂O₃ and modifiers, it participates in the glass network with triangular BiO₃ pyramidal units. In this case, the coordination of bismuth in the glass network can be viewed as tetrahedrons with the oxygen at three corners and 6s² stereo chemically active electronic lone pair at the fourth corner. However, Bi₂O₃ also participates in the network with [BiO₆] octahedral units [45]. The presence of such structural units is evident from IR and Raman spectral studies.

Earlier NMR studies on alumino silicate glasses have indicated that these ions occupy mainly tetrahedral (AlO₄) and octahedral (AlO₆) sites [46]:

\[
2\text{Al}_2\text{O}_3 \rightarrow [\text{Al}^{3+}]_3^0 + 3[\text{AlO}_{4/2}]_t
\]

It is common understanding that Al³⁺ is in tetrahedral coordination in aluminum silicate melts with sufficient modifying cations like Li⁺ for charge–balance. Coordination transformation of Al³⁺ from a network former to a network modifier in a melt with

\[(\text{Al}^{3+} + \text{Si}^{4+})_2 \text{O}_5^{2–}\] stoichiometry may be expressed with the formalized equation:

\[
5\text{Si}_2\text{O}_5^{2–} + (\text{LiAl})_2\text{O}_5^{2–} = 10[(\text{SiO}_3)^{2–} / (\text{SiO}_{2/2}\text{O}_2)^{2–}] + 2 \text{Li}^+ + 2\text{Al}^{3+}
\]
However, some previous studies on other silicate glasses containing Al$_2$O$_3$ have pointed out that Al(6) dominates the glass structure when Al$_2$O$_3$ is present in low concentrations and Al(4) structural units prevail when Al$_2$O$_3$ is present in higher concentrations [47]. Regardless of which participation is chosen, a coordination transformation of Al$^{3+}$ in any of the compositions will cause a rapid increase in the relative intensities of IR / Raman bands of Si–O$^-$ stretch vibrations.

The oxygen triclusters of such units (oxygen ion bonded to two [AlO$_4$] and one [SiO$_4$] or [BO$_4$], one [AlO$_4$] and two [SiO$_4$] or [BO$_4$] take part in inducing bonding defects in the glass containing Al$_2$O$_3$, SiO$_2$ and B$_2$O$_3$. PbO, normally in the concentration range used in the present study, acts as a modifier and as a result Si–O–Si and Si–O–Al bonds are cleaved in succession. Such behaviour also leads to the depolymerization of the glass network.

Copper ions are expected to exist mainly in Cu$^{2+}$ state in Li$_2$O–PbO–B$_2$O$_3$–SiO$_2$–Bi$_2$O$_3$–CuO: Al$_2$O$_3$ glass network. However, the oxidation or reduction of copper ions from Cu$^{2+}$ to Cu$^{3+}$ and Cu$^+$ appears to be possible during melting and annealing processes. Cu$^{2+}$ ions occupy octahedral positions, whereas Cu$^+$ and Cu$^{3+}$ ions are expected to occupy tetrahedral positions in the glass network [46–48].

The broad absorption band observed in the optical absorption spectra of titled glass is assigned to $^2B_{1g} \rightarrow ^2B_{2g}$ transition of Cu$^{2+}$ ions [39]. The broadening of
this band may be attributed to the superposition of three electron transitions in d orbitals corresponding to $^2B_{1g} \rightarrow ^2E_g$, $^2B_{1g} \rightarrow ^2A_{1g}$ and $^2B_{1g} \rightarrow ^2B_{2g}$ transitions. Further, the optical activation energy associated with $^2B_{2g} \rightarrow ^2B_{1g}$ is increased from 1.65 (sample A0) to 1.72 eV (sample A3); this is clearly a characteristic signal of inter-valence transfer or a polaronic type of absorption. This is possible when the associated electrons are trapped at deeper sites within the main band gap with higher wave-function radii; in terms of polaronic perception, this kind of situation is only possible if the local potential fluctuation is high as compared to the transfer integral, $j$. A small overlap between electronic wave functions (corresponding to adjacent sites) due to disorder is contributive to polaron formation. So from the polaronic viewpoint, the electron delivered by the impurity atom at the Cu$^{2+}$ site converts this into a lower valence state Cu$^+$, and at the next stage, the trapped electron at this Cu$^+$ site is transferred to the neighboring new Cu$^{2+}$ site by absorbing a photon energy. Thus the optical absorption in the studied glass samples is dominated by polaronic transfer between the Cu$^+$ and Cu$^{2+}$ species. As the concentration of Al$_2$O$_3$ is increased up to 3.0 mol%, a reduction in the intensity of the band due to $^2B_{2g} \rightarrow ^2B_{1g}$ transition is observed. Such decrease indicates the conversion of a part of Cu$^{2+}$ ions into Cu$^+$ ions. The two significant kinks observed in the violet region of the absorption spectra are due to $3d^{10} \rightarrow 3d^9 4s^1$ transition; these transitions are spin-forbidden transitions, but in this case they may occur due to low symmetry of local electric
field around Cu$^+$ ions [49]. Comparatively high intensity of these two kinks observed in the spectrum of glass A3 suggests the presence of larger concentration of Cu$^+$ ions in this glass.

The validity of the quadratic relation (Eq. (3.1)) related to optical band gap points out that the resulted optical band gap is caused by amorphous optical absorption edge. This result confirms a fact that the disordered amorphous glass materials have prevalingly the direct transitions between the valence 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). Some deviations observed from this dependence are understood due to trapping levels of some disordered states within the energy gap. With the increase in concentration of Al$_2$O$_3$ up to 3.0 mol%, it is evidenced from IR and Raman spectral studies that the Al$^{3+}$ ions in the glass network occupy predominantly tetrahedral positions, and alternate with SiO$_4$ and BO$_4$ structural units and form the linkages of the type Si–O–Al and B–O–Al. As a result there will be a decrease in the concentration of donor centers and subsequently, the excited states of localized electrons originally trapped on Cu$^+$ sites begin to dissociate with the empty 3d states on the neighboring Cu$^{2+}$ sites, and as a result, the impurity or polaron band becomes less extended into the main band gap. This new development might have shifted the absorption edge to the higher energy (Table 3.3) which leads up to a significant enlargement in the band gap as
the concentration of Al\textsubscript{2}O\textsubscript{3} is increased upto 3.0 mol\%. Further in this concentration range of Al\textsubscript{2}O\textsubscript{3} there is a considerable reduction of Cu\textsuperscript{2+} ions into Cu\textsuperscript{+} ions; these Cu\textsuperscript{+} ions participate in the network forming with linearly connected CuO\textsubscript{4} structural units. Such units increase the rigidity of the glass network and contribute to the enhancement of optical band gap. In 3.0 to 5.0 mol\% of Al\textsubscript{2}O\textsubscript{3} concentration range, a gradual increase in the intensity of band due to AlO\textsubscript{6} structural units is observed in the IR and Raman spectra. The octahedrally positioned Al\textsuperscript{3+} ions depolymerize the glass network by inducing bonding defects. Such higher degree of disorder in the glass network causes to decrease the optical band gap, as observed. The variation of Urbach energy with the concentration of Al\textsubscript{2}O\textsubscript{3} (Table 3.2) also supports these arguments. Another possible explanation for such low optical band gap values in case of samples A4, A5 is as follows. In silicate glasses, the transition metal ions like copper form aggregates or clusters. Comparatively weak absorption for the glass A3 indicates possible presence of more concentration of Cu\textsuperscript{2+} clusters. The observed increase of principal optical absorption peak intensity with increase in the Al\textsubscript{2}O\textsubscript{3} concentration beyond 3.0 mol\% clearly suggests that Al de–cluster copper ions and increases absorption. The possibility of admixing of wave functions of opposite parities of copper ions at these concentrations of Al\textsubscript{2}O\textsubscript{3} (which may cause more absorption) also cannot be ruled out [50].
ESR spectra of CuO doped Li$_2$O–PbO–B$_2$O$_3$–SiO$_2$–Bi$_2$O$_3$–Al$_2$O$_3$ glass exhibited the conventional characteristic signal of Cu$^{2+}$ ions coordinated by six ligands from which an octahedron elongated along the z– axis [51]. Because $g_{\|} > g_{\perp} > 2.0023$ ($g_e$), the ground state of the paramagnetic electron is $d_{x^2-y^2}$ orbital ($^2B_{1g}$ state). For the estimation of bonding parameters of copper ions we have correlated the ESR and optical absorption spectral data using the following standard equations between g tensors and the optical absorption band energies:

$$g_{\|} = 2.0023 \left[ 1 - \frac{4\lambda \alpha^2 \beta_1^2}{E(^2B_{2g})} \right]$$  \hspace{1cm} (3.5)

$$g_{\perp} = 2.0023 \left[ 1 - \frac{\lambda \alpha^2 \beta^2}{E(^2E_g)} \right]$$  \hspace{1cm} (3.6)

In Eqs. (3.5) and (3.6) $\lambda$ is the spin–orbit coupling coefficient, $\alpha^2$ is the bonding coefficient due to covalency of the $\sigma$ bonds with the equatorial ligands that measures the electron density delocalized on ligand ions, $\beta_1^2$ accounts for the covalency of $\pi$ bonding between ligands and $^2B_{2g}$ excited state and $\beta^2$ (~1.00)

The limiting values of bonding parameters $\alpha^2$ and $\beta_1^2$ are 0.5 (pure covalent) and 1.0 (pure ionic). The values of $\alpha^2$ and $\beta_1^2$ (Table 3.3) exhibited a decreasing tendency with increase in the concentration of Al$_2$O$_3$ up to 3.0 mol%. This tendency indicates a gradual adaptation of copper ions towards more covalent environment. The increasing tendency of the bonding parameters beyond 3.0 mol% of Al$_2$O$_3$ in the glass network suggests adaption of copper ions
towards ionic environment. Further, the observed decrease in the intensity of ESR signal for the glasses A0 to A3 suggests decreasing concentration of the paramagnetic Cu$^{2+}$ species (probably due to increasing redox ratio viz., Conc. Cu$^{+}$ ions/ Conc. Cu$^{2+}$ ions).

Recollecting the data on dielectric properties of CuO doped Li$_2$O–PbO–B$_2$O$_3$–SiO$_2$–Bi$_2$O$_3$–Al$_2$O$_3$ glasses with the gradual increase of Al$_2$O$_3$ beyond 3.0 mol%, the values of dielectric parameters $\varepsilon'$, tan $\delta$ and also $\sigma_{ac}$ are found to increase at any frequency and temperature and the activation energy for a.c conduction is observed to decrease; this observation indicates an increase in the space charge polarization owing to the enhanced degree of disorder in the glass network. In other words, as the concentration of Al$_2$O$_3$ is raised beyond 3.0 mol%, there is a growing presence of octahedral aluminum ions in the glass network (as is evidenced from the spectroscopic studies); these ions, as stated earlier, similar to Li$^+$ and Cu$^{2+}$ ions, disrupt the glass network by creating dangling bonds and non–bridging ions. The defects thus produced create easy path ways for the migration of charge carriers that would build up space charge polarization leading to the increase in the dielectric parameters as observed [52, 53]. The low value of dielectric constant of titled glass samples mixed up to 3.0 mol% of Al$_2$O$_3$ supports the view point that in these the concentration range Al$^{3+}$ ions mainly occupy tetrahedral positions and increase the rigidity of the glass network.
The variation of dielectric loss with temperature of CuO doped Li$_2$O–PbO–B$_2$O$_3$–SiO$_2$–Bi$_2$O$_3$–Al$_2$O$_3$ glasses exhibited the relaxation character. The relaxation effects in the studied glasses can be attributed to the Cu$^{2+}$ complexes that possess net dipole moment [18].

The increase in the breadth and the intensity of the relaxation peaks beyond 3.0 mol% of Al$_2$O$_3$ indicates that there is decreasing percentage of reduced copper ions from Cu$^{2+}$ state to Cu$^+$ state. Further, to know whether there is single relaxation time or spreading of relaxation times for the dipoles, we have adopted the pseudo Cole–Cole plot method (instead of conventional Cole–Cole plot between $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ at a fixed temperature) suggested by Sixou [54] in which $\varepsilon'(T) \text{ vs } \varepsilon''(T)$ can be plotted at a fixed frequency. The nature of variation of $\varepsilon'(T)$ and $\tan \delta$ with temperature for these glasses indicates that the Cole–Davidson equation:

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{(1 + i\omega\tau)^\beta},$$  \hspace{1cm} (3.7)$$
can safely be applied to these glasses. Separating real and imaginary terms of Eq.(3.11) and rewriting with explicit temperature dependence of terms:
\[ \varepsilon'(\omega, T) = \varepsilon_\infty + (\varepsilon_s - \varepsilon_\infty) [\cos \varphi(T)]^\beta \cos \beta \varphi(T) \]  
\tag{3.8} 

and

\[ \varepsilon''(\omega, T) = (\varepsilon_s - \varepsilon_\infty) [\cos \varphi(T)]^\beta \sin \beta \varphi(T), \]  
\tag{3.9} 

where \( \varphi(T) = \tan^{-1}(\omega \tau) = \tan^{-1}(\omega A_{o} e^{W_{d}/kT}) \).  
\tag{3.10} 

In Eq. (3.10) \( A_{o} \) is a constant and \( W_{d} \) is the activation energy for the dipoles. The plot between \( \varepsilon'(T) \) and \( \varepsilon''(T) \) given by the Eqs. (3.8) and (3.9) at a fixed frequency represents pseudo Cole–Cole plot, which cuts \( \varepsilon' \) axis at \( \varepsilon_s \) (in the high temperature region) and \( \varepsilon_\infty \) (in the low temperature region). The plot cuts \( \varepsilon' \) axis, (as per Sixou) at low temperature side at an angle of \( (\pi/2) \beta \), here \( \beta \) is the spreading factor for relaxation times. For CuO doped Li$_2$O–PbO–B$_2$O$_3$–SiO$_2$–Bi$_2$O$_3$–Al$_2$O$_3$ containing 5.0 mol% of Al$_2$O$_3$ (glass A5), a pseudo Cole–Cole plot at 1 kHz is shown in Fig. 3.11.
Fig. 3.11 A pseudo Cole–Cole plot drawn at 1 kHz for the glass A5.

The spreading factor ‘β’ estimated from this plot is 0.87 radians; such plots have also been drawn for all the glasses and the value of β is estimated in a similar way; the value of β is found to increase gradually when concentration of Al₂O₃ is raised beyond 3.0 mol % (Table 3.6). Thus the analysis indicates that there are different types of dipoles which contribute to the relaxation effects in these glasses. Earlier studies on Bi³⁺ doped samples it was proved that Bi³⁺ complexes do contribute to the dielectric relaxation effects [55]. Bismuth oxide participates in the glass network with BiO₃ structural units and can be viewed as tetrahedrons with the oxygen situated at three corners and the lone pair of electrons of bismuth (Bi³⁺) at the fourth corner localized in the third equatorial direction of Bi atom. Bi–O bonds are rich in p–character, whereas lone pair of
electrons is rich in s-character. The deformability of this pair due to the application of the electric field makes Bi$_2$O$_3$ molecule to contribute to the dipolar relaxation effects. The contribution to the dielectric relaxation effects from PbO also cannot be ruled out. In fact, PbO has two valence electrons, both nominally in $\pi$–type orbitals and no s–wave component. The spin–orbit admixes $\sigma$–type orbitals. Earlier based on first–order perturbative treatment of scalar–relativistic effects, it was shown that the spin orbit coupling contributes more substantially to the PbO dipole moment [56] and contribute to the dielectric relaxation effects.

Hence, the spreading of relaxation in CuO doped glasses may be attributed to the Bi$^{3+}$ and PbO molecules in addition to the conventional divalent copper ions. The shifting of relaxation region towards lower temperatures and decrease in the activation energy for the dipoles with increase in the concentration of Al$_2$O$_3$ from 3.0 to 5.0 mol % (Table 3.6) suggests an increasing degree of freedom for dipoles to orient in the field direction in the glass network. The decrease in the intensity of the relaxation effects below 3.0 % of Al$_2$O$_3$ supports the earlier argument that, major portion of aluminum ions take part in network forming positions with AlO$_4$ structural units and also a large part of Cu$^{2+}$ ions gets converted into Cu$^+$ state that occupy tetrahedral positions and increase the rigidity of the glass network.

The variation of log $\sigma(\omega)$ vs activation energy for conduction (in the high temperature region) is shown as the inset of Fig.3.10; the graph yields a near
straight line. This observation advocates that the conductivity enhancement is directly related to the thermally stimulated mobility of the charge carriers in the high temperature region. It appears that in the glasses under study, there is a possibility for mixed, ionic and polaronic, conductivity. Generally, electronic conduction is due to the polaron hopping between Cu$^+$ and Cu$^{2+}$ ions, whereas ionic conduction is due to migration of Li$^+$ ions.

For these glasses, the ac conductivity decreases with increasing content of Al$_2$O$_3$ upto 3.0 mol% (inset of Fig. 3.10). One of the possible explanations for such a behavior is that of Al$^{3+}$ ions enter into the network forming tetrahedral positions and reduce the concentration of dangling bonds in the glass network since some of AlO$_4$ structural units cross–link with SiO$_4$ and BO$_4$ units. This in turn leads to increase in the electrostatic binding energy and the strain energy for the easy passage of lithium ions, which consequently leads to a substantial increment in the jump distance of Li$^+$ ions. Such behavior is in good accordance with the observed increase in the activation energy for conduction. Such a structural arrangement in the glass network is more sensitive to the addition of transition metal ions resulting in the increasing role of the electronic component of conductivity. For glasses containing higher content of Al$_2$O$_3$, the increase in conductivity can be interpreted in terms of transition of the mixed conduction with high electronic contribution to the dominated ionic conduction. The progressive increase of conductivity with the increase of Al$_2$O$_3$ content beyond
3.0 mol% in the glass matrix is a manifestation of the increasing concentration of mobile electrons, or polarons, involved in the process of transfer from Cu$^+$ $\rightarrow$ Cu$^{2+}$ ions.

The frequency response of ac conductivity is usually described by power law dependence with $s$ as exponent:

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

(3.11)

$\omega_c$ is the characteristic macroscopic relaxation frequency.

The ac conductivity in the low temperature region up to nearly 360 K is almost temperature independent. In this range 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. (8) modifies to

$$\sigma(\omega) \propto \omega^s \quad (0 \leq s \leq 1)$$

(3.12)

In general, $s$ is a measure of the degree of interaction of the charge carriers with the environment. In fact this parameter depends on the glass composition and the limit of measured temperature.

Such a frequency dependent conductivity and $s$ exponent can be explained on the basis of quantum mechanical tunneling model (QMT) [57].

In the QMT model, the tunneling of electrons through barriers predicts temperature independent values for the $s$ exponent [57]. However, for the present glasses the value for $s$ varies with temperature. For example, for A5 glass the ‘$s$’ value at low temperature, 323 K, is 0.88 whereas at 383 K is 0.71. Therefore, at
lower temperatures hopping of electrons is dominant conduction for all glasses in the present study. As the concentration of Al\textsubscript{2}O\textsubscript{3} is increased beyond 3.0 mol\%, the value of ‘s’ is found to decrease. On the other hand, Sidebottom [58], while studying alkali phosphate glasses concluded that the exponent s depends upon the dimensionality of the local conduction space and it decreases with increasing dimensionality. Based on these studies the observed decrease in ‘s’ value may be attributed to enlargement in the dimensionality of conducting space with increase in the Al\textsubscript{2}O\textsubscript{3} beyond 3.0 mol\% [59].

According to QMT model the conductivity is given by [57]:

\[
\sigma(\omega) = \left(\frac{\pi}{3}\right)e^2K_T [N(E_F)]^2 \alpha^{-5}\omega \left[ \ln(\nu_0/\omega) \right]^4
\]

where \(N(E_F)\) is the density of defect energy states near the Fermi level, \(\alpha\) is the electronic wave function decay constant, \(\nu_0\) is the phonon frequency. The value of \(N(E_F)\) for a frequency of 1 k Hz at \(T = 353\) K, taking \(\alpha = 0.50 \text{ (Å)}^{-1}\) (obtained by plotting log \(\sigma_{ac}\) against \(R_i\)) and \(\nu_0 \sim 5 \times 10^{12}\) Hz, was calculated using Eq. (3.13) and presented in Table 3.7. The value of \(N(E_F)\) is found to increase from glass A3 to glass A5 indicating increase of defect energy states or free charge carriers for conduction in the glass network thus supporting earlier statement that in this concentration ranges Al\textsuperscript{3+} ions mainly act as modifiers.

When the dielectric is placed in an electric field, the heat of dielectric loss is liberated. If the applied field is an alternating field, the specific dielectric loss i.e., the loss per unit volume of the dielectric is given by [60],
\[ \rho_1 = E^2 \omega \varepsilon' \varepsilon_0 \tan \delta \text{ (W/m}^3) \]. \hspace{1cm} (3.14) 

This equation indicates that smaller the values of \( \varepsilon' \tan \delta \) of the glass at a given frequency, the lower are the specific losses. In a dielectric across which the voltage is applied, heat is liberated, the temperature of the dielectric then rises and the loss increases still more. The dielectric breakdown strength is in fact inversely proportional to the specific dielectric loss represented by Eq. (3.14).

Our studies on dielectric breakdown strengths of Li\(_2\)O–PbO–B\(_2\)O\(_3\)–SiO\(_2\)–Bi\(_2\)O\(_3\)–CuO: Al\(_2\)O\(_3\) glasses, as mentioned earlier (Table 3.7) indicate, the rate of increase of \( \varepsilon' \tan \delta \) with temperature is the lowest for glass A5 and the highest for glass A3. Though the breakdown strengths are actually measured at room temperature, the heat liberated during the breakdown, raises the temperature of the glass and hence raises the \( \varepsilon' \tan \delta \) value. Since the rate of increase of \( \varepsilon' \tan \delta \) with temperature is the highest for glass A5, the breakdown strength is the lowest when compared to that of other glasses (Table 3.7). Thus the experiments on dielectric breakdown strength of the titled glasses reveal that there is an increase in the disorderliness in the glass network with increase in the concentration of Al\(_2\)O\(_3\) beyond 3.0 mol \%. 
3.6 Conclusions

Multi–component silicate based glasses of the system Li$_2$O–PbO–B$_2$O$_3$–SiO$_2$–Bi$_2$O$_3$–CuO mixed with different concentrations of Al$_2$O$_3$ have been synthesized. Optical absorption, ESR, IR, Raman and dielectric properties have been investigated. Optical absorption and ESR studies have revealed that copper ions do exist in Cu$^{2+}$ and Cu$^+$ states. The redox ratio seems to be higher for the glasses mixed with 3.0 mol% of Al$_2$O$_3$. IR, Raman spectral studies have indicated that the aluminium ions occupy both tetrahedral and octahedral positions. The octahedral occupancy seems to be dominant when the concentration of Al$_2$O$_3$ is greater than 3.0 mol%. The rate of increase of dielectric parameters, viz., $\varepsilon'$, tan $\delta$ and also $\sigma_{ac}$ with temperature is found to be the highest in the samples mixed with 5.0 mol% of Al$_2$O$_3$ and found to be the lowest for the samples mixed with 3.0 mol% of Al$_2$O$_3$ content. Variations in these parameters with concentration of Al$_2$O$_3$ are quantitatively explained based on the deviations in the co–ordination number of aluminium ions and de–clustering influence of copper ions by aluminium ions in the glass network.
References


