Influence of Ga$^{3+}$ ions on spectroscopic and dielectric features of multi component lithium lead boro bismuth silicate glasses doped with manganese ions

Multi-component glasses of the chemical composition 19.5Li$_2$O-20PbO-20B$_2$O$_3$-30SiO- (10 - x) Bi$_2$O$_3$-0.5 MnO: x Ga$_2$O$_3$ with 0 ≤ x ≤ 5.0 have been synthesized. Spectroscopic (optical absorption, IR, Raman and ESR) and dielectric properties were investigated. Optical absorption and ESR spectral studies have indicated that manganese ions do exist in Mn$^{3+}$ state in addition to Mn$^{2+}$ state in the samples containing low concentration of Ga$_2$O$_3$. The IR and Raman studies indicated increasing degree of disorder in the glass network with the concentration of Ga$_2$O$_3$ up to 3.0 mol%. The dielectric constant, loss and ac conductivity are observed to increase with the concentration of Ga$_2$O$_3$ up to 3.0 mol%. The quantitative analysis of the results of dielectric properties have indicated an increase in the insulating strength of the glasses as the concentration of Ga$_2$O$_3$ is raised beyond 3.0 mol%. This has been attributed to adaption of gallium ions from octahedral to tetrahedral coordination.
4.1 Introduction

Ga$_2$O$_3$ is a heavy metal oxide and when introduced in the glass matrix it is expected to influence the physical properties (viz., refractive index, thermal expansion coefficient, chemical resistance, glass transition temperature, infrared transmittance and the electrical properties) of the glass to a large extent. In view of these qualities the glasses containing Ga$_2$O$_3$ are suitable for use as infrared windows, ultrafast optical switches, optical isolators and other photonic devices for communication and advanced computer applications. Many recent investigations on the role of Ga$_2$O$_3$ in various glass matrices are available in the literature [1-5].

Manganese ion is an interesting transition metal ion and is extensively investigated in various glasses. This ion exists in Mn$^{2+}$ and Mn$^{3+}$ stable states. Mn$^{2+}$ ion contains half filled $d$ orbital with $d^5$ configuration with $^6S$ as the ground state. For these reasons, the total orbital angular momentum for Mn$^{2+}$ ion is zero. Since the total spin is 5/2, this ion exhibits zero field splitting which is sensitive to the local environment. Both Mn$^{3+}$ and Mn$^{2+}$ ions are well known paramagnetic ions. Mn$^{3+}$ ion exhibits large magnetic anisotropy due to its strong spin-orbit interaction of the 3d orbital, whereas such anisotropy energy of Mn$^{2+}$ ion is small because its orbital angular momentum is zero. Recently, lasing action of Mn$^{2+}$ ions has also been reported in some inorganic glasses [6-8] with large quantum luminescence efficiencies even at room temperature. The studies on up-
conversion emission with manganese ion as sensitizer and rare-earth ions as activators in some glasses have also been reported earlier [9, 10]. The manganese ions have larger oscillator strengths than rare-earths and can therefore absorb more of the input energy and fluorescence strongly in green and red regions [6-8]. Ga\textsubscript{2}O\textsubscript{3} is considered to act as a network former if Ga\textsuperscript{3+} ion takes fourfold coordination in oxide glasses. The excess negative charges on GaO\textsubscript{4} tetrahedrons are compensated either by localization of a modifier ion nearby or by generation of threefold oxygens. The GaO\textsubscript{4} tetrahedrons may enter the glass network and alternate with BO\textsubscript{4} and SiO\textsubscript{4} tetrahedrons in borosilicate glasses. Gallium ions also take part modifier positions with GaO\textsubscript{6} structural units depending upon its concentration and other constituents of the glass matrix [11]. Overall, the variation of Ga\textsubscript{2}O\textsubscript{3} content in glass network is expected to change the local environment of the manganese ions in the glass network and there by influences the spectroscopic properties of manganese ions.

Lithium borosilicate glasses containing heavy metal oxides like Bi\textsubscript{2}O\textsubscript{3} are useful particularly in optical and optoelectronic devices such as ultrafast switches, infrared windows, optical isolators, thermal and mechanical sensors [12-14]. The most stable valence of the bismuth ion is the positive tri-valence state (Bi\textsuperscript{3+}) and its electronic configuration is 4f\textsuperscript{14}5d\textsuperscript{10}6s\textsuperscript{2}. Bismuth ion exists in various valence states from positive valence to negative valence in different compounds (e.g. Bi\textsuperscript{3+}, Bi\textsuperscript{2+}, Bi\textsuperscript{+}, Bi\textsuperscript{0}, Bi\textsuperscript{2-}). Further, bismuth ion exhibit emission
in various wavelength regions from visible to near-to-mid infrared region and even far-infrared, depending on its valence states. In view of such peculiarities, Bi$_2$O$_3$ containing glasses also offer highly suitable environment for hosting transition metal ions like manganese ions that exhibit luminescence in the green and yellow regions and bismuth ions may also act as sensitizers for up-conversion [15-19].

In the present study we have synthesized multi-component Li$_2$O–PbO–B$_2$O$_3$–SiO$_2$–Bi$_2$O$_3$: MnO glasses mixed with different contents of Ga$_2$O$_3$ and investigated the influence of variation of Ga$_2$O$_3$ concentration on spectroscopic characteristics of manganese ions. Studies are also extended to dielectric properties of the bulk material.

4.2 Brief review of the previous work on the glasses containing gallium ions

Fan et al.[20] have studied Infrared, Raman and XPS spectroscopic studies of Bi$_2$O$_3$–B$_2$O$_3$–Ga$_2$O$_3$ glasses. Their results showed that density, refractive index and optical basicity increases with the increase of Ga$_2$O$_3$. Infrared, Raman and XPS results indicate that [BiO$_6$] octahedron, [BO$_3$] triangle [BO$_4$] tetrahedron and [GaO$_4$] tetrahedron exist in the glasses. The addition of Ga$_2$O$_3$ causes a progressive coordination number change of boron atom from [BO$_3$] to [BO$_4$]. The Ga$^{3+}$ ions restrain the formation of Bi$^{5+}$ ions by Ga 4s$^2$ charge compensation effect. The average electron density and the number of non-bridging oxygens (NBOs) in glass increase with the increase of Ga$_2$O$_3$. Shi et al.
[21] have reported frequency up-conversion luminescence in Tm$^{3+}$/Yb$^{3+}$ andHo$^{3+}$/Yb$^{3+}$-codoped Ga$_2$O$_3$–GeO$_2$–Bi$_2$O$_3$–PbO glasses. The observed upconversion emission intensity as function of Yb$^{3+}$ concentration suggested that the presence of the Yb$_2$O$_3$ plays a major role in enhancing the up-conversion emission efficiency. Ling et al. [22] have investigated the effect of Ga$_2$O$_3$ on the spectroscopic properties of erbium-doped boro-bismuth glasses. In conclusion, Bi$_2$O$_3$–B$_2$O$_3$–Ga$_2$O$_3$ glass system was reported as a suitable host glass for bismuth-based broadband erbium-doped fiber amplifier material.

Kityk et al. [23] have studied new efficient materials for the luminescence on the base of PbO–Bi$_2$O$_3$–Ga$_2$O$_3$–BaO–Ho$^{3+}$ glasses. They have observed experimentally IR and red luminescence in the PGB glasses doped by 0.5% of Ho$^{3+}$. One of the advantageous of the proposed optical materials consists in high thermal stability of the IR luminescence and high quantum efficiency (up to 42%). Wang et al. [24] have studied state-selective energy transfer from Er$^{3+}$ to Eu$^{3+}$ in Bi$_2$O$_3$–GeO$_2$–Ga$_2$O$_3$–Na$_2$O glasses. The results presented in this study indicated that the improved 1.5 μm emission in Er$^{3+}$ doped BGGN glasses could be obtained with the Eu$^{3+}$ co-doped to 0.2 mol%. Bomfima et al. [25] have investigated effect of the ytterbium concentration on the upconversion luminescence of Yb$^{3+}$/Er$^{3+}$ co-doped PbO–GeO$_2$–Ga$_2$O$_3$ glasses. Shyam et al. [26] have reported the physical properties of BaO-Ga$_2$O$_3$-GeO$_2$ glasses. Duan et al. [27] have reported the photoluminescence of Eu$^{3+}$-doped ZnO–Ga$_2$O$_3$–SiO$_2$
nano-glass-ceramics. Their results showed that the as-synthesized material displays intense emission at 615 nm belonging to $^5D_0\rightarrow^7F_2$ transition. The state of Eu$^{3+}$ in the glass-ceramics was analyzed and discussed.

*Kassab et al.* [28] have carried out thermal lens study of PbO–Bi$_2$O$_3$–Ga$_2$O$_3$–BaO glasses doped with Yb$^{3+}$. The results emphasized that the thermal lens technique can be a powerful tool to study the heat generation of new glassy systems. *Zhao and Lu* [29] have reported that PbO–Bi$_2$O$_3$–Ga$_2$O$_3$–BaCl$_2$–Ho$^{3+}$ are novel glasses for high-efficient IR and red luminescence. *Park et al.* [30] have made ammonolysis of Ga$_2$O$_3$ and its application to the sublimation source for the growth of GaN film. This study demonstrated that the use of Ga$_2$O$_3$ could be possible for the preparation of GaN thick film through by the ammonolysis of Ga$_2$O$_3$. *Al Asmar et al.* [31] have prepared and characterized the high quality undoped and Ga$_2$O$_3$-doped ZnO thin films by reactive electron beam co-evaporation technique. The electrical resistivity was found to increase with the rising of the Ga$_2$O$_3$ concentration while the carrier concentration decreased which is due to chemisorptions of oxygen into the ZnO thin films. *Kityk et al.* [32] have reported IR luminescence of PbO–Bi$_2$O$_3$–Ga$_2$O$_3$–BaO–Dy$^{3+}$ glasses. *Chengyu et al.* [33] have studied photo-stimulated long-lasting phosphorescence in Mn$^{2+}$-doped zinc borosilicate glasses. They have observed the PSLLP phenomenon in Mn$^{2+}$-doped zinc borosilicate glass and conclude that new optical storage devices can be designed using these materials. *Venkat Reddy et al.* [34]
have reported the optical and thermoluminescence properties of R₂O–RF–B₂O₃ glass systems doped with MnO. All the obtained results were discussed on the basis of the glass structure and different valence states of manganese ions in the glass system.

4.3 Characterization

For the present study, a particular composition 19.5Li₂O–20PbO–20B₂O₃–30SiO₂–(10–x) Bi₂O₃–0.5MnO: x Ga₂O₃ with six values of x ranging from 0 to 5 is chosen. The detailed compositions of the glasses used in the present study are as follows:

G₀: 19.5Li₂O–20PbO–20B₂O₃–30SiO₂–10Bi₂O₃–0.5MnO
G₁: 19.5Li₂O–20PbO–20B₂O₃–30SiO₂–9Bi₂O₃–0.5MnO: 1.0Ga₂O₃
G₂: 19.5Li₂O–20PbO–20B₂O₃–30SiO₂–8Bi₂O₃–0.5MnO: 2.0Ga₂O₃
G₃: 19.5Li₂O–20PbO–20B₂O₃–30SiO₂–7Bi₂O₃–0.5MnO: 3.0Ga₂O₃
G₄: 19.5Li₂O–20PbO–20B₂O₃–30SiO₂–6Bi₂O₃–0.5MnO: 4.0Ga₂O₃
G₅: 19.5Li₂O–20PbO–20B₂O₃–30SiO₂–5Bi₂O₃–0.5MnO: 5.0Ga₂O₃

4.3.1 Physical Parameters

The density ‘d’ of the Ga₂O₃ free glass was measured to be 4.41 g/cm³ and it is found to increase with increasing concentration of Ga₂O₃ up to 3.0 mol%; beyond this concentration a slight decrease in the value of ‘d’ is observed (Table 4.1). From the measured values of the density and average molecular weight \( \bar{M} \) of the samples, various other physical parameter such as manganese ion
concentration, \( N_i \), and mean manganese ion separation, \( r_i \), in the \( \text{Li}_2\text{O}–\text{PbO}–\text{B}_2\text{O}_3–\text{SiO}_2–\text{Bi}_2\text{O}_3–\text{MnO} \): \( \text{Ga}_2\text{O}_3 \) glass samples were computed and are presented in Table 4.1.

### 4.3.2 X-ray diffraction

Fig. 4.1 shows X-ray diffraction pattern of some glass samples. The pattern shows absence of sharp Bragg peaks confirming the amorphous nature of the prepared samples.

![XRD patterns](image)

**Fig. 4.1** XRD patterns of \( \text{Li}_2\text{O}–\text{PbO}–\text{B}_2\text{O}_3–\text{SiO}_2–\text{Bi}_2\text{O}_3–\text{MnO} : \text{Ga}_2\text{O}_3 \) glasses
4.4 Results

4.4.1 Optical absorption

The optical absorption spectra of Li$_2$O–PbO–B$_2$O$_3$–SiO$_2$–Bi$_2$O$_3$–MnO: Ga$_2$O$_3$ glasses recorded in the wavelength region of 300 – 800 nm are shown in Fig. 4.2. The absorption edge observed at 333 nm for G$_0$ glass sample is found to be shifted gradually towards higher wavelength with increase of the concentration of Ga$_2$O$_3$ up to 3.0 mol%. Above this concentration, the absorption edge exhibited spectrally blue shift. The spectrum of this glass showed an intense absorption band at 534 nm corresponding to $^6A_{1g}(S) \rightarrow ^4T_{2g}(G)$ octahedral transition of Mn$^{2+}$ ions and a weak kink at about 422 nm, due to $^6A_1(S) \rightarrow ^4T_1$ (G) tetrahedral transition of Mn$^{2+}$ ions [35,36].

Additionally, a weak absorption band with a peak at about 485 nm due to $^5E_g \rightarrow ^5T_{2g}$ octahedral transition of Mn$^{3+}$ ions [37] is also observed in the spectrum of this glass. With an increase in the concentration of Ga$_2$O$_3$ up to 3.0 mol%, the octahedral band is observed to grow gradually at the expense of the tetrahedral band with minor red shift.

The summary of data on the position of various bands in the optical absorption spectra of Li$_2$O-PbO-B$_2$O$_3$-SiO$_2$-Bi$_2$O$_3$-MnO: Ga$_2$O$_3$ glasses are presented in Table 4.2.
Table 4.1
Physical parameters of $\text{Li}_2\text{O} \text{–PbO–B}_2\text{O}_3 \text{–SiO}_2 \text{–Bi}_2\text{O}_3 \text{–MnO: Ga}_2\text{O}_3$ glasses.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Conc. Ga$_2$O$_3$ (mol%)</th>
<th>Avg. Mol. wt. $\overline{M}$</th>
<th>Density $\rho$ (g/cm$^3$) (±0.01)</th>
<th>Molar Volume $V_m$ (cm$^3$) (±0.001)</th>
<th>Conc. Mn ions $N_i$ ($\times 10^{21}$ ions/cm$^3$) (±0.01)</th>
<th>Inter ionic distance of Mn ions $R_i$ (Å) (±0.01)</th>
<th>Polaron radius $R_p$ (Å) (±0.01)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$G_0$</td>
<td>0</td>
<td>129.28</td>
<td>4.41</td>
<td>0.515</td>
<td>10.28</td>
<td>4.60</td>
<td>1.85</td>
</tr>
<tr>
<td>$G_1$</td>
<td>1</td>
<td>126.50</td>
<td>4.42</td>
<td>0.516</td>
<td>10.53</td>
<td>4.56</td>
<td>1.84</td>
</tr>
<tr>
<td>$G_2$</td>
<td>2</td>
<td>123.71</td>
<td>4.44</td>
<td>0.519</td>
<td>10.82</td>
<td>4.52</td>
<td>1.82</td>
</tr>
<tr>
<td>$G_3$</td>
<td>3</td>
<td>120.93</td>
<td>4.47</td>
<td>0.430</td>
<td>11.12</td>
<td>4.48</td>
<td>1.81</td>
</tr>
<tr>
<td>$G_4$</td>
<td>4</td>
<td>118.14</td>
<td>4.31</td>
<td>0.418</td>
<td>10.97</td>
<td>4.50</td>
<td>1.82</td>
</tr>
<tr>
<td>$G_5$</td>
<td>5</td>
<td>115.36</td>
<td>4.16</td>
<td>0.487</td>
<td>10.87</td>
<td>4.52</td>
<td>1.83</td>
</tr>
</tbody>
</table>
Fig. 3 Optical absorption spectra of Li$_2$O–PbO–B$_2$O$_3$–SiO$_2$–Bi$_2$O$_3$–MnO: Ga$_2$O$_3$ glasses.

Fig. 4.2 Optical absorption spectra of Li$_2$O–PbO–B$_2$O$_3$–SiO$_2$–Bi$_2$O$_3$–MnO: Ga$_2$O$_3$ glasses.
Table 4.2

Summary of data on optical absorption spectral data of Li$_2$O–PbO–B$_2$O$_3$–SiO$_2$–Bi$_2$O$_3$–MnO: Ga$_2$O$_3$ glasses.

<table>
<thead>
<tr>
<th></th>
<th>G$_0$</th>
<th>G$_1$</th>
<th>G$_2$</th>
<th>G$_3$</th>
<th>G$_4$</th>
<th>G$_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn$^{2+}$ transitions (nm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^6$A$_1$(S) → $^4$T$_1$(G)</td>
<td>422</td>
<td>421</td>
<td>420</td>
<td>419</td>
<td>425</td>
<td>428</td>
</tr>
<tr>
<td>$^6$A$<em>{1g}$(S) → $^4$T$</em>{2g}$(G)</td>
<td>534</td>
<td>537</td>
<td>540</td>
<td>545</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Mn$^{3+}$ transition (nm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^5$E$<em>g$ → $^5$T$</em>{2g}$</td>
<td>480</td>
<td>485</td>
<td>490</td>
<td>495</td>
<td>501</td>
<td>506</td>
</tr>
<tr>
<td>cut-off wavelength (nm)</td>
<td>333</td>
<td>334.5</td>
<td>341</td>
<td>350</td>
<td>330.5</td>
<td>323.5</td>
</tr>
<tr>
<td>optical band gap, $E_o$ (eV)</td>
<td>3.28</td>
<td>3.20</td>
<td>3.09</td>
<td>3.00</td>
<td>3.40</td>
<td>3.46</td>
</tr>
</tbody>
</table>

From the observed absorption edges, we have evaluated the optical band gaps ($E_o$) of these glasses by drawing Tauc’s plot (Fig. 4.3) between $(\alpha \omega)^2$ and $\omega$ as per the equation $(\alpha(\omega)h\omega)^2 = c(h\omega - E_o)$. The values of optical band gap ($E_o$) obtained from the extrapolation of these curves are found to be the lowest for the sample G$_3$ (Table 4.2).
**Fig. 4.3** Tauc plots of Li$_2$O–PbO–B$_2$O$_3$–SiO$_2$–Bi$_2$O$_3$–MnO: Ga$_2$O$_3$ glasses. Inset shows the variation of $E_0$ with the concentration of Ga$_2$O$_3$. 
4.4.2 ESR Spectra

Fig. 4.4 represents the typical ESR spectra of MnO doped Li$_2$O–PbO–B$_2$O$_3$–SiO$_2$–Bi$_2$O$_3$–Ga$_2$O$_3$ glasses. The spectra are characterized by six-line hyperfine structure centered at $g \sim 2.008$ and another signal at $g \sim 4.29$; the relative intensity of these two signals is observed to increase in the concentration of Ga$_2$O$_3$ up to 3.0 mol%, beyond this concentration the intensity of the signals decreases. The values of $g$ obtained for Mn$^{2+}$ ions for the studied samples is comparable with that of other systems; for example Bi$_2$O$_3$-Ge$_2$O$_3$ [38], lead arsenate [39], alkali sulphate glasses [31]. The variation of $g$ corresponding to six-line hyperfine structure exhibited a decreasing trend with increase in the concentration of Ga$_2$O$_3$ up to 3.0 mol% and beyond that a clear increase in the value of $g$ could be visualized.
Fig. 4.4 EPR spectra of Li$_2$O–PbO–B$_2$O$_3$–SiO$_2$–Bi$_2$O$_3$–MnO glasses mixed with various concentrations of Ga$_2$O$_3$. Inset shows the conc. of Ga$_2$O$_3$ vs intensity of resonance value.
4.4.3 Infrared spectra

In Fig. 4.5, the IR spectra of Ga$_2$O$_3$ doped of Li$_2$O–PbO–B$_2$O$_3$–SiO$_2$–Bi$_2$O$_3$–MnO glasses are presented. The spectra have exhibited conventional vibrational band due to Si-O-Si asymmetric vibrations at about 1083 cm$^{-1}$ and another band about at 863 cm$^{-1}$ due to Si-O-Si symmetric vibrations or due to bending mode bridging oxygen situated perpendicular to Si-Si plane [40]. The spectra exhibited another band in the region of 488 cm$^{-1}$ predicted due to Si-O-Si rocking motion. In this region band due to PbO$_4$ structural units is also expected. The spectra also exhibited three distinct bands in the regions 1300-1400 cm$^{-1}$, 1000-1200 cm$^{-1}$ and at about 710 cm$^{-1}$; these bands are identified as being due to the stretching relaxation of B-O bond of the trigonal BO$_3$ units, due to the vibration of BO$_4$ structural units and due to the bending vibrations of B-O-B linkages, respectively. In the region of bending vibrational frequency of B-O-B linkages the vibrations due to MnO specific vibrations are also possible [41]. The band due to vibrations Bi-O-Bi linkages of BiO$_6$ units is also detected in these spectra at about 428 cm$^{-1}$ [42]. Another significant band identified as being due to the vibrations of GaO$_4$ structural units is also located at about 615 cm$^{-1}$ [43] in the spectra of the glasses G$_1$ to G$_5$. With addition of Ga$_2$O$_3$ in the glass sample upto 3.0 mol%, the intensity of all the asymmetrical bands of silicate groups and also that of BO$_4$ units is observed to increase, whereas that of symmetrical bands and also that of the band due to BiO$_6$ units and BO$_3$ units is observed to decrease. When the concentration of Ga$_2$O$_3$ is raised beyond 3.0 mol%, the symmetrical bands are observed to growth the expense of asymmetrical bands (Fig. 4.5) (Table 4.3).
Table 4.3

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$_3$–MnO: Ga$_2$O$_3$ glasses.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Bi-O bonds in BiO$_6$ units</th>
<th>Si-O-Si Rocking/PbO$_4$ units</th>
<th>GaO$_4$ units</th>
<th>B-O-B linkages/MnO specific vibrations</th>
<th>Si-O-Si Symmetrical</th>
<th>BO$_4$ units</th>
<th>Si-O-Si Asymmetric</th>
<th>BO$_3$ units</th>
</tr>
</thead>
<tbody>
<tr>
<td>G$_0$</td>
<td>424</td>
<td>488</td>
<td>--</td>
<td>710</td>
<td>855</td>
<td>987</td>
<td>1095</td>
<td>1312</td>
</tr>
<tr>
<td>G$_1$</td>
<td>423</td>
<td>488</td>
<td>602</td>
<td>710</td>
<td>857</td>
<td>989</td>
<td>1093</td>
<td>1308</td>
</tr>
<tr>
<td>G$_2$</td>
<td>421</td>
<td>483</td>
<td>600</td>
<td>714</td>
<td>859</td>
<td>991</td>
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<td>G$_3$</td>
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<td>1086</td>
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<td>496</td>
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<td>711</td>
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<td>987</td>
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<td>G$_5$</td>
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<td>712</td>
<td>862</td>
<td>985</td>
<td>1084</td>
<td>1316</td>
</tr>
</tbody>
</table>
Fig. 4.5 FTIR patterns of Li$_2$O–PbO–B$_2$O$_3$–SiO$_2$–Bi$_2$O$_3$–MnO: Ga$_2$O$_3$ glasses.
4.4.4 Raman spectra

The Raman spectra (Fig. 4.6) of multi-component \( \text{Li}_2\text{O–PbO–B}_2\text{O}_3–\text{SiO}_2–\text{Bi}_2\text{O}_3–\text{Ga}_2\text{O}_3 \) glasses doped with MnO have exhibited three prominent bands (Table 4.4) at about 1027, 822 and 460 cm\(^{-1}\) assigned to asymmetrical, symmetrical and rocking motion of \( \text{Si–O–Si} \) structural units, respectively [44]. The spectra also exhibited a band at 1227 cm\(^{-1}\) ascribed to diborate groups consisting of six-membered rings containing two \( \text{BO}_4 \) teterahedra and another band centered at 1327 cm\(^{-1}\) attributed to the boroxil ring oxygen breathing in which the boron coordinate atom is three [45,46]. In the region of rocking vibrations of \( \text{Si–O–Si} \) structural units (at about 460 cm\(^{-1}\)) there is a possibility for the presence of a band due to bridging oxygen breathing mode in (Si, Ga) four membered rings. A new band at about 622 cm\(^{-1}\) identified as being due to B–O–B bonding is also located in the spectra of these glasses [46]. Another new band at about 330 cm\(^{-1}\) identified due to Bi–O vibrations in \( \text{BiO}_6 \) units as well as due to \( \text{GaO}_6 \) structural units is also noticed in the spectra of these glasses [47,48]. In the same region the spectra also exhibited a weak kink at about 233 cm\(^{-1}\) due to Bi–O breathing modes in \( \text{BiO}_3 \) pyramidal units [47]. As the concentration of \( \text{Ga}_2\text{O}_3 \) is increased up to 3.0 mol\%, the intensity of \( \text{SiO}_4 \) asymmetrical band is found to be increase where as the intensity of band due to \( \text{BO}_4 \) a structural unit is found to be increasing. However, when the concentration of \( \text{Ga}_2\text{O}_3 \) is raised beyond 3.0 mol\% the intensity of all symmetrical bands is found to be increasing.
Table 4.4
Assignment of Raman bands (cm$^{-1}$) with a probable error of ± 0.1cm$^{-1}$ of Li$_2$O–PbO–B$_2$O$_3$–SiO$_2$–Bi$_2$O$_3$–MnO: Ga$_2$O$_3$ glasses.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Breathing in BiO$_3$ pyramidal units</th>
<th>Bi-O-Bi stretching vibrations in distorted BiO$_6$ units/ GaO$_6$ units</th>
<th>Si-O-Si Rocking/ /PbO$_4$ units</th>
<th>B-O-B Bonding</th>
<th>Si-O-Si Symmetricals</th>
<th>Si-O-Si Asymmetrical</th>
<th>BO$_4$ units</th>
<th>BO$_3$ units</th>
</tr>
</thead>
<tbody>
<tr>
<td>G$_0$</td>
<td>248</td>
<td>330</td>
<td>460</td>
<td>629</td>
<td>822</td>
<td>1027</td>
<td>1227</td>
<td>1318</td>
</tr>
<tr>
<td>G$_1$</td>
<td>245</td>
<td>350</td>
<td>470</td>
<td>635</td>
<td>815</td>
<td>1027</td>
<td>1212</td>
<td>1332</td>
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<tr>
<td>G$_2$</td>
<td>245</td>
<td>346</td>
<td>476</td>
<td>638</td>
<td>812</td>
<td>1027</td>
<td>1240</td>
<td>1332</td>
</tr>
<tr>
<td>G$_3$</td>
<td>251</td>
<td>360</td>
<td>470</td>
<td>629</td>
<td>809</td>
<td>1034</td>
<td>1240</td>
<td>1335</td>
</tr>
<tr>
<td>G$_4$</td>
<td>245</td>
<td>356</td>
<td>460</td>
<td>629</td>
<td>822</td>
<td>1017</td>
<td>1240</td>
<td>1317</td>
</tr>
<tr>
<td>G$_5$</td>
<td>235</td>
<td>353</td>
<td>460</td>
<td>614</td>
<td>842</td>
<td>1016</td>
<td>1251</td>
<td>1311</td>
</tr>
</tbody>
</table>
Fig. 4.6 Raman spectra of Li$_2$O–PbO–B$_2$O$_3$–SiO$_2$–Bi$_2$O$_3$–MnO: Ga$_2$O$_3$ glasses.
4.4.5 Dielectric dispersion properties

The dielectric constant $\varepsilon'$ and loss tan$\delta$ at room temperature ($\approx 30^\circ$C ) of $G_0$ glass sample at 1 MHz are measured to be 8.58 and 0.03378 respectively. The values of $\varepsilon'$ and tan$\delta$ of all the glasses are found to increase considerably with decrease in frequency. The temperature dependence of $\varepsilon'$ of the glasses containing different concentration of Ga$_2$O$_3$ at 1 kHz is shown in Fig. 4.7 and at different frequencies of glass $G_1$ is shown as the inset. The value of $\varepsilon'$ is found to exhibit a considerable increase at higher temperatures especially at lower frequencies; the rate of increase of $\varepsilon'$ with temperature is found to be the highest for the glass containing 3.0 mol% of Ga$_2$O$_3$.

The temperature dependence of dielectric loss dispersion of glass $G_4$ is shown in Fig. 4.8 (a) and at different frequencies for the glass $G_2$ as its inset. A comparison plot of variation of tan $\delta$ with frequency, measured at different temperatures is presented in Fig. 4.8 (b). The dielectric loss dispersion with frequency and temperature exhibited distinct maxima indicating dipolar relaxation character of dielectric loss of these glass samples. From these curves, it is also observed that the region of relaxation shifts towards lower temperature with broadening of relaxation peaks and increasing value of $(\tan \delta)_{\text{max}}$ up to 3.0 mol % of Ga$_2$O$_3$. The effective activation energy $W_d$ for the dipoles is evaluated for all the glass samples presented in Table 4.5. The activation energy is found to be the minimal for the glass $G_3$. 
Fig. 4.7  Variation of dielectric constant $\varepsilon'$ with temperature at 1 kHz for different concentrations of Ga$_2$O$_3$ in Li$_2$O–PbO–B$_2$O$_3$–SiO$_2$–Bi$_2$O$_3$–MnO glasses multi component glasses. Inset shows the variation of $\varepsilon'$ with temperature for different frequencies of G$_1$ sample.
Table 4.5

Summary of data on dielectric loss of Li₂O–PbO–B₂O₃–SiO₂–Bi₂O₃–MnO: Ga₂O₃ glasses.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(Tanδ)(_{\text{max}}) (±0.001)</th>
<th>Temp. region of relaxation (±1 °C)</th>
<th>AE for dipoles (±0.01) eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>G₀</td>
<td>0.0449</td>
<td>137-185</td>
<td>2.33</td>
</tr>
<tr>
<td>G₁</td>
<td>0.0452</td>
<td>123-175</td>
<td>2.03</td>
</tr>
<tr>
<td>G₂</td>
<td>0.0456</td>
<td>110-169</td>
<td>1.71</td>
</tr>
<tr>
<td>G₃</td>
<td>0.0468</td>
<td>97-162</td>
<td>1.41</td>
</tr>
<tr>
<td>G₄</td>
<td>0.0441</td>
<td>150-194</td>
<td>2.67</td>
</tr>
<tr>
<td>G₅</td>
<td>0.0430</td>
<td>163-202</td>
<td>3.16</td>
</tr>
</tbody>
</table>

The a.c conductivity, \(\sigma_{\text{a.c.}}\), values for all glasses at different temperature and frequencies are evaluated using, \(\sigma_{\text{a.c.}} = \omega \varepsilon' \varepsilon_0 \tan \delta\) (where \(\omega\) is the angular frequency and \(\varepsilon_0\) is the dielectric constant of vacuum) and its variation with 1/T of all investigated glasses at 100 kHz is shown in Fig 4.9. The variation of \(\sigma_{\text{a.c.}}\) with the concentration of Ga₂O₃ exhibited maximal effect at 3.0 mol% of Ga₂O₃ (inset (a) of Fig. 4.9). The activation energy for conduction in the higher temperature region over which a near linear dependence of log \(\sigma_{\text{a.c.}}\) with 1/T observed is calculated and presented in Table 4.6. The activation energy exhibited decreasing trend up to 3.0 mol% of Ga₂O₃ and for further increase of Ga₂O₃ content a reversal trend is observed (inset (b) of Fig. 4.9). The dielectric breakdown strength measured at room temperature in the air medium for
these glasses exhibited a decreasing trend with increase of Ga$_2$O$_3$ concentration up to 3.0 mol% (Table 4.6)

![Graph showing the variation of dielectric loss tanδ with temperature at 10 kHz for different concentrations of Ga$_2$O$_3$ in Li$_2$O–PbO–B$_2$O$_3$–SiO$_2$–Bi$_2$O$_3$–MnO multi component glasses. Inset shows the variation of tanδ with temperature of G$_4$ glass at different frequency.](image_url)
Fig. 4.8 (b) Dielectric loss dispersion at different temperatures for the G$_2$ glass.
Fig. 4.9 Variation of $\sigma_{ac}$ with $1000/T$ at 100 kHz for different concentrations of Ga$_2$O$_3$ in Li$_2$O–PbO–B$_2$O$_3$–SiO$_2$–Bi$_2$O$_3$–MnO glasses. Insets represent the (a) variation of $\sigma_{ac}$ with conc. of Ga$_2$O$_3$ (b) activation energy vs conc. of Ga$_2$O$_3$ and (c) $\sigma_{ac}$ vs activation energy.
Table 4.6
Summary of the data on ac. conductivity of Li$_2$O–PbO–B$_2$O$_3$–SiO$_2$–Bi$_2$O$_3$–MnO: Ga$_2$O$_3$ glasses.

<table>
<thead>
<tr>
<th>Glass</th>
<th>$\sigma_{ac}$ at 70°C (10$^{-8}$) (Ω-cm)</th>
<th>N(E$_F$) (10$^{-21}$, eV$^{-1}$/cm$^3$) (±0.01)</th>
<th>Relaxation time $\tau$ (μs)</th>
<th>Activation energy for conduction (eV) (±0.01)</th>
<th>Breakdown strength (±0.01) kV/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>$G_0$</td>
<td>1.71</td>
<td>6.44</td>
<td>410</td>
<td>1.02</td>
<td>10.47</td>
</tr>
<tr>
<td>$G_1$</td>
<td>1.78</td>
<td>6.58</td>
<td>399</td>
<td>0.89</td>
<td>10.16</td>
</tr>
<tr>
<td>$G_2$</td>
<td>1.85</td>
<td>6.71</td>
<td>382</td>
<td>0.78</td>
<td>9.94</td>
</tr>
<tr>
<td>$G_3$</td>
<td>1.95</td>
<td>6.90</td>
<td>356</td>
<td>0.68</td>
<td>8.80</td>
</tr>
<tr>
<td>$G_4$</td>
<td>1.65</td>
<td>6.34</td>
<td>417</td>
<td>1.13</td>
<td>10.48</td>
</tr>
<tr>
<td>$G_5$</td>
<td>1.58</td>
<td>6.19</td>
<td>432</td>
<td>1.36</td>
<td>10.77</td>
</tr>
</tbody>
</table>

4.5 Discussion

In the multi component Li$_2$O–PbO–B$_2$O$_3$–SiO$_2$–Bi$_2$O$_3$–MnO: Ga$_2$O$_3$ glass system, SiO$_2$ and B$_2$O$_3$ are well-known strong glass formers. SiO$_2$ participates in the glass network with SiO$_4$ tetrahedra, whereas B$_2$O$_3$ participates with BO$_3$ and BO$_4$ structural units. Bi$_2$O$_3$ is a weak glass former, in the presence of glass formers like SiO$_2$ and B$_2$O$_3$ and modifiers, it participates in the glass network with triangular BiO$_3$ pyramidal units with lone pair of electrons (6s$^2$ stereo chemically active electrons) at the fourth corner. Bi$_2$O$_3$ also participates in the network with [BiO$_6$] octahedral units [49].
Ga$_2$O$_3$ is considered to act as a network former if Ga$^{3+}$ ions take preferentially four fold coordination in oxide glasses with sufficient modifying cations like Li$^+$ for charge-balance. The excess negative charge on GaO$_4$ tetrahedra are compensated either by localization of a modifier ion nearby or by generation of three fold oxygens. The GaO$_4$ tetrahedrons may enter the glass network and alternate with SiO$_4$ tetrahedrons.

Coordination transformation of Ga$^{3+}$ from a network former to a network modifier in a melt with (Ga$^{3+}$ + Si$^{4+}$)$_2$O$_5^{2-}$ stoichiometry may be expressed with the formalized equation:

$$5\text{Si}_2\text{O}_5^{2-} + (\text{LiGa})_2\text{O}_5^{2-} = 10[(\text{SiO}_3)^{2-} / (\text{SiO}_2\text{O}_2)^{2-}] + 2\text{Li}^+ + 2\text{Ga}^{3+}$$

In some glass networks, the gallium ions are also found to be in modifier position with GaO$_6$ structural units [50]. PbO when incorporated into B$_2$O$_3$ glass network, normally converts sp$^2$ planar BO$_3$ structural clusters into more stable sp$^3$ tetrahedral BO$_4$ units and may also create non bridging oxygens (depending upon whether PbO goes into modifying positions or network-forming positions). In general, PbO participates in the glass network both with covalent and ionic bondings and participates in the glass network with [PbO$_4$]$^{2-}$ pyramidal units connected in puckered layers. The modifier oxide Li$_2$O de-polymerizes Si–O–Si network, with the formation of meta, pyro and ortho-silicates.

Normally, manganese ions subsist in Mn$^{2+}$ state (with five unpaired electrons [50]) with octahedral occupancy in the studied glass system. Most of the Mn$^{2+}$ complexes are octahedral and have a high spin arrangement. The presence of manganese ions in tetrahedral positions is also reported in a number of glass systems.
These tetrahedrally positioned manganese (with MnO$_4$ structural units) ions occupy network forming positions and form linkages with the other network formers. The presence of lead ions in studied glass network may provide oxidizing environment to get converted a fraction of Mn$^{2+}$ ions in to Mn$^{3+}$ ions during melting and crystallization processes described by the following reaction:

$$\text{Mn}^{2+} + \frac{1}{2}\text{O}_2 \leftrightarrow \text{Mn}^{3+} + \text{O}^{2-}$$

In octahedral symmetry, the ground state of Mn$^{2+}$ is spherically non-degenerate $^6A_{1g}$ state. In cubic crystalline field of low and moderate strengths, the five d electrons of Mn$^{2+}$ ions distribute in the t$_{2g}$ and e$_g$ orbital, with three in the former and two in the latter. Therefore, the ground state configuration is normally written as $(t_{2g})^3(e_g)^2$. This configurations gives rise to electronic states $^6A_{1g}$, $^4A_{1g}$, $^4E_g$, $^4T_{1g}$, $^4T_{2g}$, $^4A_{2g}$ and to a number of doublet states of which $^6A_{1g}$ lies lowest according to Hund’s rule. The observed optical absorption bands are from the ground state $^6A_{1g}$ to some quarter states and these are both spin and parity forbidden. The band observed at about 532 nm is assigned to octahedral $^6A_{1g}(S) \rightarrow ^4T_{2g} (G)$ transition; since this transition involves a change of configuration from $(t_{2g})^3(e_g)^2$ to $(t_{2g})^4(e_g)^1$ is therefore observed to be relatively broader [35,36]. Another weak band observed at about 422 nm can safely be ascribed to $^6A_{1}(S) \rightarrow ^4T_{2}(G)$ transition of tetrahedral Mn$^{2+}$ ions. As the concentration of Ga$_2$O$_3$ is increased up to 3.0 mol%, the octahedral band grows at the expense of tetrahedral band suggesting that there is a gradual decrease of tetrahedrally positioned Mn$^{2+}$ ions in the glass. However, when the concentration of Ga$_2$O$_3$ is raised beyond 3.0 mol% a reversal trend is observed in the intensity of these bands. The tetrahedrally
Positioned manganese ions occupy network forming positions with MnO$_4$ structural units and may form linkages with BO$_4$ and SiO$_4$ structural units.

Yet, the spectra exhibited a relatively broad band at about 490 nm. This is identified as being due to $^5E_g \rightarrow ^5T_{2g}$ octahedral transition of Mn$^{3+}$ ions [52] which arises due to the intraconfigurational transition between the two Jahn–Teller split quintet levels, viz., the $^5E$ ground state and the $^5T_2$ excited state. The intensity of this band is observed to increase with the increase in the concentration of Ga$_2$O$_3$. Thus the analysis of optical absorption spectra indicates that a part of manganese ions do exist in Mn$^{3+}$ state. The gradual growth of this Mn$^{3+}$ band with increasing content of Ga$_2$O$_3$ beyond 3.0 mol% suggests an increase in the oxidation ratio, Mn$^{3+}$/Mn$^{2+}$, in the glass matrix.

The validity of expression between $(a\hbar\omega)^2$ and $\hbar\omega$ related to optical band gap points out that the band gap is caused by amorphous optical absorption edge. This confirms the fact that the studied disordered amorphous glass materials are formed prevalingly by direct transitions between the valence band and the conduction bands and indirect inter-band transitions are quite unlikely. However, there may be some minor deviations observed from this dependence due to trapping of some disordered states within the energy gap.

The value of optical band gap ($E_o$) decreases with increasing Ga$_2$O$_3$ content in the glass network up to 3.0 mol%. This observation indicates that up to this concentration gallium ions mostly occupy octahedral positions and participate in the similar to lithium ions, depolymerize the glass network by creating more bonding
defects and non-bridging oxygens (NBO). The Mn$^{2+}$ (O$_h$) ions in the glass network (as evidenced from optical absorption studies), also contribute for the decrease of optical band gap. Mn$^{2+}$ (O$_h$) ions act as modifiers and increase in the formation of donor centers and subsequently, the excited states of localized electrons originally trapped on Mn$^{2+}$ sites begin to overlap by energy with the empty 3d Mn states on the neighboring Mn$^{3+}$ 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 shrinkage in the band gap as the concentration of Ga$_2$O$_3$ is increased up to 3.0 mol%.

The optical activation energy associated with $^6A_{1g} (S) \rightarrow ^4T_{2g} (G)$ octahedral band of Mn$^{2+}$ ions is decreased from 3.20 eV (glass G$_0$) to 2.95 eV (glass G$_3$), whereas the energy of Mn$^{3+}$ ion transition band is increased from 3.25 eV to 3.35 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 Mn$^{3+}$ site converts this one into a lower valence state Mn$^{2+}$. Afterwards the trapped electron at this Mn$^{2+}$ site is transferred to the neighboring new Mn$^{3+}$ site by absorbing a photon quantum. Thus the optical absorption in the glass
samples is dominated by polaronic transfer between the Mn\(^{2+}\) and Mn\(^{3+}\) species [53]. In addition electron–phonon interaction, including the anharmonic ones play substantial role for the variation of optical activation energy associated with the absorption bands.

The resonance signal observed at \(g\approx 2.0\) in the ESR spectra arises due to Mn\(^{2+}\) ions in an environment close to an octahedral symmetry and is known to arise from the transition between the energy levels of the lower doublet \(|\pm \frac{1}{2}\rangle\). The gradual increase observed in the value of \(g\) of this signal with the increase the concentration of Ga\(_2\)O\(_3\) beyond 3.0 mol\% suggests that there is a gradual adaption of manganese ions from ionic bonding to covalent bonding in the glass network. This result suggests that gallium ions mainly in the tetrahedral participation, alternate with Mn–O bonds and increases the rigidity of the glass network when present more than 3.0 mol\%. Contribution of orbital angular momentum to the magnetic moment of Mn\(^{2+}\) ions may also be responsible to some extent for the higher values of \(g\) obtained for these glasses [54]. The weak symmetric and isotropic line signal observed at \(g\approx 4.3\) is due to magnetically isolated Mn\(^{2+}\) ions in tetragonally (and or rhombically) distorted octahedral sites of symmetry subjected to strong crystal field effects [55] and arises from transitions between the energy levels of the middle Kramers doublet \(|\pm \frac{3}{2}\rangle\).

The intensity (\(\mathfrak{I}\)) of the ESR signal is evaluated using \(\mathfrak{I} \approx I (\Delta B)^2\), where \(I\) is the peak-to-peak height and \(\Delta B\) is the square of width of the signal and its dependence for \(g_{\text{eff}} \approx 2.0\) resonance \textit{versus} Ga\(_2\)O\(_3\) is shown as an inset of Fig. 4.4. This variation exhibited maximal effect of \(\mathfrak{I}\) at 3.0 mol\% of Ga\(_2\)O\(_3\). Dipole–dipole interaction and
exchange interaction are the two interactions that contribute 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. Exchange interactions result from mutual spin flipping, which may average out the local dipolar fields and leads to line narrowing normally insignificant when we have a system of identical ions [56]. The other mechanism which causes narrowing of the signal is supposed to be the network disordering and interaction between multivalent manganese ions (viz., Mn$^{2+}$ and Mn$^{3+}$). 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 at $g_{\text{eff}} \approx 2.0$ beyond 3.0 mol% of Ga$_2$O$_3$ shows the dominance of the exchange mechanisms which in turn indicates a gradual increase in Mn$^{3+}$ ion concentration in addition to the increasing degree of disorder in the glass network due to the increasing octahedral occupancy of Ga$^{3+}$ ions.

The dielectric parameters viz., $\varepsilon'$, tan $\delta$ are found to increase with increasing temperature for all the studied glasses. Further, at any frequency and temperature these parameters are found to increase with increase in the content of Ga$_2$O$_3$ up to 3.0 mol%. Among different polarizations (viz., electronic, ionic, dipolar and space charge polarizations) the space charge polarization which depends on defect concentration defects in the glass network influences strongly the dielectric constant at lower frequencies.

As mentioned earlier, the octahedral Ga$^{3+}$ ions and Mn$^{2+}$ ions similar to Li$^+$ ions act as modifiers and create dangling bonds and non bridging oxygen ions by disrupting
Si–O–Si and Si–O–B linkages resulting several free ions. These charge species are accumulated near the electrodes causing large surface charge polarization of the glass and contribute for the increase of dielectric parameters at higher temperatures especially at lower frequencies. Further, under the application of the electric field, electron hopping between Mn$^{2+}$ and Mn$^{3+}$ also contribute for such increase of dielectric constant. Additionally, the behaviour of dielectric permittivity dispersion is related to the application of the field. At higher frequency, the charge carriers may not be able to orient with adequate swift, so their oscillation will begin to lag behind this field and lead to the decrease of dielectric permittivity, $\varepsilon'(\omega)$.

From the analysis of results of the optical band gap, IR and Raman spectra, it is understood that a considerable proportion of Ga$^{3+}$ ions occupy tetrahedral positions when the concentration of Ga$_2$O$_3$ is greater than 3.0 mol% and alternate with SiO$_4$ structural units in the glass network. Such linkages increase the rigidity of the glass network and hinder the easy movement of charge carriers. This might be the reason for the observed decrease of dielectric constant with the increase in the content of Ga$_2$O$_3$ beyond 3.0 mol%.

The dielectric loss dispersion with frequency and temperature clearly exhibited the relaxation feature of the studied samples. The maximum in the, tan $\delta$, peak is shifted to higher frequency with increasing temperature. The frequency region under the peak maximum of, tan$\delta$, determines the range in which charge carriers are mobile on long distances. At frequency above peak maximum, the carriers are spatially confined to
potential wells, being mobile on short distances and making only localized motion within the wells.

Theses relaxation effects in the studied glasses can be attributed to the Mn$^{2+}$ ion complexes that possess net dipole moment [57]. The decrease in the breadth and the intensity of the relaxation peaks for the samples containing Ga$_2$O$_3$ beyond to 3.0 mol% supports the view point that conversion of Mn$^{2+}$ to Mn$^{3+}$ by oxidation processes is larger. The dielectric relaxation character of the samples can some times be analyzed by graphical method suggested by Cole [58]. Combination of the standard Debye’s relations gives rise to:

\[
\varepsilon''(\omega) = \frac{(\varepsilon_s - \varepsilon_\infty)\omega\tau}{1 + \omega^2\tau^2} = \frac{1}{\tau}(\varepsilon_s - \varepsilon'(\omega)), \tag{4.1}
\]

\[
\frac{\varepsilon''(\omega)}{\omega} = \frac{(\varepsilon_s - \varepsilon_\infty)\tau}{1 + \omega^2\tau^2} = \tau(\varepsilon'(\omega) - \varepsilon_\infty). \tag{4.2}
\]

As per Eqs. (4.1) and (4.2), the plots between $\varepsilon''(\omega)\omega$ vs. $\varepsilon'(\omega)$ and $\varepsilon''(\omega)/\omega$ vs. $\varepsilon'(\omega)$ yield straight lines with slope $1/\tau$ and $\tau$, respectively. Fig. 4.10 represents such plots for the glass G$_2$ drawn at 373 K. The plots observed to be straight lines. However, considerable deviation from the straight line is observed in the high frequency region. Such deviation suggests spreading of relaxation times [59]. Graphs drawn for other glasses have also exhibited nearly the same behavior. The values of relaxation time $\tau$ evaluated from these graphs are presented in Table 4.6. The value of $\tau$ exhibited minimal effect at 3.0 mol% of Ga$_2$O$_3$. 
The deviations indicate that there are different types of dipoles which contribute to the relaxation effects in these glasses. In earlier studies on Bi$^{3+}$ doped samples, it was proved that Bi$^{3+}$ complexes do contribute to the dielectric relaxation effects [60]. Bismuth oxide participates in the glass network with BiO$_3$ structural units and can be viewed as tetrahedrons with the oxygen situated at three corners and the lone pair of electrons of bismuth (Bi$^{3+}$) 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 acquire dipole moment and contribute to the dipolar relaxation effects. The contribution to the dielectric relaxation effects from PbO also cannot be ruled out. In fact, PbO posses 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 [61] and contribute to the dielectric relaxation effects. Hence, the spreading of relaxation in MnO doped glasses may be attributed to the Bi$^{3+}$ and PbO molecules in addition to the conventional divalent manganese ions.

Another contribution for the spreading relaxation is 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 [62, 63]. The shifting of relaxation region towards higher temperatures and increase in the activation energy for the dipoles with increase in the concentration of Ga$_2$O$_3$ beyond 3.0 mol % (Table 4.5) suggests a decreasing degree of freedom for dipoles to orient in the field direction in the glass network. As mentioned earlier, in G$_4$ and G$_5$ glasses, major portion of Ga$^{3+}$ ions take part in network forming positions with GaO$_4$ structural units, alternate with SiO$_4$/BO$_4$ structural units and increase the rigidity of the glass network and increases the activation energy for dipoles as observed.

The variation of log $\sigma(\omega)$ vs activation energy for conduction (in the high temperature region) is shown as the inset (c) of Fig. 4.10; the graph yields a near
straight line. Such linear nature suggests 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 Mn$^{2+}$ and Mn$^{3+}$ ions, whereas ionic conduction is due to migration of Li$^+$ ions. For these glasses, the ac conductivity increases with increasing content of Ga$_2$O$_3$ upto 3.0 mol% (inset (a) of Fig. 4.9). The increase in the conductivity can be interpreted in terms of transition of the mixed conduction with high electronic contribution (involved in the process of transfer from Mn$^{2+}$ $\rightarrow$ Mn$^{3+}$ions) to the dominated ionic conduction. The possible explanation for the decrease of conductivity with Ga$_2$O$_3$ content beyond 3.0 mol% is that the entry of Ga$^{3+}$ ions into the network forming tetrahedral positions reduces the concentration of dangling bonds in the glass network since some of GaO$_4$ 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 activation energy for conduction.

The ac conductivity in the low temperature region up to nearly 400 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.
Such a frequency dependent conductivity can be explained on the basis of quantum mechanical tunneling model (QMT) [64] as described in earlier papers from our laboratory [65, 66]. According to QMT model the conductivity by using (Eq.3.13);

where \( N(E_F) \) is the density or the concentration of energy states (formed due to the defects produced by modifier oxides) between which the conduction takes place near the Fermi level and the other symbols have the same meaning described in our earlier papers [65,66].

The value of \( N (E_F) \) evaluated at 353 K using Eq. (3.13) is found to increase from glass \( G_0 \) to glass \( G_3 \) (Table 4.6) indicating increase of defect energy states or free charge carriers for conduction in the glass network thus supporting earlier statement that in this concentration range (0 to 3.0 mol%) \( \text{Ga}^{3+} \) ions mainly occupy octahedral sites and induce bonding defects.

Our studies on dielectric properties of \( \text{Li}_2\text{O–PbO–B}_2\text{O}_3–\text{SiO}_2–\text{Bi}_2\text{O}_3–\text{MnO}: \text{Ga}_2\text{O}_3 \) glasses, as mentioned earlier indicate, the rate of increase of \( \varepsilon’\tan \delta \) (a parameter inversely proportional to dielectric breakdown strength) with temperature is the highest for glass \( G_3 \) and the lowest for glass \( G_5 \). 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 \( G_3 \), the breakdown strength is the lowest when compared to that of other glasses (Table 4.6). 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 Ga$_2$O$_3$ up to 3.0 mol%.

### 4.6 Conclusions

Optical absorption and ESR studies of Li$_2$O–PbO–B$_2$O$_3$–SiO$_2$–Bi$_2$O$_3$–MnO: Ga$_2$O$_3$ have revealed that manganese ions do exist both in Mn$^{2+}$ and Mn$^{3+}$ states. The oxidation ratio Mn$^{3+}$/Mn$^{2+}$ seems to be the lowest for the glasses mixed with 3.0 mol% of Ga$_2$O$_3$. IR, Raman spectral studies have indicated that the gallium ions occupy both tetrahedral and octahedral positions. The tetrahedral occupancy seems to be dominant when the concentration of Ga$_2$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 of the samples mixed with 3.0 mol% of Ga$_2$O$_3$ and found to be the lowest for the samples mixed with 5.0 mol% of Ga$_2$O$_3$. Variations in these parameters with concentration of Ga$_2$O$_3$ are quantitatively explained based on the deviations in the coordination number of gallium ions and influence of gallium ions on the oxidation states of manganese ions in the glass network.
References


