This chapter contains a brief outline and conclusions drawn from the investigation carried out on characterization and physical properties (viz., dielectric properties, optical absorption, IR, Raman and ESR) of Li₂O–PbO–B₂O₃–SiO₂–Bi₂O₃–M₂O₃:CuO/MnO/Fe₂O₃/V₂O₅ where M₂O₃ = (Al₂O₃, Ga₂O₃, In₂O₃ and Tl₂O₃) glasses systems.
7.1 Summary

A systematic investigation on characterization and physical properties (viz., dielectric properties, optical absorption, ESR, infrared and Raman spectra) of Li$_2$O–PbO–B$_2$O$_3$–SiO$_2$–Bi$_2$O$_3$–CuO/MnO/Fe$_2$O$_3$/V$_2$O$_5$ glasses doped with some IIIA group elemental oxides viz. Al$_2$O$_3$, Ga$_2$O$_3$, In$_2$O$_3$ and Tl$_2$O$_3$ have been carried out.

The compositions of the samples used in the present study are:

- $19.4\text{Li}_2\text{O}–20\text{PbO}–20\text{B}_2\text{O}_3–30\text{SiO}_2–(10-x)\text{Bi}_2\text{O}_3–0.6\text{CuO}: x\text{Al}_2\text{O}_3$ ($0 \leq x \leq 5$)
- $19.5\text{Li}_2\text{O}–20\text{PbO}–20\text{B}_2\text{O}_3–30\text{SiO}_2–(10-x)\text{Bi}_2\text{O}_3–0.5\text{MnO}: x\text{Ga}_2\text{O}_3$ ($0 \leq x \leq 5$)
- $19\text{Li}_2\text{O}–20\text{PbO}–20\text{B}_2\text{O}_3–30\text{SiO}_2–(10-x)\text{Bi}_2\text{O}_3–1.0\text{Fe}_2\text{O}_3: x\text{In}_2\text{O}_3$ ($0 \leq x \leq 5$)
- $19\text{Li}_2\text{O}–20\text{PbO}–20\text{B}_2\text{O}_3–30\text{SiO}_2–(10-x)\text{Bi}_2\text{O}_3–1.0\text{V}_2\text{O}_5: x\text{Tl}_2\text{O}_3$ ($0 \leq x \leq 5$)

(all in mol%)

The glasses were prepared by the usual melting, quenching and subsequent annealing techniques.

The following studies were made:

1. Dielectric properties
2. Optical absorption spectra
3. ESR spectra
4. Infrared spectra
5. Raman spectra

The samples were characterized by X-ray diffraction.

The following measurements were taken:

1) Dielectric constant ($\varepsilon'$), loss (tan $\delta$) and ac conductivity $\sigma_{ac}$ in frequency range $10^2$ to $10^6$ Hz and in the temperature range 30-300 °C.

2) Dielectric breakdown strength at room temperature in air medium.
3) Optical absorption in the UV and visible and NIR regions at room temperature.

4) Electron spin resonance spectra at room temperature.

5) Infrared spectra of all these glasses in the region 400 to 1600 cm\(^{-1}\) at room temperature.

6) Raman spectra of all the glasses in the region 100 to 1500 cm\(^{-1}\) at room temperature using He-Ne laser source of excitation wavelength 632.8 nm.

7.2 Conclusions

The main conclusions drawn from the results of above said studies for each composition are summarized below:

Chapter 3 presents the 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 is discussed and the main conclusions drawn from it are given below:

➢ 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 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., \( \text{Cu}^+ \rightarrow \text{Cu}^{2+} \) is also located in the spectra of all these glasses.

- 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.

Optical absorption and ESR studies have revealed that copper ions do exist in \( \text{Cu}^{2+} \) and \( \text{Cu}^+ \) states. The redox ratio seems to be higher for the glasses mixed with 3.0 mol\% of \( \text{Al}_2\text{O}_3 \).

- The infrared transmission spectrum of \( \text{Al}_2\text{O}_3 \) free \( \text{Li}_2\text{O}–\text{PbO}–\text{B}_2\text{O}_3–\text{SiO}_2–\text{Bi}_2\text{O}_3–\text{CuO} \) glass exhibited vibrational bands at 1284 cm\(^{-1}\) identified as being due to \( \text{BO}_3 \) structural units 1121 cm\(^{-1}\) due to \( \text{BO}_4 \) units 1032 cm\(^{-1}\) due to \( \text{Si}–\text{O}–\text{Si} \) asymmetric bending vibrations, 849 cm\(^{-1}\) due to \( \text{Si}–\text{O}–\text{Si} \) symmetrical vibrations; in this region band due to \( \text{AlO}_4 \) vibrations is also possible, 697 cm\(^{-1}\) due to \( \text{B}–\text{O}–\text{B} \) bending vibrations, 475 cm\(^{-1}\) \( \text{Si}–\text{O}–\text{Si} \) rocking motion and this region may also consisting of vibrations due to \( \text{PbO}_4 \) and \( \text{AlO}_6 \) structural units and at 449 cm\(^{-1}\) (due to vibrations \( \text{Bi}–\text{O}–\text{Bi} \) bonds of \( \text{BiO}_6 \) units).
The Raman spectra 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 at about 1053, 810 and 478 cm$^{-1}$ assigned to symmetrical, asymmetrical and rocking motion of Si–O–Si structural units, respectively. The spectra also exhibited a band at 1040 cm$^{-1}$, ascribed to diborate groups consisting of six membered rings containing two BO$_4$ teterahedra and another band centered at 805 cm$^{-1}$ attributed to the boroxil ring oxygen breathing in which the boron coordinate atom is three.

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 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.

Chapter 4 reported the Influence of Ga$^{3+}$ ions on spectroscopic and dielectric features of multi component lithium lead boro bismuth silicate glasses doped with manganese ions.
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. 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 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.

Optical absorption and ESR studies have revealed that Manganese ions do exist in Mn$^{2+}$ and Mn$^{3+}$ states. The oxidation ration Mn$^{3+}$/Mn$^{2+}$ seems to be lower 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., $\epsilon'$, tan\$\delta$ and also $\sigma_{ac}$ with temperature is found to be the highest in the samples mixed with 3.0 mole\% of Ga$_2$O$_3$ and found to be lowest for the samples 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 manganese ions by gallium ions in the glass network.
Chapter 5 narrates the influence of In$_2$O$_3$ on electrical characteristics of iron mixed Li$_2$O–PbO–B$_2$O$_3$–SiO$_2$–Bi$_2$O$_3$ multi-component glass system. The main conclusions drawn from this study are given below:

- A variety of electrical and dielectric properties including dielectric constant, $\varepsilon'(\omega)$, loss, tan $\delta$, ac conductivity $\sigma_{ac}$, and electric moduli, $M(\omega)$, over a wide continuous frequency range of $10^2$ Hz to $10^6$ Hz and in the temperature range 303 to 573 K were measured as a function of the concentration of In$_2$O$_3$. The observed increase in the dielectric constant and also dielectric loss (beyond relaxation region) with the temperature were explained using space charge polarization model. The ac conductivity has exhibited increasing trend with the increase of In$_2$O$_3$ concentration from 0 to 1.0 mol%.

- The spectrum of glass I$_0$ exhibited conventional Fe$^{3+}$ ion excitations absorption bands at 402 nm and 415 nm and 807 nm. These bands were identified as being due to $^6A_{1g}$ (S) $\rightarrow ^4E_g$ (G)$^+$$^4A_{1g}$ (G), $^4T_{1g}$ (G) and $^6A_1(t^3_2e^2_g)$$\rightarrow$$^4t_2(t^4_2e_g)$ octahedral transition of Fe$^{3+}$ (d$^5$) ions, respectively. Additionally a band, identified as being due to transition of Fe$^{2+}$ (d$^6$) ions, is also located at about 934 nm in these spectra. With the gradual increase in the concentration of In$_2$O$_3$ from 0 to 1.0 mol% the band due to Fe$^{2+}$ ion transition is observed to increase at the expense of bands due to Fe$^{3+}$ ions.
From the observed absorption edges, we have evaluated the optical band gap \( (E_o) \). The value of \( E_o \) exhibited minimal effect at 1.0 mol\% of In\(_2\)O\(_3\).

- ESR spectra of the titled glasses recorded at ambient temperature exhibited an intense spectral line situated at about \( g \approx 2.015 \) (signal-1) and a weak signal at about \( g \approx 4.513 \) (signal-2). A slight variation in the g- parameters of the signals with the content of In\(_2\)O\(_3\) is clearly observed. Further, the intensity of both signals is observed to increase with increase in the concentration of In\(_2\)O\(_3\) beyond 1.0 mol\%.

- The infrared transmission spectra of Li\(_2\)O–PbO–B\(_2\)O\(_3\)–SiO\(_2\)–Bi\(_2\)O\(_3\)–Fe\(_2\)O\(_3\):In\(_2\)O\(_3\) glasses. The spectra exhibited borate, silicate and bismuth bands exhibited. In the region of vibrations due to B-O-B linkages band due FeO\(_4\) tetrahedral units is also expected. Additionally the spectra of these glasses have exhibited an intense BiO\(_6\) units band due to vibrating at about 425 cm\(^{-1}\); in this region the vibrations of \( \nu_3\) FeO\(_6\) structural units are also possible.

The optical absorption, ESR and also IR spectral studies have revealed that Fe\(^{3+}\) ions predominantly exist in tetrahedral units, alternate with SiO\(_4\)/BO\(_4\) structural units and increase the rigidity of the glass network when the concentration of In\(_2\)O\(_3\) is raised beyond 1.0 mol\%. The overall analysis of these results concludes that Li\(_2\)O–PbO–B\(_2\)O\(_3\)–SiO\(_2\)–Bi\(_2\)O\(_3\)–Fe\(_2\)O\(_3\) glasses
containing about 1.0 mol% of In$_2$O$_3$ are more suitable for achieving of good electrical conductivity.

In Chapter 6 the Dielectric and spectroscopic investigations of V$_2$O$_5$ doped multi-component Li$_2$O–PbO–B$_2$O$_3$–SiO$_2$–Bi$_2$O$_3$–Tl$_2$O$_3$ glass system is given below:

- The optical absorption spectra of Li$_2$O–PbO–B$_2$O$_3$–SiO$_2$–Bi$_2$O$_3$–V$_2$O$_5$: Tl$_2$O$_3$ glasses recorded at room temperature in the wavelength region 300 – 1100 nm. The spectra of glass T$_0$ exhibited two broad bands with the meta-centers at 635 nm and 875 nm corresponding to $^2$B$_2$→$^2$B$_1$ and $^2$B$_2$→$^2$E$_1$ transitions of VO$^{2+}$ ions; with gradual increase in the concentration of Tl$_2$O$_3$, the half width and peak height of these bands are observed to decrease. The values of optical band gap are found to be highest for the glass T$_5$.

- The IR spectrum of Tl$_2$O$_3$ free Li$_2$O–PbO–B$_2$O$_3$–SiO$_2$–Bi$_2$O$_3$–V$_2$O$_5$ glass 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 and in the same region due to V–O–V stretching vibrations have also been observed, 615 cm$^{-1}$ due to B-O-B bending vibrations and V–O–V bending vibrations, 475 cm$^{-1}$ due to (Si–O–Si rocking motions and the PbO$_4$ units) and at 449 cm$^{-1}$ due to Bi–O–Bi vibrations bands belong to BiO$_6$.
units. With addition of Tl$_2$O$_3$ in the glass same the intensity of all the symmetric bands of silicate groups and also these of BO$_3$ units is observed to increases, where as that of the asymmetrical of bonds structural groups BiO$_6$ units and BO$_3$ units is observed to decreases.

- ESR spectra are observed to be complex made up of resolved hyperfine components arising from unpaired 3d$^1$ electron of $^{51}$V isotope having spin 7/2. As the concentration of Tl$_2$O$_3$ is increased, a decrease in the intensity of signal has been observed. The values of $g_{||}$and $g_{\perp}$ evaluated from these spectra are observed to decrease with increase in the concentration of Tl$_2$O$_3$.

- The ac conductivity is presented as a function of inverse temperature at different frequencies for T$_3$ glass. The dependence of ac conductivity at any given frequency and temperature exhibited a decrease trend with increase of Tl$_2$O$_3$ content in the glass matrix. From the plots of log $\sigma_{ac}$ vs.1/T, we have evaluated the activation energy, $w_{ac}$, for the conduction in the high temperature region over which a near linear dependence of log $\sigma_{ac}$ with 1/T could be observed; the activation energy is found to increase with the increase of Tl$_2$O$_3$ content in the glass matrix.

Optical absorption and ESR studies have revealed that vanadium ions do exist in V$^{4+}$ and V$^{5+}$ states. The redox ratio seems to be higher for glasses mixed with 5.0 mol% of Tl$_2$O$_3$. IR spectral studies have indicated that the thallium ions occupy both tetrahedral and octahedral positions. The
tetrahedral occupancy seems to be dominated. The tetrahedral occupancy seems to be dominated. The rate of increase of dielectric parameters, viz., $\varepsilon'$, $\tan \delta$ and $\sigma_{ac}$ with temperature is found to be the lowest in the sample mixed with 5.0 mol% of Tl$_2$O$_3$ and found to be the highest for the free of Tl$_2$O$_3$ sample. Variations in these parameters with concentration of Tl$_2$O$_3$ are quantitatively explained based on the deviations in the co-ordination number of thallium ions and de-clustering influence of vanadium ions by thallium ions in the glass network.

Summing up the entire work presented in this thesis it is felt that the study of various electrical properties in combination with spectroscopic properties of Li$_2$O–PbO–B$_2$O$_3$–SiO$_2$–Bi$_2$O$_3$–M$_2$O$_3$: CuO/MnO/Fe$_2$O$_3$/V$_2$O$_5$ (M$_2$O$_3$ = viz., Al$_2$O$_3$, Ga$_2$O$_3$, In$_2$O$_3$ and Tl$_2$O$_3$) glasses has yielded some valuable information which will be useful for the practical applications of these materials.