This chapter contains a brief outline and conclusions drawn from the investigation carried out on (a) electrical properties and (b) spectroscopic properties of $V_2O_5$ and CuO doped Li$_2$O-MoO$_3$-B$_2$O$_3$ glasses. Outline of optical absorption and luminescence spectroscopy of rare earth ions (viz., Pr$^{3+}$, Nd$^{3+}$, Sm$^{3+}$ and Er$^{3+}$) in Li$_2$O-MO(Nb$_2$O$_5$, MoO$_3$ and WO$_3$)-B$_2$O$_3$ glass systems is also presented.
6.1 Summary

A systematic investigation on characterization (viz., XRD, SEM and DSC) and physical properties (viz., dielectric properties, infrared, optical absorption, ESR and luminescence spectra) of Li$_2$O-MoO$_3$-B$_2$O$_3$ glasses doped with V$_2$O$_5$ and CuO; and Optical properties of Li$_2$O-MO (Nb$_2$O$_5$, MoO$_3$ and WO$_3$)-B$_2$O$_3$:Ln$^{3+}$ glasses have been carried out.

The compositions of the glasses used for the present study are:

SERIES 1: 40 Li$_2$O-4 MoO$_3$-(56-x) B$_2$O$_3$: x V$_2$O$_5$ (0 ≤ x ≤ 1.5)

SERIES 2: 40 Li$_2$O-(4-x) MoO$_3$-56 B$_2$O$_3$: x CuO (0 ≤ x ≤ 1.2)

SERIES 3: 40 Li$_2$O-4 MO-55 B$_2$O$_3$: 1 Ln$_2$O$_3$ (Ln$^{3+}$ = Pr$^{3+}$, Nd$^{3+}$, Sm$^{3+}$ and Er$^{3+}$)

where MO = Nb$_2$O$_5$, MoO$_3$ and WO$_3$.

The glasses were prepared by the usual melting, quenching and subsequent annealing techniques. The following studies were made:

1. Dielectric properties
2. Infrared spectra
3. Optical absorption
4. ESR spectra
5. Luminescence
The samples were characterized by X-ray diffraction, scanning electron microscopy and differential scanning calorimetric techniques.

The following measurements were taken:

1) Dielectric constant ($\varepsilon'$), loss (tan $\delta$) and a.c conductivity $\sigma_{ac}$ in frequency range $10^2$ to $10^5$ Hz and in the temperature range 30-250 °C.

2) Optical absorption in the UV, visible and NIR regions.

3) Electron spin resonance spectra at room temperature.

4) Infrared spectra of all these glasses in the region 400 to 4000 cm$^{-1}$.

5) Photoluminescence in the UV, visible and NIR regions.

6.2 Conclusions

The main conclusions drawn above studies on V2O5 and CuO doped samples are summarized below:

1. The scanning electron microscopic pictures and X-ray diffraction pattern of pure Li$_2$O-MoO$_3$-B$_2$O$_3$ glasses doped with V$_2$O$_5$ and CuO exhibited virtually no crystallization.

2. Differential scanning calorimetric traces of Li$_2$O-MoO$_3$-B$_2$O$_3$ glasses doped with V$_2$O$_5$, CuO have exhibited highest glass forming ability when the concentration of V$_2$O$_5$ and CuO is around 1.5 and 1.2 mol % respectively.
3. The optical absorption spectra of Li$_2$O-MoO$_3$-B$_2$O$_3$: V$_2$O$_5$ glasses recorded at room temperature in the wavelength region 300-1200 nm exhibited two broad absorption bands at 620 and 827 nm corresponding to $^2B_2 \rightarrow ^2B_1$ and $^2B_2 \rightarrow ^2E$ transitions of VO$^{2+}$ ions; with increase in the concentration of V$_2$O$_5$ up to 0.8 mol %, the half width and peak height of these bands are observed to increase. The largest intensity and the half width of these bands have been observed in the spectrum of glass V$_8$. From this observation it is concluded that the largest concentration of VO$^{2+}$ (vanadyl) ions in this glass.

The absorption spectra of CuO doped glasses have exhibited two kinks in the region 320-400 nm followed by a broad band with the metacenter between 740-760 nm. With increase in the concentration of CuO up to 0.6 mol %, the half width and peak height of broad band is observed to increase and beyond this concentration a gradual decrease in the intensity of this band could clearly be seen. The two small kinks observed in the violet region of the absorption spectra has been assigned to $3d^{10} \rightarrow 3d^9 4s^1$ transition of Cu$^+$ ion, where as The broad band observed in the region 740-760 nm is assigned to $^2B_{1g} \rightarrow ^2B_{2g}$ transition of Cu$^{2+}$ ions. The analysis of these results further indicates the presence of highest concentration of Cu$^+$ ions in the glass MC$_{12}$. 
4. The ESR spectra recorded at room temperature of pure Li$_2$O-MoO$_3$-B$_2$O$_3$ glasses have exhibited a signal consisting of a central line surrounded by smaller satellites (at $g_\perp \sim 1.930$ and $g_\parallel \sim 1.872$); this signal is identified due to Mo$^{5+}$ ions. The spectra of V$_2$O$_5$ doped glasses exhibited a complex spectra consisting of hyperfine components arising from unpaired 3d$^1$ electron with $^{51}$V isotope whose spin is 7/2. As the concentration of V$_2$O$_5$ is increased up to 0.8 mol % an increasing degree of resolution and the intensity of signal have been observed. The line shape of the ESR spectra of the glass sample changed markedly with composition. At low V$_2$O$_5$ content, the EPR spectra were observed to be asymmetrical; this has been attributed to the contribution of ESR signal at about the same region due to another paramagnetic ion Mo$^{5+}$ in the host glass network. The quantitative analysis of the ESR spectra of these glasses pointed out that the ligand environment of VO$^{2+}$ ions experiences stretching of the VO$_6$ octahedron along the z-axis.

The CuO doped glasses exhibited a strong asymmetric signal with a partially resolved hyperfine structure at $g_\perp = 2.04$ and a shallow quadruplet at about $g_\parallel = 2.33$. The quantitative analysis of these spectra indicated a gradual adaptation of Cu$^{2+}$ ions from ionic environment to
covalent environment in concentration range (0.6-1.2 %) of CuO in the glass network.

5. The infrared (IR) spectra of Li$_2$O-MoO$_3$-B$_2$O$_3$: V$_2$O$_5$ glasses recorded at room temperature have exhibited prominent bands in the regions 1300-1400 cm$^{-1}$, 1000-1200 cm$^{-1}$ and another band at about 710 cm$^{-1}$; these bands are identified due to the stretching relaxation of B-O bond of the trigonal BO$_3$ units, vibrations of BO$_4$ structural units and due to the bending vibrations of B-O-B linkages respectively. Two new bands have also been located at 886 and 820 cm$^{-1}$ in the spectrum of glass V$_2$; these bands have been attributed to $\nu_1$ and $\nu_3$ vibrational modes of MoO$_4^{2-}$ tetrahedral units respectively. The analysis of these results indicate that as the concentration of V$_2$O$_5$ is raised up to 0.8 mol %, there is a growing degree of disorder in the glass network. The analysis of IR spectral results of CuO doped glasses indicated that when the concentration of CuO is raised beyond 0.6 mol %, there is a decreasing degree of disorder in the glass network; this is attributed due to the decreasing concentration of Cu$^{2+}$ and Mo$^{5+}$ ions that act as modifiers and depolymerize the glass network.

6. Emission spectra of CuO doped glasses exhibited an intense yellow emission band centered at about 550 nm and a relatively broad blue
emission band at about 450 nm under the excitation of 271 nm. These bands have been attributed to \( ^3D_1 \rightarrow ^1S_0 \) (450 nm) transition of isolated Cu\(^+\) ions and \( ^3D_1 \rightarrow ^1S_0 \) (550 nm) transition of (Cu\(^+\))\(^2\) pairs respectively. The close examination of these results indicated that there is a gradual increase in the reduction of Cu\(^2+\) ions in to Cu\(^+\) in the samples MC\(_8\) to MC\(_{12}\).

7. The dielectric parameters viz., \( \varepsilon' \), \( \tan \delta \) and \( \sigma_{ac} \) of V\(_2\)O\(_5\) and CuO doped glasses are found to increase and the activation energy for ac conduction is found to decrease with the increase in the concentration of V\(_2\)O\(_5\) and CuO up to 0.8 mol\% and 0.6 mol\% respectively. A substantial hike in the ac conductivity is also observed when the concentration of V\(_2\)O\(_5\) and CuO are increased from 0 to 0.8 mol \% and 0 to 0.6 mol \% respectively. The analysis of dielectric relaxation effects exhibited by these glasses indicated that there is a spreading of relaxation times; the spreading has been attributed to the contribution from Mo\(^{5+}\) and V\(^{4+}\) ions in V\(_2\)O\(_5\) doped glasses and Mo\(^{5+}\) and Cu\(^{2+}\) ions in CuO doped glasses. The conduction in the high-temperature region seems to be connected with both electronic and ionic; more specifically, up to 0.8 mol \% of V\(_2\)O\(_5\) and up to 0.6 mol\% of CuO, the ionic conduction seems to be dominant while in the higher concentration range, the electronic conduction seemed to prevail.
in both the glasses. The quantum mechanical tunneling model seems to be appropriate for explaining low temperature part (temperature independent part) of the conductivity in both the systems.

Conclusions from the studies on rare earth ions doped Li$_2$O-MO (Nb$_2$O$_5$, MoO$_3$ and WO$_3$)-B$_2$O$_3$ glasses

The optical absorption and fluorescence studies are also carried out on Li$_2$O-MO (Nb$_2$O$_5$, MoO$_3$ and WO$_3$)-B$_2$O$_3$ glasses containing four rare earth ions (Pr$^{3+}$, Nd$^{3+}$, Sm$^{3+}$ and Er$^{3+}$) with a view to examine the possible use of these glasses as laser hosts.

1. The recorded optical absorption spectral profiles of rare earth ions doped Li$_2$O-MO (Nb$_2$O$_5$, MoO$_3$ and WO$_3$)-B$_2$O$_3$ glasses have revealed the following transitions:

- Pr$^{3+}$: $^3H_4 \rightarrow ^3P_2$, $^3P_1$, $^3P_0$, $^1D_2$, $^3F_4$, $^3F_3$ and $^3F_2$.
- Nd$^{3+}$: $^4I_{9/2} \rightarrow ^2P_{3/2}$, $^4G_{9/2}$, $^4G_{7/2}$, $^4G_{5/2}$, $^2H_{11/2}$, $^4F_{9/2}$, $^4F_{7/2}$, $^4F_{5/2}$ and $^4F_{3/2}$.
- Sm$^{3+}$: $^6H_{5/2} \rightarrow ^4K_{11/2}$, $^6P_{7/2}$, $^4F_{7/2}$, $^6P_{5/2}$, $^4G_{9/2}$, $^4I_{13/2}$ and $^4I_{11/2}$.
- Er$^{3+}$: $^4I_{15/2} \rightarrow ^2G_{7/2}$, $^4G_{9/2}$, $^4G_{11/2}$, $^2G_{9/2}$, $^4F_{3/2}$, $^4F_{5/2}$, $^4F_{7/2}$, $^2H_{11/2}$, $^4S_{3/2}$, $^4F_{9/2}$ and $^4I_{9/2}$.

By performing least square fitting analysis the J-O parameters for these glasses are computed and are found to show the following trend:

- Pr$^{3+}$: $\Omega_4 > \Omega_6 > \Omega_2$,
- Nd$^{3+}$: $\Omega_6 > \Omega_2 > \Omega_4$,
- Sm$^{3+}$: $\Omega_2 > \Omega_4 > \Omega_6$. 

Er\textsuperscript{3+} : \Omega_2 > \Omega_4 > \Omega_6,

2. The **luminescence spectra** recorded at room temperature for these glasses have exhibited the bands corresponding to the following transitions:

Pr\textsuperscript{3+}: \( ^3\text{P}_0 \rightarrow ^3\text{F}_2, ^3\text{H}_6, ^3\text{H}_4, ^3\text{H}_5; ^1\text{D}_2 \rightarrow ^3\text{H}_4; ^3\text{P}_1 \rightarrow ^3\text{H}_5, ^3\text{F}_3.\)

Nd\textsuperscript{3+}: \( ^4\text{F}_{3/2} \rightarrow ^4\text{I}_{11/2}, ^4\text{I}_{13/2}.\)

Sm\textsuperscript{3+}: \( ^4\text{G}_{5/2} \rightarrow ^6\text{H}_{11/2}, ^6\text{H}_{9/2}, ^6\text{H}_{7/2}, ^6\text{H}_{5/2}\)

Er\textsuperscript{3+}: \( ^2\text{G}_{9/2} \rightarrow ^4\text{I}_{11/2}, ^4\text{I}_{13/2}; ^4\text{G}_{11/2} \rightarrow ^4\text{I}_{11/2}; ^4\text{F}_{5/2} \rightarrow ^4\text{I}_{13/2}, ^4\text{I}_{15/2}; ^4\text{F}_{7/2} \rightarrow ^4\text{I}_{15/2}.\)

The transitions given in the bold letters indicate the highest branching ratio of the respective ions; the summary of various radiative parameters connected with these prominent luminescence transitions are furnished in the following Table 6.1

**Table 6.1**

*Summary of the data on various radiative properties of different rare-earth ions doped Li\textsubscript{2}O-Nb\textsubscript{2}O\textsubscript{5}-B\textsubscript{2}O\textsubscript{3} glasses*

<table>
<thead>
<tr>
<th>Glass &amp; Emission Transition</th>
<th>( \lambda ) (nm)</th>
<th>( \Delta \lambda ) (nm)</th>
<th>( A ) (s\textsuperscript{-1})</th>
<th>( \tau ) (\mu s)</th>
<th>( % )</th>
<th>( \sigma \times 10^{-20} ) (\text{m}\textsuperscript{2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr\textsuperscript{3+}: ( ^3\text{P}_0 \rightarrow ^3\text{H}_6 )</td>
<td>486</td>
<td>10.5</td>
<td>14495</td>
<td>24131</td>
<td>41.44</td>
<td>60.07</td>
</tr>
<tr>
<td>Nd\textsuperscript{3+}: ( ^4\text{F}<em>{3/2} \rightarrow ^4\text{I}</em>{11/2} )</td>
<td>813.3</td>
<td>17.5</td>
<td>3815</td>
<td>7906</td>
<td>126</td>
<td>48</td>
</tr>
<tr>
<td>Sm\textsuperscript{3+}: ( ^4\text{G}<em>{5/2} \rightarrow ^6\text{H}</em>{11/2} )</td>
<td>609</td>
<td>18.5</td>
<td>229.78</td>
<td>458.4</td>
<td>2.205</td>
<td>50.67</td>
</tr>
<tr>
<td>Er\textsuperscript{3+}: ( ^2\text{G}<em>{9/2} \rightarrow ^4\text{I}</em>{13/2} )</td>
<td>462</td>
<td>19</td>
<td>643</td>
<td>1428</td>
<td>700.14</td>
<td>45.01</td>
</tr>
</tbody>
</table>
Table 6.1 B
Summary of the data on various radiative properties of different rare-earth ions doped Li$_2$O-MoO$_3$-B$_2$O$_3$ glasses

<table>
<thead>
<tr>
<th>Glass &amp; Emission Transition</th>
<th>$\lambda$(nm)</th>
<th>$\Delta\lambda$(nm)</th>
<th>$A$($s^{-1}$)</th>
<th>$\Delta t$(us)</th>
<th>$A_{tot}$($s^{-1}$)</th>
<th>$\sigma$($10^{-20}$cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr$^{3+}$ - H$_3$</td>
<td>488</td>
<td>10</td>
<td>13711</td>
<td>44.07</td>
<td>32691</td>
<td>60.43</td>
</tr>
<tr>
<td>Nd$^{3+}$ - T$_{1g}$</td>
<td>1368</td>
<td>22</td>
<td>3547</td>
<td>149</td>
<td>6728</td>
<td>33.3</td>
</tr>
<tr>
<td>Sm$^{3+}$ - G$<em>{7/2}$ - H$</em>{5/2}$</td>
<td>612</td>
<td>21</td>
<td>200.94</td>
<td>2.550</td>
<td>392.21</td>
<td>72.17</td>
</tr>
<tr>
<td>Er$^{3+}$ - H$_{7/2}$</td>
<td>466</td>
<td>22</td>
<td>663</td>
<td>48.95</td>
<td>1381</td>
<td>7.54</td>
</tr>
</tbody>
</table>

Table 6.1 C
Summary of the data on various radiative properties of different rare-earth ions doped Li$_2$O-WO$_3$-B$_2$O$_3$ glasses

<table>
<thead>
<tr>
<th>Glass &amp; Emission Transition</th>
<th>$\lambda$(nm)</th>
<th>$\Delta\lambda$(nm)</th>
<th>$A$($s^{-1}$)</th>
<th>$\Delta t$(us)</th>
<th>$A_{tot}$($s^{-1}$)</th>
<th>$\sigma$($10^{-20}$cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr$^{3+}$ - H$_3$</td>
<td>488</td>
<td>10</td>
<td>13711</td>
<td>44.07</td>
<td>32691</td>
<td>60.43</td>
</tr>
<tr>
<td>Nd$^{3+}$ - T$_{1g}$</td>
<td>1368</td>
<td>22</td>
<td>3547</td>
<td>149</td>
<td>6728</td>
<td>33.3</td>
</tr>
<tr>
<td>Sm$^{3+}$ - G$<em>{7/2}$ - H$</em>{5/2}$</td>
<td>612</td>
<td>21</td>
<td>200.94</td>
<td>2.550</td>
<td>392.21</td>
<td>72.17</td>
</tr>
<tr>
<td>Er$^{3+}$ - H$_{7/2}$</td>
<td>466</td>
<td>22</td>
<td>663</td>
<td>48.95</td>
<td>1381</td>
<td>7.54</td>
</tr>
</tbody>
</table>

From the analysis of these results, it has been identified that WO$_3$ mixed glass network is more favourable environment for rare earth ions to give more luminescence efficiencies when compared with other two systems.
Summing up the entire work presented in this thesis it is felt that the study of various electrical and spectroscopic properties of Li$_2$O-MoO$_3$-B$_2$O$_3$ glasses doped with vanadium and copper ions, and Li$_2$O-MO (Nb$_2$O$_5$, MoO$_3$ and WO$_3$)-B$_2$O$_3$: Ln$^{3+}$ glasses has yielded some valuable information which will be useful for the practical applications.