Summary and Conclusions

7.1. Summary

Alkali fluoro strontium borate ternary glasses are doped with some 3d transition metal ions (V$_2$O$_5$, Cr$_2$O$_3$, MnO, Fe$_2$O$_3$ respectively) have been prepared. Spectroscopic and dielectric properties of 30 AF-10 SrO-(60-x) B$_2$O$_3$ [A=Na, Li] glasses doped with varying concentrations of V$_2$O$_5$, and 30 LiF-10 SrO-(60-x) B$_2$O$_3$ glasses doped with Cr$_2$O$_3$, MnO, Fe$_2$O$_3$ have been studied along with their physical properties.

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

- 30 AF-10 SrO-(60-x) B$_2$O$_3$:x V$_2$O$_5$ (A=Na, Li)  $(0 \leq x \leq 0.5)$ & $(0 \leq x \leq 1)$
- 30 LiF-10 SrO-(60-x) B$_2$O$_3$:x Cr$_2$O$_3$  $(0 \leq x \leq 0.25)$
- 30 LiF-10 SrO-(60-x) B$_2$O$_3$:x MnO  $(1 \leq x \leq 3)$
- 30 LiF-10 SrO-(60-x) B$_2$O$_3$:x Fe$_2$O$_3$  $(0 \leq x \leq 5)$

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

(a) Optical absorption spectra

(b) ESR spectra

(c) FTIR spectra

(d) Dielectric properties

The samples were characterized by X-Ray diffraction technique.

The following measurements were taken:

1) Dielectric constant ($\varepsilon'$) , loss ($\tan \delta$) and a.c conductivity $\sigma_{ac}$ in the 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 2000 cm⁻¹ at room temperature.

7. 2. Conclusions

The main conclusions drawn from the results of the various studies mentioned earlier (chapter wise) are summarized below:

In Section I of Chap-3 dielectric and spectroscopic studies have been presented to examine the sodium fluoro strontium borate glasses (30 NaF-10 SrO-60B₂O₃) doped with V₂O₅ at different lower concentrations (0 ≤ x ≤ 0.5). From the analysis of the results it has been concluded that as follows:

- The observed decrease in the optical band gap with increase in the concentration of V₂O₅ upto 0.3 mol% is due to the gradual increase in the concentration of VO²⁺ and VO⁺ ions wherever causes the V⁵⁺ ions take part network forming positions with VO₅ structural units where as V⁴⁺ ions may distort (modify) the glass network. Hence high intensity of the absorption band i.e., higher concentration of V⁴⁺ (3d¹) and V³⁺(3d²) ions is the reason for low value of optical band gap of V₃ glass sample.

- In the ESR spectra of the present glass matrices an increase in the intensity of signal up to 0.3 mol% can be attributed to the predominant presence of V⁴⁺ and V³⁺ ions that take modifier positions in the glass network. Above >0.3 mol% concentration of V₂O₅ some of these ions get converted into V⁵⁺ state that take network forming positions.
• With increase in the concentration of $V_2O_5$ in NaF-SrO-$B_2O_3$ glass network from 0.1 to 0.3 mol%, intensity of the bands due to the tetrahedral $BO_4$ units is found to decrease with a shift of the meta-center towards slightly higher wave number due to the modifying action of $VO^{2+}$ ions. Above 0.3 mol % the intensity of the bands due to $BO_4$ units is observed to increase.

• The dielectric parameters viz., $\varepsilon'$, $\tan \delta$ and $\sigma_{a.c}$ are found to increase at any frequency and temperature, while the activation energy for dipoles and that for conduction are found to decrease with the increasing content of $V_2O_5$ from 0.1 to 0.3 mol% in the 30NaF-10SrO-(60-x)$B_2O_3$ glasses. The decrease in the intensity of relaxation beyond 0.3 mol% shows an increase in the concentration of vanadyl ions in $V^{5+}$ states that take network-forming positions. The conductivity is increased with increasing concentration of $V_2O_5$ up to 0.3 mol% and beyond this concentration the conductivity is observed to decrease gradually.

In Section II of Chap-3 dielectric and spectroscopic studies have been reported to examine the lithium fluoro strontium borate glasses (30 LiF-10 SrO-60$B_2O_3$) doped with $V_2O_5$ at different lower concentrations ($0 \leq x \leq 1$). From the analysis of the results the following conclusions are drawn.

• From optical absorption spectra the observed decrease in the optical band gap energy with increase in the concentration of $V_2O_5$ upto 0.8 mol% is due to the gradual increase in the concentration of $VO^{2+}$ and $VO^+$ ions, which in turn causes the $V^{5+}$ ions take part network forming positions with VO$_5$ structural units where as $V^{4+}$ ions may distort (modify) the glass network. Hence high intensity of the
absorption band is observed due to increase with higher concentration of $V^{4+}$ ($3d^1$) and $V^{3+}(3d^2)$ ions. Due to this reason for low value of optical band gap energy for $V_8$ glass sample is noticed.

- ESR spectra of the present glass matrices an increase in the intensity of signal up to 0.8 mol % can be attributed to the predominant presence of $V^{4+}$ ions that take modifier positions in the glass network. Above >0.8 mol% concentration of $V_2O_5$ some of these ions get converted into $V^{5+}$ state that take network forming positions. The values of $g_{∥}$ and $g_{⊥}$ evaluated from these spectra are found to be in the ranges of 1.948 to 1.950 and 1.969 to 1.970 respectively.

- The analyzed FTIR spectra with increase in the concentration of $V_2O_5$ in LiF-SrO-B$_2$O$_3$ glass network from 0.1 to 0.8 mol%, showed that the intensity of the bands due to the tetrahedral BO$_4$ units is found to decrease with a shift of the meta-center towards slightly higher wave number due to the modifying action of VO$_{2+}$ ions. Above 0.8 mol % the intensity of the bands due to BO$_4$ units is observed to increase.

- The dielectric parameters viz., $\varepsilon'$, tan $\delta$ and $\sigma_{a.c}$ are found to increase at any frequency and temperature, where as the activation energy for dipoles and that for conduction are found to decrease with the increasing content of $V_2O_5$ upto 0.2 to 0.8 mol% in the 30LiF- 10SrO-(60-x)B$_2$O$_3$ glasses. The observed decrease in the relaxation peak intensity intensity beyond 0.8 mol% is due to the increase in the concentration of vanadyl ions in $V^{5+}$ states that take network-forming positions. The conductivity is increased with increasing concentration.
of V₂O₅ up to 0.8 mol% and beyond this concentration the conductivity is observed to decrease gradually.

In Chap-4 present the role of chromium ions on the structure of LiF-SrO-B₂O₃ glass system by means of spectroscopic and dielectric studies is discussed and the main conclusions drawn from it are given below:

- By optical absorption spectra the observed bands are characteristic of Cr³⁺ ions in octahedral symmetry. More specifically, for C5 glass sample at lower doping concentration of Cr₂O₃ the bridging oxygens (BO) develop bonds with Cr³⁺ which in turn lead to the gradual breakdown of the glass network. This breakdown seems to account for the decrease in the Eg value, i.e., edge shifts to longer wavelengths.

- The low field portion of the ESR spectrum is attributed to the isolated Cr³⁺ ions and the high field portion mainly attributed to exchange coupled Cr³⁺ ion pairs and are related to strongly distorted sites. More specifically, in the present investigation ESR studies indicate that the concentration of isolated Cr³⁺ ions is found to increase for C5 glass.

- More precisely from FTIR spectra at the concentration 0.05 mol% of Cr₂O₃ (for C5 sample) the increase in line of vibrational bands intensity reaches to maximum due to conversion of BO₄ units into BO₃ units and also function of CrO₆ octahedral units in the glass matrices. It causes the decrease in optical band gap, increase in Urbach energy and EPR signal intensity by forming non bridging oxygen in the C5 glass matrix.
With the introduction of Cr$_2$O$_3$ (0.05 mol%), we observed a large increase in the dielectric parameters, the values of $\varepsilon'$, tan$\delta$ and $\sigma_{ac}$ (ac conductivity) are found to increase at any frequency with raise in temperature, and the values of breakdown strength and activation energy for ac conduction are observed to decrease for the glass C5 when compared to that glasses C10-C25. Such behaviour has been attributed to the decrease in the magnitude of space charge polarization, possibly due to the presence of a part of chromium ions in Cr$^{6+}$ state that participate in the network forming with CrO$_4$ structural units. At this particular concentration chromium ions mostly exist in Cr$^{3+}$ state which act as modifiers (evidenced from ESR and optical absorption measurements); the defects thus produced create easy path ways for the migration of charges that would build up space charge polarization and lead to an increase in the dielectric parameters as observed.

**Chap-5** narrates the influence of manganese ions on spectroscopic and dielectric properties of LiF-SrO-B$_2$O$_3$ glasses. The main conclusions drawn from these study are given below:

- In the present glass system, the red shift of the absorption edge or cutoff wavelength and the decrease of optical band gap energy $E_g$ with doping of MnO is due to formation of octahedral Mn$^{2+}$ and Mn$^{3+}$ ions which in turn causes the increase in non-bridging oxygen (NBO) atoms and decrease of optical band gap along with an increase in Urbach energies.

- The intensity of the observed sharpline in the hyperfine splitting of MnO doped glasses is found to decrease with an increase in the concentration of MnO and is
due to the increase of Mn$^{3+}$ species which occupy the octahedral symmetry in the glass network. It is also supported by the observed pronounced absorption band due to single spin allowed transition $^{5}E_{g} \rightarrow ^{5}T_{2g}$ of Mn$^{3+}$ ions from the optical absorption spectra of the glasses.

- Interestingly, from FTIR spectra, with increasing in the concentration of MnO, the intensity of the bands at around 1383 cm$^{-1}$ is increased at the expense of the band at 982 cm$^{-1}$ is due to conversion of BO$_4$ units into BO$_3$ units. However, with the doping of MnO two new feeble bands at 542 and 469 cm$^{-1}$ are noticed and their intensity is found to increase with increase in the concentration of MnO due to specific vibrations of Mn-O bonds of different lengths in MnO$_6$ octahedra. It causes the decrease in optical band gap, increase in Urbach energy and EPR signal intensity by forming non bridging oxygens in the glass matrix.

- In the dielectric properties of LiF-SrO-B$_2$O$_3$: MnO glasses, we observed a large increase of the dielectric parameters with increase in the concentration of MnO. The values of breakdown strength and activation energy for ac conduction are observed to decrease with increase in concentration of MnO. The defects which are produced create easy path ways for the migration of charges that would build up space charge polarization and lead to an increase in the dielectric parameters as observed. The shifting of relaxation region towards lower temperatures and decrease in the activation energy for the dipoles with the addition of MnO, suggests an increase in the degree of freedom for dipoles to orient in the field direction in the glass network.
In *Chap-6* the influence of iron ions on spectroscopic and dielectric properties of LiF-SrO-B$_2$O$_3$ glasses is discussed and the main conclusions drawn from these investigations are given below:

- With increase in the concentration of Fe$_2$O$_3$ up to 3 mol%, the intensity of bands due to Fe$^{3+}$ ions is observed to increase; with further addition beyond 3 mol%, a gradual decrease in the intensity of the band is found with a redshift of the band position to 450 nm. Moreover, the band is disappeared at higher concentration (5 mol%) of Fe$_2$O$_3$. In the present investigation increase in the intensity of the bands due to Fe$^{3+}$ ions, in the spectra of the glass samples from F1 to F3 indicates that iron ions predominantly exist in trivalent state.

- From ESR spectra, the gradual increase of iron content in the matrix destroys the local ordering of Fe$^{3+}$ ion vicinities, thereby, the structural units as characteristic entities become less represented, and consequently, a decrease in the intensity of the resonance signal at $g\approx 4.2$ is observed. The decay of the intensity of this signal in the spectra of the glasses F4 and F5 clearly suggests the increase in presence of iron ions in the divalent state (Fe$^{2+}$) in these glasses. The redox ratio, therefore, of iron ions (Fe$^{2+}$/Fe$^{3+}$) is increased considerably beyond 3 mol% of Fe$_2$O$_3$.

- The FTIR transmission spectra represents the increase in intensity of such vibrational bands with increase in Fe$_2$O$_3$ concentration suggests the increase of FeO$_6$ octahedra. It causes the decrease in optical band gap energy and increase in Urbach energy by forming non bridging oxygens due to increase of FeO$_6$ octahedral units observed from FTIR studies in the glass matrix.
Dielectric parameters are increased considerably in the concentration of Fe$_2$O$_3$. The values of breakdown strength and activation energy for ac conduction are observed to decrease with increase in concentration of Fe$_2$O$_3$. The defects which are produced create easy path ways for the migration of charges that would build up space charge polarization and lead to an increase in the dielectric parameters as observed. The shifting of relaxation region towards lower temperatures and decrease in the activation energy for the dipoles with the addition of Fe$_2$O$_3$, suggests an increase in the degree of freedom for dipoles to orient in the field direction in the glass network. The redox ratio, therefore, of iron ions (Fe$^{2+}$/Fe$^{3+}$) is increased considerably beyond 3 mol% of Fe$_2$O$_3$. When the concentration of Fe$_2$O$_3$ is raised beyond 3 mol% of Fe$_2$O$_3$, the iron ions are found to existing predominantly in divalent state, such ions occupy octahedral positions and act as modifiers in the glass structure. As a result decrease in the insulating strength of the glass network is observed with increasing concentration of Fe$_2$O$_3$.

Summing up the entire work presented in this thesis, it is felt that the synthesis, characterization and the study of dielectric and spectroscopic properties of LiF-SrO-B$_2$O$_3$ ternary glasses doped with some 3d transition metal ions viz, V$_2$O$_5$, Cr$_2$O$_3$, MnO, Fe$_2$O$_3$ respectively have yielded some valuable information which may be useful for make use of these glasses for practical applications.