PREFACE

The present thesis deals with the studies on “Electrical, dielectric and spectroscopic studies on LiI–AgI–B₂O₃ glasses doped with some transition metal ions”. This work has been carried out in the Department of Physics, Acharya Nagarjuna University – Dr. M.R.A.R Campus, Nuzvid. The thesis contains the methods of preparation, studies on electric and spectroscopic properties of LiI–AgI–B₂O₃ glass systems doped with varying concentration of Fe₂O₃, V₂O₅ and MnO.

Study of electrical properties of solid electrolytes has received wide attention due to their potential applications in solid state ionic devices such as fuel cells, gas sensors, electrochemical capacitors, electro chromic displays, analog devices, cathodes in electro chemical cells, smart windows etc. The conductivity of LiI–AgI mixed glasses especially, has been the subject of extensive investigation in recent years as a quest for new solid electrolytes with super ionic properties [21, 22]. The silver / lithium ions surrounded by iodide ions diffuse very rapidly and are the main contributors of the conductivity in the glasses; on the other hand, the silver ions interlocked with the oxide glass network are almost immobile and contribute poorly to the conductivity. Further, when these glasses are doped with multivalent transition metal ions like Fe, V, Mn mixed electronic and ionic, pure electronic or pure ionic conduction is
expected depending upon the composition of the glass constituents. Electronic conduction in this type of materials is predicted due to polaron hopping between different valent states of transition metal ions, where as the ionic conduction is expected due to the diffusion of Li and Ag ions.

When LiI–AgI glasses are doped with transition metal ions like iron, vanadium and manganese, the electrical conductivity consists of mixed electronic and ionic, pure electronic or pure ionic conduction depending on the composition of the glass constituents. The electronic conduction is described by the polaron hopping between different valence states of these ions, whereas the ionic conduction should be proportional to the concentration and diffusion of Li and Ag ions.

Among various transition metal ions, the iron ions are considered as effective and useful dopant ions in the conducting glass materials owing to the fact that they exist in different valence states with different coordinations simultaneously in the glass network; for example as Fe$^{3+}$ with both tetrahedral and octahedral and as Fe$^{2+}$ with octahedral environment.

Similarly another interesting transition metal ion viz., vanadium for the simple reason that the presence of vanadium ions makes the material to exhibit semiconducting behavior with the electrical conductivity $>10^{-3}$ to $10^{-5}$ (ohm cm)$^{-1}$ due to electron hopping between V$^{4+}$ to V$^{5+}$ ions. V$_2$O$_5$ containing glasses
are being extensively used in memory and switching devices. Presence of such complexes facilitate to accelerate the rate of hopping of electron between $V^{4+}$ and $V^{5+}$ ions which ultimately lead to the enhancement of conductivity. The process of hopping of the electrons between $V^{4+}$ and $V^{5+}$ ions in the presence of larger concentrations of mobile cations like lithium and silver ions is highly interesting and useful to investigate in the ionic conducting glass systems like LiI–AgI–B$_2$O$_3$ in view of their huge technological importance as a potential glassy cathode material in Li-ion rechargeable batteries.

Like wise manganese ions exist in different valence states with different coordinations in glass matrices, for example as Mn$^{3+}$ in borate glasses with octahedral coordination where as in silicate and germinate glasses as Mn$^{2+}$ with both tetrahedral and octahedral environment and are expected to influence the electrical properties of ionic conducting glasses.

The clear objective of the present study is to explore the changes in conduction mechanism that take place with the varied oxidation states of iron, vanadium and manganese ions in the glass network and the role of silver and lithium ions in this process by a systematic study on d.c conductivity and dielectric properties (viz., dielectric constant, loss and a.c conductivity over a wide range of frequency and temperature) coupled with the data on ESR,
optical absorption of LiI–AgI–B\textsubscript{2}O\textsubscript{3} glasses doped with varied concentrations of Fe\textsubscript{2}O\textsubscript{3}, V\textsubscript{2}O\textsubscript{5} and MnO.

The chemical compositions of the samples used for the present study are:

1. (39–x)LiI–1.0AgI–60 B\textsubscript{2}O\textsubscript{3}: x Fe\textsubscript{2}O\textsubscript{3} (0 ≤ x ≤ 2.0)
2. (39–x)LiI–1.0AgI–60 B\textsubscript{2}O\textsubscript{3}: x V\textsubscript{2}O\textsubscript{5} (0 ≤ x ≤ 1.0)
3. (39–x)LiI–1.0AgI–60B\textsubscript{2}O\textsubscript{3}: x MnO (0 ≤ x ≤ 0.8)

The details of the studies are

(i) Dielectric properties viz., dielectric constant \( \varepsilon' \), dielectric loss tan δ and ac conductivity \( \sigma_{ac} \) in the frequency range 0.01 Hz to 1 MHz and in temperature range from 173 to 523 K

(ii) Impedance spectra and evaluation of dc conductivity over a wide temperature range

(iii) Electron spin resonance measurements at room temperature

(iv) Optical absorption studies in the wavelength range 250-1000 nm to identify the valence states of the dopant ions.

For the sake of convenience, the thesis is divided into six chapters.

**CHAPTER–I** presents the General Introduction, Scope, Contents and the Aim of the present work. In this chapter, the basic theory related to electrical and spectroscopic properties of LiI–AgI–B\textsubscript{2}O\textsubscript{3}: Fe\textsubscript{2}O\textsubscript{3}/V\textsubscript{2}O\textsubscript{5}/MnO glasses are presented systematically.
CHAPTER–II gives the description of experimental methods employed in the preparation and characterization of LiI–AgI–B\textsubscript{2}O\textsubscript{3}: Fe\textsubscript{2}O\textsubscript{3}/V\textsubscript{2}O\textsubscript{5}/MnO. The details of the apparatus used and the techniques adopted for characterization and for measuring electrical properties, optical absorption, ESR are described in detail in this chapter.

Amorphous nature of all the samples prepared is confirmed by X-ray diffraction studies. The differential scanning calorimetric (DSC) studies of all the glass samples exhibited endothermic change due to the glass transition followed by exothermic effects due to the crystal growth.

The main objective of CHAPTER-III is to explore the changes in conduction mechanism that take place with the varied oxidation states of iron ions in the glass network and the role of silver and lithium ions in this process by a systematic study on d.c conductivity and dielectric properties (viz., dielectric constant, loss and a.c conductivity over a wide range of frequency and temperature) of LiI–AgI–B\textsubscript{2}O\textsubscript{3} glasses mixed with varied concentrations of Fe\textsubscript{2}O\textsubscript{3} from 0 to 2.0 mol %. Auxiliary experimental data viz., optical absorption and ESR that help to have some pre-assessment over the valence states of iron ions and their environment in the glasswork have also been reported.
For this study, a particular composition (39–x) LiI–1.0 AgI–60 B₂O₃: x Fe₂O₃ with seven values of x ranging from 0 to 2.0 is chosen. The detailed compositions are as follows:

F₀: 39 LiI–1.0 AgI–60 B₂O₃
F₃: 38.7 LiI–1.0 AgI–60 B₂O₃: 0.3 Fe₂O₃
F₆: 38.4 LiI–1.0 AgI–60 B₂O₃: 0.6 Fe₂O₃
F₉: 38.1 LiI–1.0 AgI–60 B₂O₃: 0.9 Fe₂O₃
F₁₂: 37.8 LiI–1.0 AgI–60 B₂O₃: 1.2 Fe₂O₃
F₁₅: 37.5 LiI–1.0 AgI–60 B₂O₃: 1.5 Fe₂O₃
F₂₀: 37.0 LiI–1.0 AgI–60 B₂O₃: 2.0 Fe₂O₃

The optical absorption spectra of Fe₂O₃ doped LiI–AgI–B₂O₃ glasses exhibited three absorption bands at about 776 (6A₁(t₂g⁹e₈g) → a⁴T₁(t₂g⁶e₈g) (O_h₁)), 566 (6A₁(t₂g⁹e₈g) → a⁴T₂(t₂g⁶e₈g) and 528 nm (6A₁(e²t₂g) → a⁴T₁(e³t₂g) identified due to transitions of Fe³⁺ (d⁵) ions; additionally, a band at 976 nm, identified due to ⁵T₂g → ⁵E₉ transition of Fe²⁺ (d⁶) ions. With the gradual increase in the concentration of Fe₂O₃ up to 0.9 mol%, the intensity of bands due to Fe³⁺ ions has been observed to decrease with the shift of meta-centers towards slightly higher energy; further with the increase of the concentration of Fe₂O₃ up to 0.9 mol%, the band due to Fe²⁺ ions is observed to grow at the expense of bands due to Fe³⁺ ions. Such variations indicate that, trivalent iron ions that
participate in the glass network forming, dominate over the divalent ions in the
glasses F\textsubscript{12} and F\textsubscript{15} where as in the glass F\textsubscript{3} to F\textsubscript{9} the concentration of Fe\textsuperscript{3+} ions
is higher.

ESR spectra of LiI–AgI– B\textsubscript{2}O\textsubscript{3}: Fe\textsubscript{2}O\textsubscript{3} glass series recorded at room
temperature exhibited an intense signal centered at about \( g \approx 2.0 \). This signal is
predicted due to the Fe\textsuperscript{3+}–O–Fe\textsuperscript{3+} spin pair. Additionally, a weak signal at about
\( g \approx 4.3 \) identified to the isolated tetrahedral Fe\textsuperscript{3+} ions in the orthorhombic
crystal field, could be detected in the spectra of all the glasses. The variation of
intensity and the half width of this signal with the concentration of Fe\textsubscript{2}O\textsubscript{3}
exhibited a downward kink at \( x = 0.9 \) mol\%. Change in the Fe\textsuperscript{3+}/Fe\textsubscript{tot} ratio
seems to be one of the reasons for the variations in the line–shape.

D.C conductivity of Fe\textsubscript{2}O\textsubscript{3} doped LiI–AgI–B\textsubscript{2}O\textsubscript{3} glasses is increased up
to 0.9 mol\% of Fe\textsubscript{2}O\textsubscript{3} and beyond that the conductivity is found to decrease. The
analysis of the d.c. conductivity results indicated that there is a mixed
conduction (both ionic and electronic) and the ionic conduction seems to
prevail over polaron hopping in the glasses containing Fe\textsubscript{2}O\textsubscript{3} more than 0.9
mol\%. The quantitative analysis of the dc conductivity of all the three series of
glasses indicated that the hopping is adiabatic and the conduction is mainly
controlled by the activation energy only.
The variation of dielectric constant $\varepsilon'$ of the glasses containing different concentrations of Fe$_2$O$_3$ indicated that the highest value is for the glass doped with 0.9 mol% of Fe$_2$O$_3$. The variation of tan $\delta$ with temperature of these glasses have exhibited dielectric relaxation character; these effects are attributed to Fe$^{3+}$ complexes. The activation energy for the dipoles is found to be minimum for the glass F$_9$.

A.C conductivity in the high temperature region is observed to be progressively increasing with the content of Fe$_2$O$_3$ (up to 0.9 mol %). This is attributed to the predominant presence of iron ions in divalent state. At the larger concentrations of Fe$_2$O$_3$ (> 0.9 mol %) the conductivity is found to decrease. This has been attributed to the larger presence of iron ions in Fe$^{3+}$ state that participate in the glass network with tetrahedral structural units.

The purpose of the CHAPTER IV is to study the electrical conductivity and dielectric properties over a wide frequency range from 0.01 Hz to 1 MHz and in temperature range from 173 to 523 K for Li–AgI–B$_2$O$_3$ glasses doped with various concentration of V$_2$O$_5$ (0 to 1.0 mol %). Auxiliary experimental data on optical absorption, ESR, that help to have some pre-assessment over the valence states of vanadium ions and their environment in the glass network have also been included.
The detailed compositions are as follows:

\[ V_0: 39 \text{LiI–}1.0 \text{AgI–}60 \text{B}_2\text{O}_3 \]

\[ V_2: 38.8 \text{LiI–}1.0 \text{AgI–}60 \text{B}_2\text{O}_3: 0.2 \text{V}_2\text{O}_5 \]

\[ V_4: 38.6 \text{LiI–}1.0 \text{AgI–}60 \text{B}_2\text{O}_3: 0.4 \text{V}_2\text{O}_5 \]

\[ V_6: 38.4 \text{LiI–}1.0 \text{AgI–}60 \text{B}_2\text{O}_3: 0.6 \text{V}_2\text{O}_5 \]

\[ V_8: 38.2 \text{LiI–}1.0 \text{AgI–}60 \text{B}_2\text{O}_3: 0.8 \text{V}_2\text{O}_5 \]

\[ V_{10}: 38.0 \text{LiI–}1.0 \text{AgI–}60 \text{B}_2\text{O}_3: 1.0 \text{V}_2\text{O}_5 \]

Optical absorption spectra of \( \text{V}_2\text{O}_5 \) doped \( \text{LiI–AgI–B}_2\text{O}_3 \) glasses exhibited two absorption bands at 651 (\( ^2\text{B}_2\rightarrow ^2\text{B}_1 \)) and 1070 nm (\( ^2\text{B}_2\rightarrow ^2\text{E}_1 \)). With the gradual increase in the concentration of \( \text{V}_2\text{O}_5 \) up to 0.8 mol% in the glass matrix, the intensity of these bands is observed to increase with the shift of meta-centers towards slightly higher wavelength. This observation clearly indicates an increase in the rate of reduction of \( \text{V}^{5+} \) ions to \( \text{V}^{4+} \) ions in these glasses.

The ESR spectra of \( \text{LiI–AgI–B}_2\text{O}_3: \text{V}_2\text{O}_5 \) glasses recorded at room temperature are observed to be complex made up of resolved hyperfine components arising from unpaired 3d\(^1\) electron of \(^{51}\text{V} \) isotope. The values of \( g_\parallel \) and \( g_\perp \) evaluated from these spectra are found to be in the ranges of 1.910 to 1.919 and 1.943 to 1.952 respectively. As the concentration of dopant \( \text{V}_2\text{O}_5 \) is increased (up to 0.8 mol%), an increasing degree of resolution and the intensity
of the signal have been observed. Such variations have been attributed to the variation in the concentration of V$^{4+}$ ions and also due to structural and microstructural modifications, which produce fluctuations of the degree of distortion or even of the coordination geometry of V$^{4+}$ sites.

D.C. conductivity as a function of the V$_2$O$_5$ concentration exhibited the maximal effects at x = 0.8 mol%. The analysis of the conductivity results of V$_2$O$_5$ mixed glasses indicated that there is a mixed ionic and electronic conduction where the ionic conduction seems to prevail over polaron hopping in the glasses containing V$_2$O$_5$ more than 0.8 mol%.

The dielectric studies of these glasses indicated that with the gradual increase of dopant V$_2$O$_5$ (up to 0.8 mol%), the values of $\varepsilon'$, tan $\delta$ and $\sigma_{ac}$ are found to increase at any frequency and temperature and the activation energy for ac conduction is observed to decrease; this observation indicates an increase in the space charge polarization owing to the enhanced degree of disorder in the glass network. The value of the effective activation energy associated with the dipoles is observed to decrease with increase in the content of vanadyl ions in the glass ceramic network; from this observation it is concluded that there is an increasing freedom for dipoles to orient in the field direction due to increasing degree of disorder in glass ceramic network. When the concentrations of V$_2$O$_5$ is > 0.8 mol%, the ac conductivity is found to decrease. This has been attributed
to the larger presence of vanadium ions in $V^{5+}$ state that participate in the glass network with tetrahedral structural units.

Further, the relaxation effects exhibited by these glasses have been analysed quantitatively by graphical methods and the spreading of relaxation time has been established for all the three series of glasses. Such spreading is attributed to the coupling of individual relaxation processes, one site needing to relax before the other can do so.

In **CHAPTER V**, we have reported the results of the extensive investigations on electrical conductivity and dielectric properties over a wide frequency range from 0.01 Hz to 1 MHz and in temperature range from 173 to 523 K for LiI–AgI–B$_2$O$_3$ glasses doped with different concentration of MnO. The studies were also extended to spectroscopic properties viz., optical absorption, ESR and photoluminescence spectra so as to have some pre-assessment over the valance states of manganese ions and their coordination in the glass network; such information will facilitate the analysis of the results of electrical properties quantitatively.

In this study, a particular composition $(39-x)$LiI–$1.0$AgI–$60$B$_2$O$_3$: $x$MnO with $x$ ranging from 0 to 0.8 ( in mol%) is chosen. The detailed compositions are as follows:
Mn₀: 39 LiI–1.0 AgI–60 B₂O₃
Mn₁: 38.9 LiI–1.0 AgI–60 B₂O₃: 0.1 MnO
Mn₂: 38.8 LiI–1.0 AgI–60 B₂O₃: 0.2 MnO
Mn₃: 38.6 LiI–1.0 AgI–60 B₂O₃: 0.4 MnO
Mn₄: 38.4 LiI–1.0 AgI–60 B₂O₃: 0.6 MnO
Mn₅: 38.2 LiI–1.0 AgI–60 B₂O₃: 0.8 MnO

Optical absorption spectra of MnO doped LiI–AgI–B₂O₃ glasses exhibited an intense absorption band at 523 nm corresponding to \( ^6A_{1g}(S) \rightarrow ^4T_{1g}(G) \) octahedral transition of \( Mn^{2+} \) ions; the spectrum also exhibited a weak kink at about 418 nm due to \( ^6A_1(S) \rightarrow ^4T_2(G) \) tetrahedral transition of \( Mn^{2+} \) ions. Additionally a weak absorption band with a peak at about 498 nm due to \( ^5E_g \rightarrow ^5T_{2g} \) octahedral transition of \( Mn^{3+} \) ions is also observed in the spectrum of this glass. With increase in the concentration of MnO up to 0.8 mol %, the tetrahedral band is observed to grow gradually at the expense of the octahedral band with minor red shift.

ESR spectra of LiI–AgI–B₂O₃: MnO glasses are characterized by six-line hyperfine structure centered at \( g \sim 2.005 \). This signal is attributed 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 \( \pm \frac{1}{2} \). The spectra also exhibited another signal at \( g \sim 4.3 \) due to magnetically isolated
Mn$^{2+}$ ions in tetragonally (and or rhombically) distorted octahedral sites of symmetry subjected to strong crystal field effects and arises from transitions between the energy levels of the middle Kramers doublet $|\pm \frac{3}{2}\rangle$. The intensity of the resonance signal at $g \sim 2.005$ decreases with increase in the concentration of MnO. This is attributed either due to the decreasing presence of Mn$^{2+}$ ions in octahedral distorted positions or due to increasing presence of trivalent manganese ions.

D.C conductivity is found to decrease with increase in the concentration of MnO. The decreasing trend of conductivity is understood due to the gradual increase in the concentration of tetrahedrally positioned manganese ions in the glass network. Further, the quantitative analysis of the dc conductivity of these glasses indicated that the hopping is adiabatic and the conduction is mainly controlled by the activation energy only.

The dielectric constant is observed to decrease continuously with the concentration of MnO. The variation of dielectric constant with temperature for these samples exhibited considerable increase especially at lower frequencies. This variation has been analysed in terms of various polarization mechanisms and the space charge polarization is found to be responsible for increase of $\varepsilon'$ with temperature. The space charge polarization is attributed mainly to Mn$^{2+}$ ions that act as modifiers in the glass network.
A.C conductivity has been found to decrease whereas the activation energy for conduction, found to increase gradually with the increase in the content of manganese ions in the glass network. Such decrease is attributed to the increasing proportions in the concentration of tetrahedral Mn\(^{2+}\) ions that take part network forming positions by cross linking with BO\(_4\) structural units. The low temperature part of conductivity is analyzed quantitatively based on quantum mechanical tunneling model.

References closely related to the present work have been compiled to the extent possible and given at the end of the relevant chapter.