LiI–AgI–B$_2$O$_3$ glasses mixed with different concentrations of V$_2$O$_5$ (ranging from 0 to 1.0 mol %) were prepared. Electrical and dielectric properties over wide ranges of frequency ($10^2$ – $10^7$ Hz) and temperature (173- 523 K) have been studied. Additionally spectroscopic properties viz., optical absorption and ESR spectra have also been investigated. The optical absorption and ESR studies have revealed that vanadium ions do exist in both V$^{4+}$ and V$^{5+}$ states and the redox ratio is the highest in the glasses containing 0.8 mol% of V$_2$O$_5$. The results of conductivity measurements have indicated that there is a mixed conduction (both ionic and electronic). The ionic conduction seems to be dominant over polaron hopping only in the glasses containing V$_2$O$_5$ more than 0.8 mol% of V$_2$O$_5$. The impedance spectra have also indicated that the conduction is predominantly polaronic in nature. The frequency and temperature dependence of the electrical moduli as well as dielectric loss parameters have exhibited relaxation character attributed to the vanadyl complexes. The relaxation effects have been analyzed by the graphical method and from this analysis it has been established that there is a spreading of relaxation times. The results have been further discussed quantitatively in the light of different valence states of vanadium ions with the aid of the data on spectroscopic properties.
The role of vanadium valence states and coordination on electrical conduction in lithium iodide borate glasses mixed with small concentration of silver iodide

4.1 Introduction

The study on electrical conductivity of super ionic glasses like LiI, AgI has been the subject of the extensive investigation in the recent years due to their potential applications in solid state batteries [1-4] as mentioned earlier. When these glasses are doped with transition metal ions like vanadium, the electrical conductivity consists of mixed electronic and ionic, pure electronic or pure ionic conduction depending on the composition of the glass constituents [5]. The electronic conduction is described by the polaron hopping between different valence states of vanadium ions, whereas the ionic conduction should be proportional to the concentration and diffusion of Li and Ag ions [6]. Among various transition metal ions, the vanadium ions are considered as effective and useful dopant ions owing to the fact that they exist not only in different valence states but also in different coordinations (viz., \(\text{VO}_4\), \(\text{VO}_5\)) simultaneously in the glass networks [7]. Further, \(\text{V}_2\text{O}_5\) containing glasses are being extensively used in the memory and switching devices [8].

Presence of vanadium ions in two valence states viz., \(\text{V}^{4+}\) and \(\text{V}^{5+}\) facilitate the rate of electron hopping between ions which ultimately lead to the enhancement of electronic conductivity. The process of electron hopping
between $V^{4+}$ and $V^{5+}$ ions in the presence of high concentration of mobile cations like lithium and silver is highly interesting and useful for investigation in view of the technological importance as a potential glassy cathode material in Li-ion rechargeable batteries.

Although a considerable number of recent studies on AgI, LiI mixed borate, phosphate and silicate glasses are available in the literature [9-12], there is still a lot of scope to investigate in detail the electrical and dielectric properties of $V_2O_5$ doped AgI–LiI–$B_2O_3$ glasses. The main objective of this investigation is to explore the changes in conduction mechanism that takes place by electron hopping from low to high valence state of vanadium ions and the role of silver and lithium ions in this process. The purpose of the present work 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 LiI–AgI–$B_2O_3$ glasses doped with various concentration of $V_2O_5$ (0 to 1.0 mol %). The understanding of the charge carriers transport phenomenon in mixed ion-electron conducting glasses is a challenging and unsolved task because of the complexity of structure. 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.
For the present study, a particular composition (39–x) LiI–1.0AgI–60B₂O₃: x V₂O₅ with x ranging from 0 to 1.0 (in mol%) is chosen. The detailed compositions are as follows:

V₀: 39 LiI–1.0 AgI–60 B₂O₃
V₂: 38.8 LiI–1.0 AgI–60 B₂O₃: 0.2 V₂O₅
V₄: 38.6 LiI–1.0 AgI–60 B₂O₃: 0.4 V₂O₅
V₆: 38.4 LiI–1.0 AgI–60 B₂O₃: 0.6 V₂O₅
V₈: 38.2 LiI–1.0 AgI–60 B₂O₃: 0.8 V₂O₅
V₁₀: 38.0 LiI–1.0 AgI–60 B₂O₃: 1.0 V₂O₅

4.2 Brief Review of the recent work on V₂O₅ glass systems

The studies as such on vanadium containing LiI-AgI-B₂O₃ glasses are limited. However in this review, the studies on different glass systems containing vanadium ions, has been described briefly.

Agarwal et al [13] have recently reported the electron paramagnetic resonance studies of vanadyl doped alkali niobium borate glasses. In this study it was observed that the tetragonality of V⁴⁺O₆ complex decreases with increasing concentration of Nb₂O₅. Lin-Hua et al [14] have recently reported electron paramagnetic resonance spectra of vanadyl doped zinc phosphate glass. In this study the compressed defect structure of V⁴⁺ center is discussed in detail. Kerkouri et al [15] have reported spectroscopic studies and the structural
aspects of $V_2O_5$-CdO-P$_2$O$_5$ glasses. In their study it was reported that the glasses containing more than 20% of $V_2O_5$, the VO$_4$ and VO$_5$ structural units with $V-O-V$ bridges were formed in the glass network. Gouda et al [16] have investigated the effect of replacing vanadium by Cu$^{2+}$ ion on the dc-electrical conductivity ($\sigma$) and I–V characteristics of $(V_2O_5)_{0.7}(GeO_2)_{0.3}(CuO)_x$ glasses. In this report the electrical conduction is interpreted on the basis of electrons hopping from reduced to unreduced vanadium and/or copper ions. Behzad et al [17] have studied the conductivity of $50P_2O_5-xV_2O_5-(50-x)Li_2O$ glass system as a function of temperature and composition. Isothermal variation of conductivity as a function of composition of this study showed a minimum for a molar ratio $x$ near 20. Probable mechanisms for decrease of conductivity with decrease of vanadium oxide concentration were explained in detail. Ali and Ezz-Eldin [18] have studied some physical properties of the lithium disilicate ($Li_2Si_2O_5$) glasses doped with different ratios of $V_2O_5$ before and after gamma-rays irradiation. The observed variations in the physical properties with the change in the concentration of $V_2O_5$ were correlated with the changes in internal glass network. Abd El-Aal and Afifi [19] have reported the elastic properties of vanadium tellurite glasses, $65TeO_2-(35-x)V_2O_5-xCuO$, with different compositions of copper at room temperature by ultrasonic methods. Khattak et al [20] have studied X-ray photoelectron spectroscopy (XPS) and
magnetic susceptibility studies of vanadium phosphate glasses. From the analysis of the results of these studies, the authors have proposed a glass structure model consisting of a mixture of vanadate phosphate phases that include \( \text{V}_2\text{O}_5 \), \( \text{VOPO}_4 \), \( (\text{VO})_2\text{P}_2\text{O}_7 \), \( \text{VO(PO}_3) \), and \( \text{V(PO}_3) \) with the abundance of orthophosphate \( (\text{PO}_4)^{3-} \) units increasing with increasing vanadium content. In another report [21] these authors have also reported the results of X-ray photoelectron spectroscopy (XPS) of vanadium tellurite glasses. Quantitative analysis of the results of these studies has indicated that there is a change of \( \text{TeO}_4 \) tp to \( \text{TeO}_3 \) tp upon \( \text{V}_2\text{O}_5 \) addition.

Bogomolova et al [22] have reported electron paramagnetic resonance studies of \( \text{V}^{4+} \) ions in lanthanum-aluminosilicate glasses. From the detailed analysis of EPR spectra it was concluded that in the samples containing low content of \( \text{La}_2\text{O}_3 \) lanthanum acts predominately as modifying ion where as in glass with a high \( \text{La}_2\text{O}_3 \) concentration lanthanum gradually occupies a glass forming site in the network. Saddeek [23] has recently reported FTIR and elastic properties by ultrasonic methods on \( \text{MoO}_3-\text{V}_2\text{O}_5-\text{PbO} \) glasses. The observed compositional dependence of the elastic moduli was interpreted in terms of the effect of \( \text{MoO}_3 \) on the coordination number of the vanadate units. A good correlation was observed between the experimentally determined elastic moduli and those computed according to the Makishima-Mackenzie model.
Feng [24] has reported detailed theoretical studies of the optical and EPR spectra for vanadyl ions in alkaline-earth aluminoborate glasses. In this study the Optical spectra and electron paramagnetic resonance (EPR), g and A factors of calcium aluminoborate glasses (CaAB): VO$^{2+}$ are calculated using a complete diagonalization (of the energy matrix) process. Good agreement between the theoretical values and experimental results attributed effectiveness of the CDP method for theoretical studies of optical and EPR spectra of 3d$^1$ (or V$^{4+}$) ions in glasses. Shapaan et al [25] have investigated hyperfine structure and electric transport properties of vanadium iron phosphate glasses and interpreted the results with the aid of the data on Mössbauer spectroscopy. Increase of V$_2$O$_5$ content, resulted the increase in dc conductivity while the activation energy was found to decrease. The observed increase of dielectric constant $\varepsilon'(\omega)$ with increasing V$_2$O$_5$ content was attributed to the increase in the deformation of glass network. Kartashov and Vysloukh [26] have investigated the propagation of laser beams in SiO$^2$VO$_2$ nanocomposite waveguides with thermo-optical nonlinearity. These studies have indicated that the large modifications of the absorption coefficient as well as notable changes of the refractive index of VO$_2$ nanoparticles embedded into the SiO$_2$ host media that accompany the semiconductor-to-metal phase transition. At the end they have
concluded that such changes may lead to optical limiting in the near-IR wave range.

Sung et al [27] have investigated a variety of thermal properties of P2O5–V2O5–ZnO/B2O3 glasses that include glass transition temperature, dilatometer softening point, coefficient of thermal expansion and aqueous durability. From these studies it was observed that the aqueous durability was improved through the addition of some additives such as Al2O3 and TiO2. ElBatal et al [28] have prepared V2O5-doped sodium phosphate glasses of various compositions and studied various spectroscopic properties that include UV-vis and infrared, Raman and electron spin resonance. In this study the changes observed in UV-vis and infrared spectral data were discussed in relation to the structural evolution caused by the change in the V2O5 content or glass composition. Kim et al [29] have investigated the local structures of the boron and vanadium sites in the ternary xV2O5–B2O3–yNa2O glass by means of magic angle spinning (MAS) nuclear magnetic resonance (NMR) techniques. In this study it was observed that with increasing x, the mol. ratios of the BO3 and BO4 structures were enhanced, as were the quadrupole asymmetry parameters for the BO3 structures, while the quadrupole coupling constants for the sites were reduced. Moawad et al [30] have investigated dc conductivity the mixed electronic-ionic conduction in 0.5[xAg2O–(1–x)V2O5]–0.5TeO2 glasses. In this study it was
observed that the mechanism of dc conductivity changes from predominantly electronic to ionic within the $30 \leq \text{Ag}_2\text{O} \leq 40$ range. Taibi et al [31] have investigated the influence of the $\text{V}_2\text{O}_5/\text{Sb}_2\text{O}_3$ substitution on the physical properties of the $(70-x)\text{Sb}_2\text{O}_3-x\text{V}_2\text{O}_5-30\text{K}_2\text{O}$ glasses. From these studies the authors have suggested that there is a change in the coordination number of the vanadium cations in relation to the network topology. Farah [32] has studied the relationship between glass composition and optical basicity by redox analysis of vanadium in Na$_2$O and CaO based Al$_2$O$_3$–SiO$_2$ glasses/melts. In this study it was found that the $V^{4+}/V^{5+}$ equilibrium was more affected by a change in the calculated optical basicity compared with that of the $V^{3+}/V^{4+}$ in both sodium and calcium silicate series. However, Alumina saturation from the crucible did not affect the calculated optical basicity of the sodium silicate glasses, although there was a change in the corresponding redox ratios. The results were compared using different experimental parameters and were found to be useful in glass production and extractive metallurgy of vanadium.

Vedeanu et al [33] have investigated structural changes induced by CuO and V$_2$O$_5$ in the phosphate glass network by means of Raman spectroscopy. In this study it was observed that at higher concentrations of V$_2$O$_5$ a strong depolymerization of the phosphate network was taking place. Kumar et al [34] have reported thermal and electrical properties of tellurium-based glasses doped
with vanadium and vanadium-cobalt oxides. From the thermal properties the authors have estimated that the thermal stability, fragility and glass-forming tendency of the glass system. The results of dc conductivity have been analyzed in the light of Mott's small polaron hopping (SPH) and Mott's and Greave's variable range hopping (VRH) models. Kundu et al [35] have investigated effect of V₂O₅ on structural, physical and electrical properties of bismuth borate glasses. In this study the dc conduction was found to increase with increase in vanadium content and the mechanism was explained in terms of polaron hopping. Rao et al [36] have reported dielectric dispersion in Li₂O–MoO₃–B₂O₃ glass system doped with V₂O₅. The observed dielectric relaxation effect was analyzed quantitatively by pseudo Cole-Cole plot method and the spreading of relaxation times was established. Li et al [37] have studied the effect of lanthanum on structure of vanadate-phosphate glass by means of Fourier infrared spectroscopy, Raman spectroscopy and nuclear magnetic resonance. The analysis of these results have indicated that vanadium existed in the glass in the form of (VO₃)ₙ single chains, (V₂O₈)ₙ zigzag chains, VO₄ branches and groups. Rada et al [38] have investigated the effect of the introduction of vanadium pentoxide on structural changes in phospho-tellurite glasses containing gadoloniunm ions. In these studies it was found that the addition of V₂O₅ resulted in gradual depolymerization of the phosphate chains and
formation of short phosphate units in the glass network. Ardelean et al [39] reported the EPR study of V$_2$O$_5$–P$_2$O$_5$–Li$_2$O glass system. In this study it was found that at high V$_2$O$_5$ content, the vanadium hyperfine structure disappears and only the broad line could be observed in the spectra. Spin Hamiltonian parameters $g_{||}$, $g_{\perp}$, $A_{||}$, $A_{\perp}$, dipolar hyperfine coupling parameters, $P$, and Fermi contact interaction parameters, $K$, have been calculated. The composition dependence of line widths of the first two absorptions from the parallel band and of the broad line characteristic to the cluster formations was also discussed in detail.

Al-Assiri [40] has studied electrical properties of vanadium-copper-phosphate glasses. In this study the dc conductivity was found to increase while the activation energy is found to decrease with the increase of the V$_2$O$_5$ content. Further, it was reported that the dc conductivity in these glasses is electronic in nature and depends strongly upon the average distance, $R$, between the vanadium ions. Tian et al [41] have investigated the effect of V$_2$O$_5$ content on the phase-transformation and the microstructural development in the SiO$_2$–MgO–Al$_2$O$_3$–K$_2$O–V$_2$O$_5$–F glass by XRD, SEM and EPMA measurements. In this study it was found that the incorporation of V$_2$O$_5$ leads to the precipitation of mullite (Al$_6$Si$_2$O$_{13}$) crystalline phases at lower temperatures. Further, it was reported that although the types of crystalline phases, which are formed as
mullite and mica, were less influenced by $V_2O_5$ contents, the morphology, volume fraction and sizes of crystals were dependent sensitively on the $V_2O_5$ content. Hager [42] has reported the region of glass formation of ternary $V_2O_5$–BaF$_2$–RF (RF=LiF, NaF and mixed NaF–LiF) and has also measured a variety of physical parameters that include density, molar volume, characteristic temperatures, average thermal expansion coefficient, $\alpha$, and specific heat, $C_p$. In this study it was observed that the glass-transition temperature, $T_g$, decreased by increase of RF while thermal expansion, $\alpha$, and specific heat, $C_p$, near $T_g$ were increased. Jung et al [43] have carried out NMR investigations on PbO–B$_2$O$_3$ glasses containing $V_2O_5$ and they have calculated the ratio of BO$_4$ and BO$_3$ units as a function of $V_2O_5$ concentration. Mekki et al [44] have investigated the magnetic properties of vanadium-sodium silicate glasses. Ferrari et al [45] have probed the effect of $V_2O_5$ on the crystallization of CaO–ZrO$_2$–SiO$_2$ glasses. Abd El-Moneim [46] has carried out DTA and IR spectra of vanadium tellurite glasses. Hoppe et al [47] have reported the details on structure of vanadium tellurite glasses by using neutron and X–ray diffraction. Cozar et al [48] have studied the IR and EPR studies on some lithium borate glasses with vanadium ions. Salim et al [49] have carried out X–ray photoelectron spectroscopy and magnetization studies of iron–vanadium phosphate glasses. Khattak et al [50] have studied X–ray photoelectron spectroscopy (XPS) and magnetic properties
of copper-vanadium phosphate glasses. Krasowski et al [51] have measured electrical conductivity of silver vandate glasses. Maria-Camelja et al [52] have investigated the ionic and electronic conductivity of P$_2$O$_5$–V$_2$O$_5$–Na$_2$O glasses.

Sudarsan et al [53] have carried out a study on the structural aspects of V$_2$O$_5$–P$_2$O$_5$–B$_2$O$_3$ glasses by using MAS NMR and IR spectral studies. Sega et al [54] have studied the electrical conduction in V$_2$O$_5$–NiO–TeO$_2$ glasses. Mori et al [55] have discussed the conduction phenomenon in V$_2$O$_5$–Sb–TeO$_2$ glasses on the basis of small polaron hopping model. Rajendran et al [56] have carried out ultrasonic investigations in V$_2$O$_5$–PbO glasses containing BaTiO$_3$. Simockova et al [57] have investigated complex impedance response of V$_2$O$_5$–P$_2$O$_5$ glasses. Takahashi et al [58] have investigated the structure of AgI–Ag$_2$O–V$_2$O$_5$ glasses. Moustafa et al [59] have reported the spectroscopic studies of semiconducting barium vandate glasses doped with iron oxide. Attos et al [60] have investigated the structure of borovanadate glasses by Raman spectroscopy. Murawski et al [61] has investigated the dielectric relaxation in semiconducting glasses. Seth et al [62] have studied the EPR study of vanadyl ion in CoO–PbO–B$_2$O$_3$ glasses. Prakash et al [63] have carried out the EPR study of vanadyl ion in CoO-PbO-B$_2$O$_3$ glasses. Amano et al [64] have studied the electrical properties of Sb$_2$O$_3$–CaO–V$_2$O$_5$ glasses and glass ceramics. Bogomolova et al [65] have investigated the role of V$_2$O$_5$ on the structure of fluoro germinate
glasses using ESR measurements. Yoko et al [66] have studied the IR and NMR spectral studies on lead vanadate glasses. Ghosh et al [67] have reported the spectral studies of binary iron vanadate glasses. Gupta et al [68] reported the influence of $V^{4+}$ ion concentration on the EPR spectra of vanadate glasses. Adams et al [69] have studied the silver ion conductivity during the crystallization of AgI–Ag$_2$O–V$_2$O$_5$ glasses. Dimitrov et al [70] have analyzed V$_2$O$_5$–GeO$_2$–Bi$_2$O$_3$ glass structure by IR spectra.

4.3 Results

4.3.1 DSC analysis

Fig. 4.1 represents differential scanning calorimetric (DSC) curves of LiI–AgI– B$_2$O$_3$: V$_2$O$_5$ glasses. DSC traces indicate an inflection due to the glass transition temperature $T_g$ in the region from 593 to 608 K followed by a well defined exothermic effect due to the crystallization temperature ($T_c$) between 653 and 683 K. The glass transition temperature $T_g$ and the parameter ($T_c$–$T_g$) that give the information on the glass forming ability exhibited minimal effects at 0.8 mol % of V$_2$O$_5$ (inset of Fig. 4.1).

4.3.2 Physical parameters

From the measured values of density, D, and calculated average molecular weight $\overline{M}$, various physical parameters such as vanadium ion concentration $N_i$ and mean vanadium ion separation $r_i$ for these glasses are
determined using the conventional expressions and are presented in Table 4.1.

**Table 4.1 Various physical parameters of LiI-AgI-B$_2$O$_3$:V$_2$O$_5$ glasses**

<table>
<thead>
<tr>
<th>Glass</th>
<th>$V_0$</th>
<th>$V_2$</th>
<th>$V_4$</th>
<th>$V_6$</th>
<th>$V_8$</th>
<th>$V_{10}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm$^3$)</td>
<td>2.672</td>
<td>2.664</td>
<td>2.650</td>
<td>2.607</td>
<td>2.606</td>
<td>2.605</td>
</tr>
<tr>
<td>Average molecular weight $M$</td>
<td>96.32</td>
<td>96.41</td>
<td>96.51</td>
<td>96.60</td>
<td>96.70</td>
<td>96.55</td>
</tr>
<tr>
<td>Vanadium ion concentration $N_i$ (10$^{20}$ ions/cm$^3$)</td>
<td>--</td>
<td>0.332</td>
<td>0.661</td>
<td>1.000</td>
<td>1.29</td>
<td>1.62</td>
</tr>
<tr>
<td>Inter–ionic distance of vanadium ions $R_i$ (Å)</td>
<td>--</td>
<td>31.08</td>
<td>24.72</td>
<td>21.54</td>
<td>19.75</td>
<td>18.33</td>
</tr>
<tr>
<td>Field strength (10$^{14}$ cm$^2$)</td>
<td>--</td>
<td>3.186</td>
<td>5.038</td>
<td>6.637</td>
<td>7.892</td>
<td>9.156</td>
</tr>
<tr>
<td>Molar vol. (cm$^3$/mol)</td>
<td>36.04</td>
<td>36.19</td>
<td>36.41</td>
<td>37.06</td>
<td>37.11</td>
<td>37.15</td>
</tr>
<tr>
<td>Refractive index</td>
<td>1.650</td>
<td>1.649</td>
<td>1.648</td>
<td>1.647</td>
<td>1.646</td>
<td>1.645</td>
</tr>
</tbody>
</table>
4.3.3 Electrical conductivity

The impedance spectra for the V₆ glass at 473 K and its corresponding electrical circuit used to generate the spectrum are shown in Fig. 4.2(a). The spectrum for the V₆ glass consists of a single semicircle typical for semiconducting glasses. The dc resistance (R) of all glasses in this series was obtained from fitting procedure. The dc conductivity, \( \sigma_{dc} \), was calculated using sample dimensions. It should be noted that the complex impedance plot in the wide frequency range was single semicircle for all glasses with no straight spur typical for ionic conductors. This means that the dominant mechanism is polaronic around this temperature.

Fig. 4.2(b) shows the frequency dependence of the ac conductivity at different temperatures for V₆ glass. The ac conductivity spectra, generally, show a universal feature [71] where at low frequency the conductivity is independent of frequency and corresponds to the dc conductivity, \( \sigma_{dc} \) of glass, whereas at higher frequency exhibits dispersion in power law fashion. It is noted that the dispersion starts at a higher frequency as the temperature increases. However, at low temperature and frequency the leveling-off of the conductivity is not distinct. Moreover, the dc conductivity calculated from equivalent circuit modeling corresponds to the dc conductivity obtained from low frequency plateau at higher temperature.
Fig. 4.1 DSC traces of LiI-AgI-B$_2$O$_3$ glass doped with different concentrations of V$_2$O$_5$ and inset shows the variation of the glass transition temperature $T_g$ and $T_c$-$T_g$ with the concentration of V$_2$O$_5$. 
The evaluated dc conductivity variation with 1/T is shown in Fig. 4.3(a). The activation energy for dc conduction, $W_{dc}$, for each glass sample was determined from the slope of log $\sigma_{dc}$ vs.1/T using Arrhenius equation $\sigma_{dc} = \sigma_o \exp(-W_{dc}/k_B T)$ where $\sigma_{dc}$ is the dc conductivity calculated using fitting procedure, $\sigma_o$ is the pre-exponent, $k_B$ is the Boltzmann constant and T is the temperature (K). The values for $W_{dc}$ for each glass are given in Table 4.2. The activation energy evaluated from these graphs is found to decrease with increase in the concentration of $V_2O_5$ up to 0.8 mol% and then after a slight increase of activation energy is observed (Table 4.2).

Fig. 4.4 exhibits the measured ac conductivity, $\sigma_{ac}$, as a function of inverse temperature at different frequencies. The inset of Fig. 4.4 shows the variation of the $\sigma_{ac}$ with the concentration of $V_2O_5$ measured at 1.3 kHz and 523 K. It can be seen from the inset that the dependence of the ac conductivity, $\sigma_{ac}$, upon the addition of $V_2O_5$ passes through the maximum at 0.8 mol%. In the high temperature region where the linear dependence of log $\sigma_{ac}$ with 1/T is observed, the activation energy (A.E.) for ac conductivity, $W_{ac}$, was calculated and presented in Table 4.2. The lowest value of the activation energy ($W_{ac}$), was found for the glass $V_8$. 
Fig. 4.2. (a) The impedance spectrum for the V$_6$ glass at 473 K and its corresponding electrical circuit and (b) frequency dependence of the ac conductivity at different temperatures for V$_6$ glass.
Fig. 4.3. (a) The variation of dc conductivity with 1/T for LiI-AgI-B$_2$O$_3$ glass doped with different concentrations of V$_2$O$_5$ (b) variation of dc conductivity with the concentration of V$_2$O$_5$ (c) variation of dc conductivity with activation energy
Fig. 4.4. The variation of ac conductivity, $\sigma_{ac}$, with $1/T$ for $V_6$ glass. Inset represents variation of ac conductivity with the concentration of $V_2O_5$ measured at $T = 523$ K and $\nu = 1.3$ kHz.
4.3.4 Dielectric properties

The complex permittivity $\varepsilon^*(\omega)$ can be expressed as a complex number:

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - j\varepsilon''(\omega)$$

where $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ are the real part known as dielectric constant and imaginary part known as dielectric loss of the complex permittivity. The frequency dependence of dielectric constant $\varepsilon'(\omega)$ and dielectric loss peak $\tan \delta(\omega)$ (or $\varepsilon'/\varepsilon''$) for V$_6$ glass at various temperatures is shown in Figs. 4.5 (a) and (b). At higher frequency the $\varepsilon'(\omega)$ approaches a constant value, $\varepsilon'_\infty(\omega)$, which results from rapid polarization processes occurring in the glasses under applied field [72]. With decreasing frequency, $\varepsilon'(\omega)$ increases and reaches a low-frequency plateau, $\varepsilon_s$, usually associated with the polarization effects of the mobile ions with respect to the immobile glass matrix. This low frequency shoulder is more pronounced for glasses containing higher V$_2$O$_5$ content, from 0.6 to 1.0 mol%. At further decrease of frequency, $\varepsilon'(\omega)$ begins to increase significantly due to the electrode polarization arising from space charge accumulation at the glass-electrode interface. It should be noted that the loss peak shifts toward higher frequency side as the temperature increases, indicates a thermally activated behavior. Nature of the variation of the dielectric parameters with frequency and temperature is found to be similar for all the other samples in this study.
Fig. 4.5. The frequency dependence curves of (a) dielectric constant, $\varepsilon'(\omega)$ and (b) dielectric loss, $\tan\delta$, at different temperatures for $V_4$ glass.
Figs. 4.6 (a) and (b) exhibit the variation of $\varepsilon'(\omega)$ and Tan $\delta$ as a function of temperature at different frequencies, respectively. It can be seen that $\varepsilon'(\omega)$ is less dependent of frequency at lower temperature whereas exhibits the plateau at higher temperature. With increasing temperature especially at lower frequency $\varepsilon'(\omega)$ shows an increase attributed to the electronic polarization. The variation of dielectric loss, tan $\delta$, with temperature, shows a distinct maximum (Fig. 4.6(b)). With increasing frequency and temperature maxima shift towards higher temperature indicating the dielectric relaxation character of dielectric loss peak for these glasses. It should be noted that the dielectric loss peak is positioned at low frequency region where the conductivity is dominated by dc conductivity. Following the relation, $\nu = \nu_0 \exp (-W_d/kT)$, (here $\nu_0$ is a constant, $k_B$ is the Boltzmann constant, $T$ is absolute temperature and $\nu$ is relaxation frequency) the effective activation energy, $W_d$, for the dipoles is evaluated for all the glasses by drawing the plots of $\log \nu$ vs $1/T$. The activation energy $W_d$ is found to be the lowest for the sample $V_8$ (Table 4.2).
Fig. 4.6. (a) The variation of dielectric constant, $\varepsilon'(\omega)$, and (b) dielectric loss, $\tan\delta$, with temperature at different frequencies for the glass $V_6$. 
Table 4.2 Various activation energies and relaxation times obtained from the dielectric properties of LiI–AgI–B\textsubscript{2}O\textsubscript{3}: V\textsubscript{2}O\textsubscript{5} glasses

<table>
<thead>
<tr>
<th>Glass</th>
<th>A.E. for dipoles W\textsubscript{d} (eV) (± 0.01)</th>
<th>A.E. for ac conduction W\textsubscript{ac} (eV) (± 0.01)</th>
<th>A.E. for dc conduction W\textsubscript{dc} (eV) (± 0.01)</th>
<th>Relaxation time τ (μs)</th>
<th>Exponent s (at 373 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V\textsubscript{2}</td>
<td>1.85</td>
<td>1.17</td>
<td>1.06</td>
<td>128</td>
<td>0.82</td>
</tr>
<tr>
<td>V\textsubscript{4}</td>
<td>1.84</td>
<td>1.15</td>
<td>1.05</td>
<td>125</td>
<td>0.85</td>
</tr>
<tr>
<td>V\textsubscript{6}</td>
<td>1.54</td>
<td>1.00</td>
<td>1.01</td>
<td>120</td>
<td>0.89</td>
</tr>
<tr>
<td>V\textsubscript{8}</td>
<td>1.50</td>
<td>0.96</td>
<td>0.98</td>
<td>115</td>
<td>0.94</td>
</tr>
<tr>
<td>V\textsubscript{10}</td>
<td>1.65</td>
<td>1.20</td>
<td>1.05</td>
<td>118</td>
<td>0.83</td>
</tr>
</tbody>
</table>

The electrical modulus formalism is being extensively used for studying electrical relaxation behavior in ion conducting materials. The advantage of this representation is that the electronic polarization effects are minimized in this formalism [73]. In the modulus formalism, an electric modulus M* is defined in terms of the reciprocal of the complex dielectric constant ε* as:

\[
M^* = 1/\varepsilon^*(\omega) = M'(\omega) + i M''(\omega) \tag{4.1}
\]

where \[
M'(\omega) = \frac{\varepsilon'(\omega)}{(\varepsilon'(\omega))^2 + (\varepsilon^*(\omega))^2} \tag{4.2}
\]

and \[
M''(\omega) = \frac{\varepsilon^*(\omega)}{(\varepsilon'(\omega))^2 + (\varepsilon^*(\omega))^2} \tag{4.3}
\]

are the real and imaginary parts of complex modulus respectively.
The frequency dependence of $M'(\omega)$ and $M''(\omega)$ at different temperatures for $V_8$ glass is presented in Figs. 4.7 (a) and (b). These figures clearly exhibit the relaxation character of dielectric properties of these glasses. It should be noted that the $M'(\omega)$ increases with increasing temperature and at sufficient high temperature reaches a plateau which corresponds to the limiting value of $M_\infty$. The maximum in the $M''(\omega)$ peak shifts to higher frequency with increasing temperature. The frequency region below peak maximum $M''(\omega)$ determines the range in which charge carriers are mobile on long distances. At frequency above peak maximum $M''(\omega)$, the carriers are spatially confined to potential wells, being mobile on short distances making only localized motion within the wells. Fig. 4.8 shows the variation of $M'(\omega)$ and $M''(\omega)$ with frequency at 523 K. From the point of intersection of two curves at $(M'')_{\text{max}}$, at characteristic frequency which is equal to the relaxation frequency given by $\omega_{\text{max}} = 1/\tau_M$ the relaxation time $\tau_M$ can be extracted for the $V_6$ glass as is shown in Fig. 4.8. The relaxation times, $\tau_M$, obtained for all glasses measured at 523 K are shown in Table 4.2. The lowest value for the relaxation time is found for the $V_8$ glass.
Fig. 4.7. The frequency dependence of (a) $M'$ and (b) $M''$ at different temperatures for $V_8$ glass.
Fig. 4.8. Frequency dependence of the real and imaginary part of electrical moduli $M'$ and $M''$ for the glass sample $V_6$ measured at 523 K.
4.3.5. Spectroscopic properties

4.3.5 (a) Optical absorption spectra

The optical absorption spectra of LiI–AgI–B₂O₃ glasses doped with different concentrations of V₂O₅ recorded in the wavelength region 300–1100 nm are shown in Fig. 4.9. The absorption edge observed at 380 nm for the glass doped with 0.2 mol % of V₂O₅ is found to be shifted to slightly higher wavelength side with increase in the concentration of V₂O₅ up to 0.8 mol%. The spectrum of glass V₂ exhibited two absorption bands at 651 and 1070 nm. With the gradual increase in the concentration of V₂O₅ 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. From the observed absorption edges, we have evaluated the optical band gaps (Eₒ) of these glasses by drawing Urbach plot between (αℏω)¹/² and ℏω. Fig. 4.10 represents the Urbach plots of all these glasses in which a considerable part of each curve is observed to be linear. From the extrapolation of the linear portion of these curves, the values of optical band gap (Eₒ) are determined and presented in Table 4.3. The value of optical band gap is found to be the lowest for the glass V₈ (inset of Fig. 4.10).
Fig. 4. Optical absorption spectra of LiI-AgI-B$_2$O$_3$: V$_2$O$_5$ glasses recorded at room temperature.
Fig. 4.10. Urbach plots of LiI-AgI-B2O3: V2O5 glasses. Inset shows the variation of optical band gap with the concentration of V2O5.
Table 4.3 Summary of data on optical absorption spectra of LiI-AgI-B$_2$O$_3$:V$_2$O$_5$

<table>
<thead>
<tr>
<th>Glass</th>
<th>Cut-off Wavelength (nm)</th>
<th>Band position (nm) $^2$B$_2$$\rightarrow$$^2$B$_1$</th>
<th>Band position (nm) $^2$B$_2$$\rightarrow$$^2$E$_1$</th>
<th>Optical band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_2$</td>
<td>380</td>
<td>653</td>
<td>1070</td>
<td>3.26</td>
</tr>
<tr>
<td>$V_4$</td>
<td>394</td>
<td>656</td>
<td>1075</td>
<td>3.15</td>
</tr>
<tr>
<td>$V_6$</td>
<td>399</td>
<td>659</td>
<td>1078</td>
<td>3.11</td>
</tr>
<tr>
<td>$V_8$</td>
<td>407</td>
<td>662</td>
<td>1081</td>
<td>3.05</td>
</tr>
<tr>
<td>$V_{10}$</td>
<td>403</td>
<td>657</td>
<td>1073</td>
<td>3.08</td>
</tr>
</tbody>
</table>

4.3.5. (b) ESR spectra

The ESR spectra of LiI–AgI–B$_2$O$_3$: V$_2$O$_5$ glasses recorded at room temperature are shown in Fig. 4.11. Spectra are observed to be complex made up of resolved hyperfine components arising from unpaired 3d$^1$ electron of $^{51}$V isotope. As the concentration of dopant, V$_2$O$_5$, is increased (up to 0.8 mol%) an increasing degree of resolution and the intensity of the signal have been observed. The values of $g_{\parallel}$ and $g_{\perp}$ evaluated from these spectra are observed to increase with increase in the concentration of V$_2$O$_5$, Table 4.4
Fig. 4.11. ESR spectra of LiI-AgI-B$_2$O$_3$ glasses doped with different concentrations of V$_2$O$_3$ recorded at room temperature.
Table 4.4 Data on ESR spectra of LiI–AgI–B₂O₃: V₂O₅ glasses

<table>
<thead>
<tr>
<th>Glass</th>
<th>g∥</th>
<th>g⊥</th>
<th>Δg∥</th>
<th>Δg⊥</th>
<th>Δg⊥/Δg∥</th>
</tr>
</thead>
<tbody>
<tr>
<td>V₂</td>
<td>1.914</td>
<td>1.946</td>
<td>0.090</td>
<td>0.056</td>
<td>0.622</td>
</tr>
<tr>
<td>V₄</td>
<td>1.915</td>
<td>1.947</td>
<td>0.089</td>
<td>0.053</td>
<td>0.596</td>
</tr>
<tr>
<td>V₆</td>
<td>1.919</td>
<td>1.949</td>
<td>0.086</td>
<td>0.051</td>
<td>0.593</td>
</tr>
<tr>
<td>V₈</td>
<td>1.923</td>
<td>1.952</td>
<td>0.085</td>
<td>0.049</td>
<td>0.576</td>
</tr>
<tr>
<td>V₁₀</td>
<td>1.910</td>
<td>1.943</td>
<td>0.088</td>
<td>0.052</td>
<td>0.591</td>
</tr>
</tbody>
</table>

4.4 Discussion

In LiI–AgI–B₂O₃: V₂O₅ glasses, B₂O₃ is a well known network former, participates in the network forming with BO₃ and BO₄ structural units. AgI and LiI do act as modifiers like any conventional modifiers and create bonding defects. In some of the recent investigations it has also been reported that Ag⁺ and Li⁺ ions in oxysalt glass matrices experience mixed oxygen–iodine coordination and do not induce any defects in the glass network [74,75]. According to this model AgI and LiI mainly act to expand the glass network and increase in the accessible volume for the fraction of mobile charge carriers [76].
Vanadium ions are expected to exist mainly in $V^{5+}$ state in the LiI–AgI–B$_2$O$_3$: V$_2$O$_5$ glasses. However, during the melting and annealing processes it is quite certain that the following redox equilibrium takes place:

$$2V^{5+} + O^{2-} \rightarrow 2V^{4+} + \frac{1}{2} O_2$$

The $V^{5+}$ ions take part network forming positions with VO$_5$ structural units and form linkages of the type V–O–B. The $V^{4+}$ ions form vanadyl complexes (VO$_2^+$), act as modifiers and distort the glass network similar to lithium ions. In this type of glasses there is also a possibility to reduce a small fraction of $V^{5+}$ ions to diamagnetic $V^{3+}$ ions [77-79].

The entry of Ag$^+$ into the glass network may be represented as follows:

$$B–O–V + AgI \rightarrow B–O^–Ag^+ + V–O^–Ag^+$$

As a consequence, there is a disruption in the chains of BO$_4$ and BO$_3$ structural units with the creation of number of non–bridging oxygens [75].

The progressive introduction of V$_2$O$_5$ caused a slight decrease in the density (or increase in molar volume) of the glass. The variation in the degree of structural compactness, the modification of the geometrical configuration of the glassy network, changes in the coordination of the glass forming ions and the fluctuations in the dimensions of the interstitial holes are the some of the factors that are responsible for the observed decrease in the density.
The parameters $T_g$ and $T_c - T_g$ evaluated from DSC traces, exhibited a decreasing trend with increase in the concentration of $V_2O_5$ up to 0.8 mol%. Such trend indicates the decrease of augmented cross-link density of various structural groups and closeness of packing. This is possible only if there is a gradual increasing proportion of $V^{4+}$ ions that act as modifiers in the glass network.

On the basis of energy level scheme provided by Ballhausen and Gray [80], for molecular orbitals of $VO^{2+}$ ($3d^1$) ion in a ligand field of $C_{4v}$ symmetry situated in an octahedral field with tetragonal distortion, three bands corresponding to the $^2B_2 \rightarrow ^2B_1 (\Delta \perp)$, $^2B_2 \rightarrow ^2E (\Delta \parallel)$ and $^2B_2 \rightarrow ^2A_1$ transitions were predicted in the absorption spectra. In the spectra of the investigated glasses, only the first two bands are observed. As the content of the $V_2O_5$ continues to increase up to 0.8 mol%, a gradual growth of these bands could clearly be seen; this observation clearly indicates an increase in the rate of reduction of $V^{5+}$ ions to $V^{4+}$ ions in the glasses. Further, the optical activation energy associated with $^2B_2 \rightarrow ^2B_1$ is decreased with the increase in the content of $V_2O_5$ up to 0.8 mol% (Table 4.3); this is clearly a characteristic signal of inter valence transfer or a polaronic type of absorption. This is possible when the associated electrons are trapped at shallow sites within the main band gap with smaller wave-function radii; in terms of polaronic perception, this kind of situation is only
possible if the local potential fluctuation is small as compared to the transfer integral, \( j \). A small overlap between electronic wavefunctions (corresponding to adjacent sites) due to strong disorder is contributive to polaron formation. So from the polaronic viewpoint, the electron delivered by the impurity atom at the \( V^{5+} \) site converts this into a lower valence state \( V^{4+} \), and at the next stage, the trapped electron at this \( V^{4+} \) site is transferred to the neighboring new \( V^{5+} \) site by absorbing a photon energy (Fig. 4.12). Thus the optical absorption in the glass samples is dominated by polaronic transfer between the \( V^{4+} \) and \( V^{5+} \) species [81].

Fig. 4.12. An illustration of transfer of electron from \( V^{4+} \) site to the neighboring new \( V^{5+} \) site.
The vanadyl cations similar to lithium and silver ions are expected to depolymerize the glass network by creating more bonding defects and non-bridging oxygens (NBOs). With the increase in concentration of vanadyl cations in the glass network, a large number of donor centers are thus created, and subsequently, the excited states of localized electrons originally trapped on V$^{4+}$ sites begin to overlap with the empty 3d states on the neighboring V$^{5+}$ sites, and 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, Table 4.3, which leads up to a significant shrinkage in the band gap as the concentration of V$_2$O$_5$ is increased.

The variation of ESR line intensity and the resolution with the concentration of V$_2$O$_5$ is obviously due 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. The observed increase in the intensity of ESR signal with the concentration of V$_2$O$_5$ indicates the growing presence of V$^{4+}$ ions and may also be due to exchange coupling between V$^{3+}$ ions (if any) and V$^{4+}$ ions [82].

The ESR and optical absorption spectral data can be correlated to understand the environment of vanadium ions in LiI-AgI- B$_2$O$_3$: V$_2$O$_5$ glass
network are described below. The \( g \) parameters are connected with the optical band energies by the relations [82]:

\[
g_{\parallel} = g_e \left[ 1 - \frac{4\lambda \alpha^2}{E(\gamma B_e)} \right] \tag{4.4}
\]

\[
g_{\perp} = g_e \left[ 1 - \frac{\lambda \gamma^2}{E(\gamma E)} \right] \tag{4.5}
\]

where \( \lambda \) is the spin-orbit coupling coefficient (249 cm\(^{-1}\) for \( V^{4+} \) ion) and the bonding coefficients \( \alpha^2, \gamma^2 \) characterize respectively, the in–plane \( \sigma \) bonding and out of –plane \( \pi \) bonding of the \( V^{4+} \) ions.

The bonding scheme between vanadium and oxygen ions can be further illustrated as follows: a very strong \( \sigma \) bond will be formed between the \((2p_z + 2s)\) hybrid of the oxygen and the \( (3d_z + 4s) \) hybrid of the vanadium ion. Furthermore, the \( 2p_x \) and \( 2p_y \) orbitals on the oxygen do make a strong \( \pi \) bond with the \( 3d_{xz}, 3d_{yz} \) orbitals on the metal ion, as a result vanadyl becomes a highly stable complex. The \( (3d_z - 4s) \) hybrid, together with the orbitals \( (3d_{x-y^2}, 4p_x, 4p_y, 4p_z) \) are then just capable of five \( \sigma \) bonds directed in a tetragonal pyramid with the \( V^{4+} \) ion located at its base.

From Eqs. (4.4) and (4.5),

\[
\frac{\Delta g_{\perp}}{\Delta g_{\parallel}} = \frac{4E(\gamma B_e)\gamma^2}{E(\gamma E)\alpha^2} \propto \frac{\gamma^2}{\alpha^2} \tag{4.6}
\]
The values of $\Delta g_\perp/\Delta g_\parallel$ obtained for the glasses containing different concentrations of $V_2O_5$ are presented in Table 4.4; the ratio is observed to decrease gradually with increase in the concentration of $V_2O_5$ up to 0.8 mol%.

As it can be seen from the Table 4.4, $\Delta g_\perp$ is always less than one indicating $\gamma^2$ is always less than $\alpha^2$ or the covalence factor $(1 - \gamma^2)$ is always greater than $(1 - \alpha^2)$. In other words the ratio of $(1 - \gamma^2)/(1 - \alpha^2)$ increases with increasing concentration of $V_2O_5$. Such result indicates a progressive weakening of the bonding between $V^{4+}$ ion and equatorial oxygen as the concentration of $V_2O_5$ is increased up to 0.8 mol% [83]; this leads to an increase in the degree of disorder of the octahedral and in the glass network as a whole.

When the concentration of $V_2O_5$ is increased beyond 0.8 mol%, suppression in the hyperfine structure has been observed. Such suppression may be due to the various interactions of electronic spins with their surroundings. In electronically conducting vanadate glasses such interaction occurs via so-called super-exchange of an electron, i.e. hopping of a mobile electron along a $V^{4+}$ - O - $V^{5+}$ bond as mentioned before. This mechanism in fact was earlier reported in different glass systems [83].
Thus, both optical absorption and ESR studies clearly suggest that there is an increasing fraction of vanadyl cations in the glass network with the increase in the concentration of V$_2$O$_5$ up to 0.8 mol%.

Recollecting the data of dielectric properties for LiI–AgI–B$_2$O$_3$: V$_2$O$_5$ glasses, with the gradual increase of V$_2$O$_5$ up to 0.8 mol%, the values of dielectric parameters are observed to increase at any frequency and temperature whereas the activation energy for conduction decreases. This indicates an increase in the space charge polarization owing to the enhanced degree of disorder in the glass network [84-87] due to the increasing proportions of vanadyl cations that act as modifiers.

The variation of dielectric loss with the temperature of LiI–AgI–B$_2$O$_3$: V$_2$O$_5$ glasses exhibited the relaxation character. Theses relaxation effects in the studied glasses can be attributed to the vanadyl complexes that possess net dipole moment [88]. The increase in the breadth and the intensity of the relaxation peak also supports the view point that there is a gradual increase in the concentration of vanadyl cations (which participate in the relaxation effects) with increasing content of V$_2$O$_5$ in these glasses. Although the Cole-Cole plot is very useful for describing relaxation effects, it is preferable sometimes to determine the relaxation parameters by a graphical method suggested by Cole [89]. Combination of the standard Debye’s relations,
\[ \varepsilon'(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + \omega^2 \tau^2} \] (4.7)

\[ \varepsilon''(\omega) = \frac{(\varepsilon_s - \varepsilon_\infty) \omega \tau}{1 + \omega^2 \tau^2} \] , (4.8)

gives rise to:

\[ \varepsilon''(\omega) \omega = \frac{(\varepsilon_s - \varepsilon_\infty) \omega \tau}{1 + \omega^2 \tau^2} = \frac{1}{\tau} (\varepsilon_s - \varepsilon'(\omega)) , \] (4.9)

\[ \varepsilon''(\omega) / \omega = \frac{(\varepsilon_s - \varepsilon_\infty) \tau}{1 + \omega^2 \tau^2} = \tau (\varepsilon'(\omega) - \varepsilon_\infty) . \] (4.10)

Eqs. (4.9) and (4.10) yield straight lines with slope 1/\(\tau\) and \(\tau\), respectively. In Fig. 4.13 the plots between \(\varepsilon''(\omega) \omega\) vs. \(\varepsilon'(\omega)\) and \(\varepsilon''(\omega) / \omega\) vs. \(\varepsilon'(\omega)\) for the V_6 glass are presented. 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 [72]. Graphs drawn for other glasses have also exhibited nearly the same behaviour. Such spreading is possibly due to 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 [90, 91].
The decreasing value of activation energy for dipoles and also the relaxation time with increase in the content of V$_2$O$_5$ (Table 4.3), suggests an increasing degree of freedom for dipoles to orient in the field direction.

Within the framework of the linear–response theory, the frequency–dependent conductivity can be related to

\[
\sigma(\omega) = -\frac{q^2n_e\omega^2}{6kTH_R} \int_0^\infty \langle r^2(t) \rangle e^{-i\omega t} dt \tag{4.11}
\]

where \( q \) is the charge, \( n_e \) is the mobile ion density, \( \langle r^2(t) \rangle \) is the mean square displacement of the mobile ions and \( H_R \) is the Haven ratio (lies in between 0.2 and 1.0) [92] which represents the degree of correlation between successive hops.

At short times, when the mean square displacement \( \langle r^2(t) \rangle \) of ions is small then it is \( \sim t^{1-s} \); the ion transport is characterized by the non–random forward–backward hopping process. Under these conditions Eq. (4.11) modifies to

\[
\sigma(\omega) \propto \omega^s \tag{4.12}
\]

The variation of the exponent ‘s’ (obtained by plotting \( \log \sigma(\omega) \) vs \( \omega \)) is found to be the largest for the glass V$_8$ (Table 4.2). Such largest value suggests that dimensionality of conduction space is the highest for this glass [93, 94].
Fig. 4.13. Variation of the quantities $\omega \varepsilon''(\omega)$ and $\varepsilon''(\omega)/\omega$ with $\varepsilon'(\omega)$ of glass $V_6$ at 373 K.
When a plot is made between log $\sigma_{dc}$ vs. activation energy for conduction, a near linear relationship is observed (Fig. 4.3 (a)). This suggests that the conductivity enhancement is also related to the thermally stimulated mobility of the charge carriers in the high temperature region. Either dc conductivity, Fig. 4.3 (b), or ac conductivity, inset to Fig. 4.4, as a function of the V$_2$O$_5$ concentration exhibited the maximal effects at x = 0.8 mol%. These effects suggest that at this point there is a changeover of conduction mechanism.

The dc conductivity of the LiI–AgI–B$_2$O$_3$: V$_2$O$_5$ glasses for the hopping of the small polarons is given by [95, 96].

$$\sigma_{dc} = \sigma_0 \exp(-W_{dc}/kT) \quad (4.13)$$

$$\text{Where } \sigma_0 = v_o N_i e^2 R^2 C /kT (1-C) \exp(-2\alpha R_i) \quad (4.14)$$

In the Eq. 4.14, $N_i$ is the concentration of ions that contribute to the conductivity, $v_o$ is the phonon frequency ($= \theta_D$ K/h); C is the mole fraction of the sites occupied by electron and $\alpha$ is the electron wave function decay constant, R is the mean separation between iron ions. The term $\exp(-\alpha R_i)$ represents electron overlap integral.

The variation of $\sigma_{dc}$ with 1/T for LiI–AgI–B$_2$O$_3$: V$_2$O$_5$ glasses shown in Fig. 4.3 (a) is in accordance with Eq. (4.13). To explore the nature of the hopping conduction in LiI–AgI–B$_2$O$_3$: V$_2$O$_5$ glasses, a graph between log $\sigma_{dc}$ at
455 K and the activation energy ‘$W_{dc}$’ is plotted in the inset of Fig. 4.3 (c). The graph obtained is a straight line. From the slope of this curve, the value of $1/k_B T$ is obtained and the temperature $T$ is estimated. The value of $T$ is found to be 463 K which is very close to the actual temperature. This suggests that the hopping is adiabatic.

Earlier NMR studies by Olsen et al [97] and Kamitsos et al [98] on the oxide glasses containing AgI, indicated that a part of Ag$^+$ and Li$^+$ ions have oxygen and iodine in their coordination sphere, which do not affect the borate glass network. These studies have also revealed that the fraction of the Ag$^+$ and Li$^+$ ions contributing to the transport process is independent of temperature and the content of AgI and LiI in the glass matrix. However, VO$_2^-$ ions act as modifiers, create dangling bonds and increase the accessible free volume with the enhancement of the number of conduction pathways available for the migration of Ag$^+$ and Li$^+$ ions. Thus, the presence of higher proportions of vandyl ions in the glass network lead to decrease the electrostatic binding energy that traps Ag$^+$ and Li$^+$ ions to the charge compensating oxygen ions and also decrease in the strain energy for the easy passage of these ions. Such decrease leads to a substantial decrement in the jump distance of Ag$^+$ and Li$^+$ ions. This is principal factor for the increase in the conductivity in the Zone I (0.2 to 0.8 mol% of V$_2$O$_5$) in addition to polaron hopping. Further the ionic
conduction in this type of glasses depends upon the height of the energy barrier that conducting ions (Li$^+$ and Ag$^+$ in this case) should overcome. According to Anderson and Stuart model [99], the two principal controlling factors are, (i) the electrostatic binding energy that arises from Coulombic force acting on the ions as they move away from their charge compensation sites and (ii) the migration energy against the mechanical forces acting on the ion as it dilates the structure sufficiently to allow it to move between equilibrium sites in the glass network.

Moreover, the polarons involved in the transfer process from V$^{4+}$ to V$^{5+}$, are attracted by the oppositely charged Ag$^+$ and Li$^+$ ions. This cation–polaron pair moves together as a neutral entity. As expected, the migration of this pair is not associated with any net displacement of the charge and thus does not contribute to electrical conductivity. As a result, there is a decrease in the conductivity in the zone–II (0.8 to 1.0 mol% of V$_2$O$_5$) [100]. The decrease of conductivity may further be interpreted as the entry of network modifying Ag$^+$ and Li$^+$ ions into the glass network, the electronic paths are progressively blocked which causes an inhibition of the electronic current in this region.
4.5 Conclusions

LiI–AgI–B₂O₃ glasses mixed with different concentrations of V₂O₅ (ranging from 0 to 1.0 mol %) were prepared. Electrical and dielectric properties, DSC, optical absorption, ESR of these glasses as a function of concentration of V₂O₅ have been investigated. Optical absorption and ESR studies have indicated that vanadium ions exist in V⁴⁺ state in addition to V⁵⁺ state. Conductivity (both ac and dc) is observed to increase up to 0.8 mol% of V₂O₅ and beyond that the conductivity is found to decrease. The analysis of the conductivity results indicated that there is a mixed ionic and electronic conduction where the ionic conduction seems to prevail over polaron hopping in the glasses containing V₂O₅ more than 0.8 mol%. The electrical moduli and dielectric loss parameters with the frequency and temperature have exhibited relaxation character and these effects have been attributed to vanadyl complexes. The relaxation effects exhibited by these glasses have been analyzed quantitatively by the graphical method and from this analysis it has been established that there is spreading of relaxation times.
References


