Electrical, dielectric and spectroscopic studies on MnO doped LiI–AgI–B2O3 glasses

Citation: J. Appl. Phys. 111, 013714 (2012); doi: 10.1063/1.3676254
View online: http://dx.doi.org/10.1063/1.3676254
View Table of Contents: http://jap.aip.org/resource/1/JAPIAU/v111/i1
Published by the American Institute of Physics.

Related Articles
Inversion of the direction of photo-induced mass transport in As20Se80 films: Experiment and theory
J. Appl. Phys. 110, 063502 (2011)
Proton conduction in hydrous glasses of the join CaAl2Si2O8–CaMgSi2O6: An impedance and infrared spectroscopic study
Dielectric and conductivity relaxation in AgI doped silver selenite superionic glasses
Self-diffusion of poly(propylene glycol) in nanoporous glasses studied by pulsed field gradient NMR: A study of molecular dynamics and surface interactions
Sodium migration pathways in multicomponent silicate glasses: Car–Parrinello molecular dynamics simulations

Additional information on J. Appl. Phys.
Journal Homepage: http://jap.aip.org/
Journal Information: http://jap.aip.org/about/about_the_journal
Top downloads: http://jap.aip.org/features/most_downloaded
Information for Authors: http://jap.aip.org/authors

ADVERTISEMENT

Explore AIP’s new open-access journal
- Article-level metrics now available
- Join the conversation! Rate & comment on articles

Submit Now
Electrical, dielectric and spectroscopic studies on MnO doped LiI–AgI–B₂O₃ glasses

A. Moguš-Milanković,1,a) L. Pavić,1 K. Srilatha,2 Ch. Srinivasa Rao,2 T. Srikumar,2 Y. Gandhi,2 and N. Veeraiah2

1Ruder Bošković Institute, Department of Chemistry, Zagreb, Croatia
2Department of Physics, Acharya Nagarjuna University–Nuzvid Campus, Nuzvid–521 201, A.P., India

(Received 9 September 2011; accepted 14 December 2011; published online 12 January 2012)

LiI–AgI–B₂O₃ glasses doped with different concentrations of MnO (ranging from 0 to 0.8 mol%) were prepared. Electrical and dielectric properties have been studied over a wide frequency range of 10⁻² – 10⁶ Hz and in the temperature range from 173 to 523 K. The valence states of manganese ions and their coordination in the glass network have been investigated using optical absorption, luminescence, and ESR spectroscopy. The analysis of the spectroscopic results has indicated that the manganese ions exist in both Mn²⁺ and Mn³⁺ states and occupy octahedral and tetrahedral positions. With increasing MnO concentration there is a gradual increase in the tetrahedral occupancy of Mn³⁺ ions at the expense of octahedral occupancy in the glass network. The results of dc conductivity have indicated that when T > θD/2, the small polaron hopping model is appropriate and the conduction is adiabatic in the nature. Further, the analysis of experimental data indicates that there is a mixed, ionic and electronic, conduction. It has been observed that the electrical conductivity decreases as the concentration of MnO increases suggesting the electronic conduction controlled by polaron hopping between manganese ions. In the low temperature region, up to 250 K, the ac conductivity is nearly temperature independent and varies linearly with frequency, which can be explained by the quantum mechanical tunneling (QMT) model. The dielectric properties have been analyzed in the framework of complex dielectric permittivity and complex electrical modulus formalisms. The evolution of the complex permittivity as a function of frequency and temperature has been investigated. © 2012 American Institute of Physics. [doi:10.1063/1.3676254]

I. INTRODUCTION

In recent years there have been extensive investigations on the influence of manganese ions on electrical properties and other physical properties of various inorganic glass systems that include silicate, borate, arsenate, phosphate, tellurite, etc.1–7 Manganese ions exist in different valence states occupying tetrahedral or octahedral sites in a glass network. For example, Mn³⁺ ions in borate glasses exist only in octahedral coordination, whereas in silicate and germanate glasses are in both a tetrahedral and octahedral environment.8 Tetrahedral and octahedral Mn²⁺ ions exhibit luminescence emission in the green and red regions for various glasses, respectively.9–11 On the other hand, Mn³⁺ and Mn²⁺ ions are well known paramagnetic ions. The Mn³⁺ ion has a large magnetic anisotropy due to its strong spin-orbit interaction of the 3d orbital, whereas such anisotropy energy of Mn²⁺ ion is small because its orbital angular momentum is zero.

The study of electrical properties of solid electrolytes mixed with transition metal ions has received wide attention due to their potential applications in solid state devices, such as fuel cells, gas sensors, electrochemical capacitors, electrochromic displays, analog devices, cathodes in electrochemical cells, smart windows, etc.1–4 The conductivity of LiI–AgI glasses has been the subject of extensive investigation in recent years as a quest for new solid electrolytes with superionic properties.5,6 The silver/lithium ions surrounded by iodide ions diffuse very rapidly and are the main contributors to the conductivity in the glasses. On the other hand, the silver ions in the oxide glass network get interlocked, become almost immobile, and contribute poorly to the electrical conductivity. Further, when these glasses are doped with multivalent transition metal ions like manganese, the mixed, electronic and ionic, conduction is expected depending upon the glass composition. Electronic conduction in this type of materials is predicted due to polaron hopping between different valence states of transition metal ions whereas the ionic conduction is due to the diffusion of Li and Ag ions. 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 the structure.

The content of manganese in various environments and valence states in the glasses depends on the quantitative properties of modifiers and glass formers, size of the ions in the glass structure, their field strength, mobility of the modifier cation, etc. Hence, the connection between the state and the position of the manganese ion and the electrical properties of the host glass containing highly mobile ions like Ag⁺ and Li⁺ is expected to be interesting.

a)Author to whom correspondence should be addressed. Electronic mail: mogus@irb.hr. Fax: ++385-1-4680-114.
In this study, we have undertaken the extensive investigations on electrical conductivity and dielectric properties over a wide frequency from 0.01 Hz to 1 MHz and temperature range from 173 to 523 K for LiI–AgI–B2O3 glasses doped with various concentration of MnO. The studies were also extended to the spectroscopic investigations of the valence states and coordination of manganese ions in the glass network. Such information will facilitate the analysis of the results of electrical properties quantitatively.

II. EXPERIMENTAL

For the present study, a particular composition (39–x) LiI–1.0AgI–60B2O3: xMnO with x ranging from 0 to 0.8 (in mol%) is chosen. The detailed compositions are as follows:

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

Analytical grade reagents of H3BO3, LiI, AgI, and MnCO3 powders in appropriate amounts were thoroughly mixed in an agate mortar and melted in a platinum crucible at 1473 ± 10 K in a proportional integral derivative (PID) temperature controlled furnace for about 1 h. The resultant bubble free melt was then poured in a brass mold and subsequently annealed at 625 K. The amorphous nature of the samples was verified by X-ray diffraction technique using Xpert’s PRO panalytical X-ray diffractometer with CuKα radiation. It may be noted here that when the concentration of MnO is raised beyond 0.8 mol%, transparent glasses could not be obtained.

The density of the glasses was determined using Ohaus digital balance Model AR2140 to an accuracy of ±0.0001 by the standard principle of Archimedes’ with o-xylene (99.99% pure) as the buoyant liquid. Thermal analysis (differential scanning calorimetry (DSC)) of these samples was carried out by TÁ instruments Model Q20 V24.2 Build 107. Heating rate was 10 K/min in the temperature range from 303 to 923 K. The electron spin resonance (ESR) spectra of the samples were recorded at liquid nitrogen temperature on JEOL JES–TES100 X–band EPR spectrometer. For optical absorption and electrical measurements the samples were cut and (mechanically and optically) polished to the dimensions of 1 cm × 1 cm × 0.2 cm. The optical absorption spectra of the glasses were recorded at room temperature in the spectral wavelength range covering 400–1200 nm with a spectral resolution of 0.1 nm using JASCO Model V–670 UV–vis–NIR spectrophotometer.

The luminescence spectra of the samples were recorded at room temperature on a Photon Technology International fluorescence spectrophotometer. This instrument contains an auto calibrated quadrascopic monochromator for wavelength selection and quadcentric sample compartment. The light source is high intensity continuous xenon lamp with high sensitivity thermoelectric (TE)–cooled InGaAs detector with lock-in amplifier and chopper for noise suppression and an additional emission mono with a 600 groove grating blazed at 1.2 microns. The system provides unmatched near infrared (NIR) luminescence recording capability from 500 nm to 2.2 μm. The spectral resolution is 0.1 nm.

For electrical/dielectric measurements the gold electrode were sputtered onto both sides of the samples using Sputter Coater SC7620. The samples were stored in a desiccator until the electrical conductivity measurements were performed. Dielectric properties were obtained by measuring complex impedance using an impedance analyzer (Novocontrol Alpha-AN Dielectric Spectrometer) over a frequency range from 0.01 Hz to 1 MHz and in temperature range from 173 to 523 K. The temperature was controlled to an accuracy of ±0.5 K. The equivalent circuit that represents a depressed semicircle is a parallel combination of resistor (R) and constant-phase element (CPE). The CPE is an empirical impedance function of the type \( Z_{CPE} = \frac{1}{A(j\omega)^{-z}} \), where A and \( \omega \) are the constants. The impedance spectra were analyzed by means of equivalent circuits modeling and parameters were obtained by the complex non-linear least square (CNLLSQ) fitting. The values of the resistance, R and electrode dimensions (d is sample thickness and A is electrode area) were used to calculate the dc conductivity, \( \sigma_{dc} = \frac{d}{(R \times A)} \).

III. RESULTS AND DISCUSSION

A. Physical parameters

From the measured values of density, D, and calculated average molecular weight, various physical parameters such as manganese ion concentration, \( N_i \), and mean manganese ion separation \( R_i \) for these glasses are determined using the conventional expressions, are presented in Table I. The density of the glasses increases considerably with the concentration of MnO. The increase of structural compactness, the modification of the geometrical configuration of the glassy network, changes in the coordination of the glass forming ions are the factors responsible for the observed increase in the density.

B. DSC analysis

Figure 1 represents DSC curves of LiI–AgI–B2O3: MnO glasses. DSC traces indicate an inflection due to the glass transition temperature, \( T_g \), in the region from 586 to 615 K followed by a well-defined exothermic effect due to the crystallization temperature, \( T_c \), between 679 and 733 K. The glass transition temperature, \( T_g \), and the parameter, \( T_c−T_g \), as a measure of thermal stability of glass against devitrification, increase with an increase in the concentration of MnO, inset of Fig. 1. Such trend indicates the increase of augmented cross-link density of various structural groups in the glass network and closeness of packing.

C. Spectroscopic properties

1. Optical absorption

Figure 2 shows the optical absorption spectra of glasses in the wavelength region of 280–600 nm. The absorption edge observed at 381 nm for the glass M1 is shifted gradually to a lower wavelength with increase in the concentration of
MnO. The spectrum of this glass exhibited an intense absorption band at 523 nm corresponding to $^6\text{A}_1g(S) \rightarrow ^4\text{T}_{1g}(G)$ octahedral transition of Mn$^{2+}$ ions. The spectrum also exhibits a weak kink at about 418 nm due to the $^6\text{A}_1(S) \rightarrow ^4\text{T}_{2}(G)$ tetrahedral transition of Mn$^{2+}$ ions.\textsuperscript{12–14} Additionally, a weak absorption band with a peak at about 498 nm due to $^5\text{E}_g \rightarrow ^5\text{T}_{2g}$ octahedral transition of Mn$^{3+}$ ions is also observed in the spectrum of this glass.\textsuperscript{15} With an 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 redshift. In general, the Mn$^{2+}$ ($3d^5$) complexes with five unpaired electrons are expected to occupy octahedral positions in the glass network.\textsuperscript{16} However, the presence of these ions in tetrahedral positions is also reported in a number of glass systems.\textsuperscript{17} The summary of data on the positions of various bands in the optical absorption spectra of LiI–AgI–B$_2$O$_3$: MnO glasses is presented in Table II.

The observed optical absorption bands are from the Mn$^{2+}$ ion ground state $^6\text{A}_{1g}$ to some quartet states, both spin and parity forbidden. The transitions $^6\text{A}_{1g}(S) \rightarrow ^4\text{T}_{1g}(G)$ involves a change of configuration from $(t_2g)^3(e_g)^2$ to $(t_2g)^4(e_g)^1$ and is therefore observed to be comparatively broad.\textsuperscript{12,13} Since all the excited states are spin quartet states, no spin allowed transitions would occur for Mn$^{2+}$ ions. Hence, Mn$^{2+}$ ions are characterized by weak bands, which arise due to the spin forbidden transitions.

The appearance of a clear broad band in the spectra of the glasses at about 490 nm (due to spin allowed $^5\text{E}_g \rightarrow ^5\text{T}_{2g}$ transition) indicates that a part of manganese ions exist in Mn$^{3+}$ ($d^4$) and occupy octahedral positions.\textsuperscript{18,19} From the observed absorption edges, we have evaluated the optical band gaps ($E_\text{o}$) of these glasses by drawing the Tauc plot (Fig. 3) between $(\alpha h\nu)^{1/2}$ and $h\nu$. The value of the optical bandgap ($E_\text{o}$) increases gradually with increasing MnO content in the glass network. The octahedrally positioned manganese ions, similar to lithium and silver ions, depolymerize

![FIG. 1. (Color online) DSC traces of LiI-AgI-B$_2$O$_3$ glass doped with different concentrations of MnO. Inset shows the variation of the glass transition temperature $T_g$ and $T_c-T_g$ with the concentration of MnO.](image1)

![FIG. 2. (Color online) Optical absorption spectra of LiI-AgI-B$_2$O$_3$: MnO glasses recorded at room temperature.](image2)
the glass network by creating more bonding defects and non-bridging oxygens (NBO). With the decrease in concentration of Mn$^{2+}$\textsuperscript{(Oh)} in the glass network, a decrease in the formation of donor centers is expected, and subsequently, the excited states of localized electrons originally trapped on Mn$^{2+}$ sites begin to separate with the empty 3d states on the neighboring Mn$^{3+}$ sites. As a result, the impurity or polaron band becomes less extended into the main bandgap. This new polaronic development might have shifted the absorption edge to the higher energy, Table II, which leads up to a significant enlargement in the bandgap as the concentration of MnO increased.

### 2. ESR spectra

Figure 4 represents the typical ESR spectra of LiI–AgI–B$_2$O$_3$: MnO glasses. The spectra are characterized by six-line hyperfine structure centered at $g \approx 2.005$ and another signal at $g \approx 4.3$. The values of $g$ obtained for Mn$^{2+}$ ions in the present glass system is comparable with that of other glass systems, such as Bi$_2$O$_3$–GeO$_2$,\textsuperscript{20} lead phosphate,\textsuperscript{21} alkali sulfate glasses.\textsuperscript{13}

For Mn$^{2+}$ ion, if we neglect the nuclear Zeeman term, the spin Hamiltonian term can be written as

$$H = \mu_B g BS + ASI + D S_z^2 - \frac{1}{3} S(S + 1) + E(S_x^2 - S_y^2),$$  \hspace{0.5cm} (1)

where $\mu_B$ is the Bohr magneton, $g$ is the electronic $g$ factor, $B$ is the Zeeman field, $S$ is the Mn$^{2+}$ electronic spin = 5/2, $I$ is the Mn$^{2+}$ nuclear spin = 5/2, $A$ is the hyperfine interaction tensor, and $D$ and $E$ are the non-axial zero field splitting parameters. In case of d$^5$ metal ions, it is known that the axial distortion of octahedral symmetry gives rise to three Kramers doublets $|\pm \frac{5}{2}\rangle$, $|\pm \frac{3}{2}\rangle$ and $|\pm \frac{1}{2}\rangle$.\textsuperscript{22} An application of Zeeman field will split the spin degeneracy of the Kramers doublets. As the crystal field splitting is normally much greater than the Zeeman field, the resonances observed are due to transitions within the Kramers doublets split by the Zeeman field. The resonance at $g = 2.0$ is due 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 $|\pm \frac{1}{2}\rangle$. This line with well resolved hyperfine splitting (due to $^{55}$Mn) can be further interpreted in terms of this spin-Hamiltonian described by Eq. (1) by assuming that the parameters of the fine structure $D$ and $E$ are $|D| \approx |E| < g\beta H$, i.e., the non-cubic crystalline electric fields are weak. The signal observed at $g = 4.3$ corresponding to $|D| \geq g\beta H$ and $E/D = 1/3$ is due to magnetically isolated Mn$^{2+}$ ions in tetragonally or rhombically distorted octahedral sites of symmetry subjected to strong crystal field effects,\textsuperscript{23} and arises from transitions between the energy states.

### Table II. Summary of data on optical absorption for the LiI–AgI–B$_2$O$_3$: MnO glasses.

<table>
<thead>
<tr>
<th>Glass</th>
<th>Mn$_{1s}$</th>
<th>Mn$_{2s}$</th>
<th>Mn$_{14}$</th>
<th>Mn$_{6s}$</th>
<th>Mn$_{9s}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn$^{2+}$ transitions (nm)</td>
<td>523.1</td>
<td>520.6</td>
<td>518.1</td>
<td>516.4</td>
<td>515.8</td>
</tr>
<tr>
<td>(a) $^6A_{1g}(S) \rightarrow ^4T_{1g}(G)$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(b) $^6A_1(S) \rightarrow ^4T_2(G)$</td>
<td>414.0</td>
<td>415.1</td>
<td>416.8</td>
<td>418.0</td>
<td>420.0</td>
</tr>
<tr>
<td>Mn$^{3+}$ transition (nm)</td>
<td>498.2</td>
<td>499.4</td>
<td>500.0</td>
<td>501.1</td>
<td>502.3</td>
</tr>
<tr>
<td>$^5E_g \rightarrow ^5T_{2g}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cut-off wavelength (nm)</td>
<td>381</td>
<td>334</td>
<td>326</td>
<td>304</td>
<td>299</td>
</tr>
<tr>
<td>Optical band gap $E_o$ (eV)</td>
<td>3.18</td>
<td>3.66</td>
<td>3.74</td>
<td>3.98</td>
<td>4.08</td>
</tr>
</tbody>
</table>

FIG. 3. (Color online) Tauc plots of LiI–AgI–B$_2$O$_3$: MnO glasses. Inset shows the variation of optical bandgap with the concentration of MnO.

FIG. 4. (Color online) ESR spectra of LiI–AgI–B$_2$O$_3$ doped with different concentrations of MnO recorded at room temperature.
levels of the middle Kramers doublet \( |\pm \frac{3}{2}\rangle\). The intensity (\( I \)) of the EPR signal is assumed to be proportional to the product of the peak-to-peak height (\( I \)) and the square of its width (\( \Delta B \)),

\[
I \propto I(\Delta B)^2. \tag{2}
\]

The dependence of this factor, for \( g_{\text{eff}} \approx 2.0 \) resonance is shown as an inset of Fig. 4. The figure shows that the intensity of the resonance signal decreases with increase in the concentration of MnO. This may be either due to the decreasing presence of Mn\(^{2+}\) ions in octahedral distorted positions or due to increasing presence of trivalent manganese ions (as evidenced from optical absorption studies). The effective value of \( g \) obtained from ESR spectra show a gradual increase from 2.0027 for Mn\(_1\) to 2.007 for Mn\(_8\) as the concentration of MnO increases in the glass matrix, Table III. This is partly ascribable to the contribution of orbital angular momentum to the magnetic moment of Mn\(^{2+}\) ions.\(^{24}\) The value of \( g \) for hyperfine splitting may also give some information about the nature of the bonding with which the manganese ions participate in the glass network. High shift in the \( g \) value toward positive side from 2.0027 corresponds to more covalent bonding in nature.\(^{25}\) The close examination of the \( g \) values obtained for the present glasses indicates the increasing covalent environment of Mn\(^{2+}\) ions with the increase in the concentration of MnO in the glass matrix.

### 3. Luminescence studies

The room temperature fluorescence spectra of LiI–AgI–B\(_2\)O\(_3\): MnO glasses excited at the wavelength corresponding to their absorption edge are shown in Fig. 5. The spectrum of glass Mn\(_1\) exhibited two emission bands at about 628 nm and 546 nm assigned to \( ^4T_{1g}(G) \rightarrow ^6A_{1g}(S) \) spin forbidden transition of octahedrally positioned Mn\(^{2+}\) ions, where the green emission band is identified due to \( ^4T_{1g}(G) \rightarrow ^6A_{1g}(S) \) spin allowed transition of tetrahedrally positioned Mn\(^{2+}\) ions.\(^{28–30}\) As the concentration of MnO is increased gradually up to 0.8 mol%, the tetrahedral band is observed to grow at the expense of the octahedral band. Thus, the luminescence studies indicate that as the concentration of MnO increased there is gradual transformation of Mn\(^{2+}\) ions from octahedral to tetrahedral positions in the glass network.

Thus, the summary of the results of spectroscopic studies is as follows: the manganese ions do exist in both Mn\(^{2+}\) and Mn\(^{3+}\) states in the LiI–AgI–B\(_2\)O\(_3\) glass network. Mn\(^{2+}\) ions occupy both octahedral and tetrahedral positions in the glass network. With the increase in the concentration of MnO in the glass network, there is a gradual increase in the tetrahedral occupancy of Mn\(^{2+}\) ions at the expense of the octahedral ones.

### D. Impedance spectra

#### 1. Ac conductivity

The impedance spectra for the Mn\(_1\), Mn\(_4\), and Mn\(_8\) glasses at 523 K and its corresponding electrical circuit used to generate each spectrum are shown in Figs. 6(a)–6(c). The spectrum for the Mn\(_1\) glass contains the semicircle and inclined spur at low frequency. This spectrum is characteristic for glasses with two types of charge carriers. The semicircle arc corresponds to the bulk conduction whereas the spur is due to the electrode polarization. The presence of the spur at high temperature points to the blocking of Li\(^+\) and/or Ag\(^+\) ions at gold electrodes. It should be noted that the spur appears in the high temperature region suggesting the thermally stimulated mobility of Li\(^+\) and Ag\(^+\) ions. With increasing MnO content the low-frequency linear spur decreases, Fig. 6(b), and for the Mn\(_8\) glass almost disappeared, Fig. 6(c). However, in this case, even at high temperature, 523 K, the observed contribution of ionic mobility is too low for the formation of an electrode spike. The evolution of characteristic features in impedance spectra for glasses in this study indicates that the nature of conduction undergoes a transition from predominantly electronic transport. So, as the MnO content increases the ionic contribution of the conductivity decreases.

### Table III. Summary on ESR spectra of LiI-AgI-B\(_2\)O\(_3\): MnO glasses.

<table>
<thead>
<tr>
<th>Glass</th>
<th>( g ) (due to the dipole-dipole and super exchange interaction)</th>
<th>( g ) (due to the rhombic distortion)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(_1)</td>
<td>2.0027</td>
<td>4.2999</td>
</tr>
<tr>
<td>Mn(_2)</td>
<td>2.0046</td>
<td>4.3002</td>
</tr>
<tr>
<td>Mn(_3)</td>
<td>2.0058</td>
<td>4.3030</td>
</tr>
<tr>
<td>Mn(_4)</td>
<td>2.0064</td>
<td>4.3058</td>
</tr>
<tr>
<td>Mn(_6)</td>
<td>2.0070</td>
<td>4.3086</td>
</tr>
</tbody>
</table>

FIG. 5. (Color online) Photoluminescence spectra of LiI-AgI-B\(_2\)O\(_3\) glasses doped with different concentrations of MnO recorded at room temperature.
Figure 7 exhibits the measured ac conductivity, $\sigma_{ac}$, as a function of inverse temperature at different frequencies for the glass $\text{Mn}_1$. From these plots, the activation energy, $W_{ac}$, for the conduction in the high temperature region over which a linear dependence of $\log \sigma_{ac}$ with $1/T$ is observed, was calculated and presented in Table IV. The activation energy is found to increase with increasing MnO concentration. When $\log \sigma_{ac}$ is plotted against activation energy, $W_{ac}$, a near linear relationship is found (inset (a) of Fig. 7). This means that the conductivity enhancement is directly related to the thermally stimulated mobility of the charge carriers in the high temperature region.

As mentioned earlier, the glasses under study show mixed, ionic and polaronic, conductivity. Generally, electronic conduction is due to the polaron hopping between $\text{Mn}^{2+}$ and $\text{Mn}^{3+}$ ions whereas ionic conduction is due to migration of $\text{Li}^+$ and $\text{Ag}^+$ ions. For these glasses, the ac conductivity decreases with increasing content of MnO, inset (b) of Fig. 7. One of the possible explanations for such behavior is that the entry of $\text{Mn}^{2+}$ ions into the network forming tetrahedral positions reduces the concentration of dangling bonds in the glass network since some of the MnO$_4$ structural units cross-link with BO$_4$ units. This is consistent with the ESR, optical absorption, and photoluminescence studies, which suggested the gradual increase of tetrahedral manganese ions with increasing MnO content in the glass network. This in turn leads to an increase in the electrostatic binding energy and the strain energy for the easy passage of lithium and silver ions, which consequently leads to a substantial increment in the jump distance of $\text{Li}^+$ and $\text{Ag}^+$ ions. Such behavior is in good accordance with the observed increase in activation energy for conduction. Therefore, the increase in activation energy and decrease in conductivity with increasing MnO content is probably caused by a stronger degree of cross-link in the glass network. Such a structural arrangement in the glass network is more sensitive to the addition of transition metal ions resulting in the increasing role of the electronic component of conductivity. For glasses containing higher manganese ions content, the decrease in conductivity can be interpreted in terms of transition of the mixed conduction with high ionic contribution to the dominate electronic conduction.

![Figure 6](image6.png)  
**FIG. 6.** The impedance spectra for the $\text{Mn}_1$, $\text{Mn}_4$ and $\text{Mn}_8$ glasses measured at 473 K. The solid line: fit using equivalent circuit.

![Figure 7](image7.png)  
**FIG. 7.** The variation of ac conductivity with $1000/T$ for the $\text{Mn}_1$ glass. Insets: the variation of ac conductivity with activation energy (a); the variation of ac conductivity with concentration of MnO measured at $T = 523 \text{ K}$ and $\nu = 1.3 \text{ kHz}$ (b). The solid lines are guides for the eye.

**TABLE IV.** Summary of data on ac conductivity studies and dielectric properties of Li$_2$Ag$_{1-x}$B$_2$O$_{6}$: MnO glasses.

<table>
<thead>
<tr>
<th>Glass</th>
<th>$W_{ac}$ (eV)</th>
<th>Exponent $s$</th>
<th>$W_d$ (eV)</th>
<th>$\tau_m$ (s)</th>
<th>$N(E_F)$ ($\times 10^{20}$ cm$^{-3}$ eV$^{-1}$ cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Mn}_1$</td>
<td>0.489</td>
<td>0.69</td>
<td>0.93</td>
<td>$5.6 \times 10^{-3}$</td>
<td>1.39</td>
</tr>
<tr>
<td>$\text{Mn}_2$</td>
<td>0.494</td>
<td>0.70</td>
<td>1.01</td>
<td>$7.9 \times 10^{-3}$</td>
<td>1.34</td>
</tr>
<tr>
<td>$\text{Mn}_4$</td>
<td>0.519</td>
<td>0.79</td>
<td>1.09</td>
<td>$8.9 \times 10^{-2}$</td>
<td>0.59</td>
</tr>
<tr>
<td>$\text{Mn}_6$</td>
<td>0.552</td>
<td>0.77</td>
<td>1.05</td>
<td>$3.9 \times 10^{-2}$</td>
<td>0.68</td>
</tr>
<tr>
<td>$\text{Mn}_8$</td>
<td>0.577</td>
<td>0.92</td>
<td>1.29</td>
<td>3.9</td>
<td>0.19</td>
</tr>
</tbody>
</table>

$^a$Exponent calculated at 383 K.

$^b$Relaxation time calculated at 383 K.
The ac conductivity in the temperature region up to 250 K, where the ac conductivity is nearly temperature independent and varies linearly with frequency, can be described by the power low relation,

$$\sigma(\omega) = A\omega^s,$$

where $A$ is the temperature dependent constant and the exponent $s < 1$. In general, $s$ is a measure of the degree of interaction of the charge carriers with the environment. In fact this parameter depends on the glass composition and the limit of measured temperature.

Such a frequency dependent conductivity and $s$ exponent can be explained on the basis of quantum mechanical tunneling model (QMT). In the QMT model the tunneling of electrons through barriers predicts temperature independent values for the $s$ exponent. However, for the present glasses the value for $s$ varies with temperature. For example, for Mn$_1$ glass the $s$ value at low temperature, 323 K is 0.86, whereas at 383 K is 0.69. Therefore, at lower temperatures hopping of electrons is dominant conduction for all glasses in the present study. Thus, as the concentration of MnO increases the $s$ values increase as well, confirming the electron hopping conduction for these glasses. On the other hand, Sidebottom studying alkali phosphate glasses concluded that the exponent $s$ depends upon the dimensionality of the local conduction space and it increases with decreasing dimensionality. Based on these studies the observed increase in $s$ values may be attributed to shrink in the dimensionality of conducting space with increase in the MnO.

According to QMT model the conductivity is given by

$$\sigma(\omega) = (\pi/3)\varepsilon^2K[T(N(E_F))^{-1/2}]\omega^{-2}\omega[\ln(\nu_0/\omega)]^4,$$

where $N(E_F)$ is the density of defect energy states near the Fermi level, $\varepsilon$ is the electronic wave function decay constant, $\nu_0$ is the phonon frequency. The value of $N(E_F)$ for a frequency of 1 kHz at $T=253$ K, taking $\gamma=0.52$ (A)$^{-1}$ (obtained by plotting log $\sigma_{dc}$ against $\nu_0$) and $\nu_0 \sim 5 \times 10^{12}$ Hz, was calculated using Eq. (4) and presented in Table IV. The value of $N(E_F)$ is found to decrease from glass Mn$_1$ to glass Mn$_8$ indicating reduction of defect energy states or free charge carriers for conduction in the glass network.

2. Dc conductivity

The values of dc resistance, $R$, for all glasses in this series obtained from fitting analysis were used to determine dc electrical conductivity. The dc conductivity, $\sigma_{dc}$, was calculated using sample dimensions. The activation energy, $W_{dc}$, for each glass was determined from the slope log $\sigma_{dc}$ versus $1/T$ using equation for the hopping of the small polarons,

$$\sigma_{dc} = \sigma_0\exp\left(-\frac{W_{dc}}{k_BT}\right).$$

Figure 8 shows the changes in the dc conductivity, $\sigma_{dc}$, measured at 415 K and activation energy, $W_{dc}$, upon the addition of MnO. Similar to ac conductivity the dc conductivity decreases with increase in MnO concentration. The decrease of the dc conductivity, $\sigma_{dc}$, and increase in activation energy, $W_{dc}$, indicates the gradual loss of the ionic component of conductivity. However, the dc conductivity measured for MnO$_6$ glass shows a slight shoulder, which probably corresponds to the changes in glass network observed from the optical measurements.

Based on earlier NMR studies on the oxide glasses containing AgI, one can imagine that a part of Ag$^+$ and Li$^+$ ions having oxygen and iodine in their coordination sphere 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. Nevertheless, the octahedral Mn$^{2+}$ 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. As mentioned earlier the decrease of octahedral Mn$^{2+}$ ions in the glass network caused an increase in the electrostatic binding energy that traps Ag$^+$ and Li$^+$ ions to the charge compensating oxygen ions as well as an increase in the strain energy for the easy passage of ions. Consequently, this leads to a significant increment in the jump distance between Ag$^+$ and Li$^+$ ions and a decrease in the ionic component of conductivity. It seems that the glass network is more open for the electronic hopping and less favorable for ion motion as the amount of Mn$^{2+}$ ions in tetrahedral coordination increases.

To be more quantitative, the ionic conduction in this type of glasses represents the height of the energy barrier that the conducting ions, Li$^+$ and Ag$^+$, should overcome. According to the Anderson and Stuart model, the two principal conductivity controlling factors are, the electrostatic binding energy that arises from Columbic force acting on the ions as they move away from their charge compensation sites and 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.

According to another interpretation the polarons involved in the process of transfer from Mn$^{2+}$ to Mn$^{3+}$ 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 other words, with the presence of network modifying Ag⁺ and Li⁺ ions and addition of manganese ions into a glass network the ionic and electronic motion are progressively blocked by electrostatic interactions between mobile ions and polaron. However, such a decrease of the effective mobility that is manifested as the decrease in dc conductivity is effective in the case of comparable concentration of both types of charge carriers.

Going further in the interpretation of the origin, the hopping conduction was investigated. It is well known that the activation energy, \( W_{\text{dc}} \), for the dc conductivity is expressed as

\[
W_{\text{dc}} = W_H + (1/2)W_D \quad \text{for} \quad T > \theta_D/2
\]
\[
W_{\text{dc}} = W_D \quad \text{for} \quad T < \theta_D/4
\]

(6)

where \( W_H \) is the polaron hopping energy, \( W_D \) is the disorder energy, and \( \theta_D \) is the Debye temperature. The polaron hopping energy is evaluated using the equation,

\[
W_H = W_p/2 = \frac{\varepsilon^2}{4\varepsilon_p} \left( \frac{1}{r_p} - \frac{1}{R_i}\right).
\]

(7)

where \( W_p \) is the polaron binding energy, \( r_p \) is the polaron radius, and \( \varepsilon_p \) is effective dielectric constant. The calculated values for \( W_H \), presented in Table V, increase with increasing concentration of MnO in the glass network.

In order to determine the nature of the hopping conduction in LiI–AgI–B₂O₃: MnO glasses, a graph between log \( \sigma_{\text{dc}} \) at 413 K and the activation energy, \( W_{\text{dc}} \), is plotted in the inset of Fig. 8. The graph obtained is a straight line. From the slope the value of \( 1/k_B T \) is obtained and the temperature \( T \) is found to be 419 K, which is very close to the actual temperature (413 K). This suggests adiabatic hopping and the conduction mainly controlled by the activation energy.

In small polaron hopping model (SPH), the polaron bandwidth, \( J \), for the adiabatic process is given by

\[
J > (2k_B T W_H / \pi)^{1/4} (h\nu_0 / \pi)^{1/2}.
\]

(8)

The polaron bandwidths can also be calculated from the relation \( \log J = \log J_0 - \alpha R \), where \( J_0 = W_H/4 \) (Ref. 42) as shown in Table V. It should be noted that the \( J \) for all glasses satisfies Eq. (8) and hence the conduction can be taken as adiabatic. This means that there is non-compatibility between the hopping rate of polaron and phonon frequency. According to a more general polaron hopping model, where \( W_D > 0 \), the optical multiphonon determines the dc conductivity at high temperatures, while at low temperatures, charge carrier transport is via an acoustical phonon-assisted hopping process.

### E. Dielectric properties and relaxation studies

The frequency dependence of dielectric constant, \( \varepsilon'(\omega) \), and dielectric loss, tan \( \delta \), for Mn₂ glass at various temperatures is shown in Figs. 9(a) and 9(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. With decreasing frequency, \( \varepsilon'(\omega) \) increases and reaches a low-frequency plateau, \( \varepsilon_\infty \) associated with the polarization effects of the long range hopping of mobile ions with respect to the immobile glass matrix. The bulk polarization of the glass sample results from the presence of metallic electrodes, which do not permit transfer of the charge species into the external circuit. Consequently, charge species are accumulated near the electrodes causing large polarization of the glass. The increase in \( \varepsilon'(\omega) \) occurs at higher temperatures and is more pronounced at lower frequency. The behavior of dielectric permittivity with frequency is related to the application of the field, which assists electron hopping between two different sites in the glasses. This leads to an increase of the electronic component in dielectric dispersion. At high frequency, the charge carriers will no longer be able to rotate sufficiently rapidly.

### TABLE V. Summary of data on dc conductivity studies of LiI–AgI–B₂O₃: MnO glasses.

<table>
<thead>
<tr>
<th>Glass</th>
<th>( W_{\text{dc}} ) (eV)</th>
<th>( W_H ) (eV)</th>
<th>( J ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn₁</td>
<td>0.876</td>
<td>0.516</td>
<td>0.015</td>
</tr>
<tr>
<td>Mn₂</td>
<td>0.884</td>
<td>0.521</td>
<td>0.024</td>
</tr>
<tr>
<td>Mn₄</td>
<td>0.945</td>
<td>0.525</td>
<td>0.038</td>
</tr>
<tr>
<td>Mn₆</td>
<td>0.921</td>
<td>0.563</td>
<td>0.045</td>
</tr>
<tr>
<td>Mn₈</td>
<td>1.088</td>
<td>0.663</td>
<td>0.060</td>
</tr>
</tbody>
</table>

FIG. 9. (Color online) The frequency dependence curves of dielectric constant, \( \varepsilon'(\omega) \) (a) and dielectric loss, tan \( \delta \), at different temperatures for the Mn₂ glass (b). The solid lines are guides for the eye.
so their oscillation will begin to lay behind this field resulting in a decrease of dielectric permittivity, \( \varepsilon'(\omega) \).

The factor, which means the phase difference due to the loss of energy within the sample at a particular frequency is the loss factor tangent, \( \tan \delta = \varepsilon''/\varepsilon' \). The frequency dependence of \( \tan \delta \) at different temperatures for Mn\(_2\) glass is shown in Fig. 9(b). The maximum in the \( \tan \delta \) peak shifts to higher frequency as the temperature increases indicating a thermally activated behavior. The nature of the variation of the dielectric parameters with frequency and temperature is found to be similar for all the other glasses in this study. Generally, the dielectric losses at high frequency are much lower than those occurring at low frequencies at specific temperature. This kind of dependence of \( \tan \delta \) on frequency is typically associated with losses by conduction.

For better understanding the temperature dependencies of \( \varepsilon'(\omega) \) and \( \tan \delta \) at different frequencies are shown in Figs. 10(a) and 10(b). It can be seen that the \( \varepsilon'(\omega) \) is less dependent of frequency at lower temperature which exhibits the plateau at higher temperature. With increasing temperature especially at lower frequency, \( \varepsilon'(\omega) \) shows an increase attributed to the electrode polarization. On the other hand, the variation of dielectric loss, \( \tan \delta \), with temperature, shows a distinct maximum, Fig. 10(b). With increasing frequency and temperature, the maxima are shifted toward higher temperatures 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. The relaxation effects in the studied glasses are obviously due to octahedrally positioned divalent manganese ions.45

The comparison of temperature dependence of dielectric loss, \( \tan \delta \), at different frequencies indicates that with the increase in the concentration of MnO in the glass network, the relaxation maxima are shifted toward the higher temperature indicating the decrease in the breadth of the dielectric relaxation peaks. Following the relation, \( v = v_0 \exp(-W_d/\kappa_b T) \), where \( v_0 \) is the constant, \( \kappa_b \) is the Boltzmann constant, \( T \) is absolute temperature, and \( v \) is relaxation frequency, the effective activation energy, \( W_d \), for the dipoles is determined for all glasses from the plots of \( \log v \) versus \( 1/T \). The activation energy for dipoles, \( W_d \), increases with the increase in the concentration of MnO in the glass network, Table V.

Generally, the relaxation phenomena in dielectric materials are associated with a frequency dependent orientational polarization. At low frequency, the permanent dipoles align themselves along the field and contribute fully to the total polarization of the dielectric. At higher frequency, the variation in the field is too rapid for the dipoles to align themselves, so their contribution to the polarization and hence, to dielectric permittivity can become negligible. Therefore, the dielectric permittivity, \( \varepsilon'(\omega) \), decreases with increasing frequency.

In addition, for glasses where polaronic conductivity is dominant, it is assumed that the electrons interact strongly with the network to form small polarons. These polarons can form positively and negatively charge defects, which act as dipoles in glass.46,47 It should be mentioned that the electron, which creates a polaron is the same electron that later separates from its neighborhood by hopping motion producing conduction at lower frequency. Before a polaron has overcome the potential well, it is effectively trapped and contributes to the dielectric polarization.

At lower frequency, an increase in the magnitude of \( \varepsilon'(\omega) \) is caused by dipolar effects. The dipoles formed between two different manganese valence states act as a relaxing species, which have a distribution of relaxation times. With gradual increase in the MnO content in glass matrix, the values for the \( \varepsilon'(\omega) \) and \( \tan \delta \) decrease at any frequency and temperature resulting in the reduction of electrode polarization. This behavior may be either related to the distribution of relaxation times or ion-polaron interaction between mobile Ag\(^+\) and/or Li\(^+\) and manganese ions in glasses that contain higher concentration of tetrahedral Mn\(^{2+}\) ions in network forming positions. It seems that the cross-linking between tetrahedral Mn\(^{2+}\) ions and BO\(_3\) structural units favors the formation of ion-polaron species resulting in the decrease conductivity and dielectric parameters. This less disrupted glass network is more open for the polaron hopping resulting in dominate electronic over ionic conduction.

An alternative formalism that may be used for analyzing electrical relaxation behavior in glasses is the electrical modulus model. The advantage of this representation is that the electrode polarization effects are minimized in this formalism.48 In the modulus formalism, an electric modulus \( M^* \) is defined in terms of the reciprocal of the complex dielectric constant \( \varepsilon^* \) as

\[
M^*(\omega) = \frac{1}{\varepsilon^*(\omega)} = F(\omega) + \frac{1}{i \omega \varepsilon_0 \delta(\omega)}
\]
\[ M(\omega) = 1/\varepsilon(\omega) = M'(\omega) + iM''(\omega), \quad (9) \]

where \[ M'(\omega) = \frac{\varepsilon'(\omega)}{(\varepsilon'(\omega))^2 + (\varepsilon''(\omega))^2}, \quad (10) \]

and \[ M''(\omega) = \frac{\varepsilon''(\omega)}{(\varepsilon'(\omega))^2 + (\varepsilon''(\omega))^2}, \quad (11) \]

are the real and imaginary part of complex modulus, respectively.

The frequency dependence of \( M'(\omega) \) and \( M''(\omega) \) at different temperatures for Mn\(_2\) glass is presented in Figs. 11(a) and 11(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 sufficiently high temperature reaches a plateau that 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. From the characteristic frequency, which is equal to the relaxation frequency at which the maximum \( M''(\omega) \), occurs, given by \( \omega_{\text{max}} = 1/\tau_M = \sigma_{dc}/\varepsilon_\infty \), the relaxation time, \( \tau_M \), can be extracted as shown in Fig. 11(b). It is clear, that at any chosen temperature, \( \tau_M \) for Mn\(_1\) and Mn\(_2\) glasses exhibit lower values, whereas \( \tau_M \) for Mn\(_8\) glasses is almost two orders of magnitude higher. The relaxation times, \( \tau_M \), for the glasses measured at 383 K, are shown in Table V.

Moreover, the way the dielectric loss, \( \tan \delta \), and \( M''(\omega) \) vary either with frequency or temperature suggests the spreading of relaxation times, 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 \( \tau_M \) the coupling between them ensures that the time domain is effectively stretched leading to the spreading of relaxation times as observed.\(^{49,50}\)

**IV. CONCLUSIONS**

LiI–AgI–B\(_2\)O\(_3\) glasses mixed with different concentrations of MnO (ranging from 0 to 0.8 mol%) were synthesized. A variety of properties, electrical, dielectric, and spectroscopic along with optical absorption, ESR, and photoluminescence studies have been investigated.

1. The differential thermal analysis of these samples has indicated an increase in thermal stability of glass against devitrification with increase in the concentration of MnO.
2. The optical absorption and ESR studies indicated that a part of the manganese ions do exist in the Mn\(^{2+}\) and Mn\(^{3+}\) state in these glasses. The results of these studies along with luminescence spectral results have indicated that as the concentration of MnO increased there is gradual transformation in coordination of Mn\(^{2+}\) ions from octahedral to tetrahedral in the glass network. The higher concentration of MnO and lower LiI content causes a strong cross-link in the glass network.
3. The ac and dc conductivities have been found to decrease, whereas the activation energy for conduction increases gradually with the increase in the content of manganese ions in the glass network. This trend has been understood due to the gradual increase in the concentration of tetrahedrally positioned manganese ions in the glass network.
4. The analysis of the results of dc conductivity has indicated that when \( T > \theta_D/2 \), the small polaron hopping model is appropriate and the conduction is adiabatic in nature. These results further indicated that there is a mixed conduction both ionic and electronic with increasing MnO content. As the glass network becomes less and less disrupted, the conditions for electronic conduction are more favorable.
5. The ac conductivity in the low temperature region up to 250 K is explained based on QMT.
6. The variations of dielectric constant, \( \varepsilon'(\omega) \), and loss, \( \tan \delta \), with temperature have been analyzed on the basis of dielectric polarization. The frequency and temperature dependence of the electrical moduli as well as dielectric loss parameters have exhibited relaxation character; these effects have been attributed to the octahedral Mn\(^{2+}\) complexes.

Finally it is concluded that there is an increasing electrical rigidity (or insulating strength) of LiI–AgI–B\(_2\)O\(_3\) glass samples with increase in the content of MnO in the glass network.
ACKNOWLEDGMENTS

K. Srilatha wishes to thank UGC, Government of India and the Management of St. Theresa’s College, Eluru for sanctioning study leave to carry out this work. A. Mogus-Milanković and L. Pavić would like to acknowledge the Croatian Ministry for Science, Education and Sport for the financial support, Grant No. 098-0982929-2916.