Role of TeO\textsubscript{2} on Conduction Mechanism in AgI-Ag\textsubscript{2}O-B\textsubscript{2}O\textsubscript{3} Glasses

E. Ramesh Kumar, K. Rajani Kumari, B. Appa Rao and G. Bhikshamaiah
Department of Physics, Osmania University, Hyderabad-500 007, India
E mail: esrameshraj@gmail.com, apparaobojja@gmail.com

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Abstract
Glasses containing TeO\textsubscript{2} as a network former have got many applications particularly when they are mixed with superconducting halides and oxides. In the present study we have synthesized AgI-Ag\textsubscript{2}O-B\textsubscript{2}O\textsubscript{3}-TeO\textsubscript{2} (SBT) glass system with different concentrations of TeO\textsubscript{2} by melt quenching technique and studied their electrical properties. All the prepared glasses were characterized by X-ray diffraction. X-ray diffraction confirmed the amorphous nature of the prepared samples. The DC and AC conductivity was measured for all SBT samples in the temperature region 300 to 503K and activation energies were evaluated. The AC conductivity measurements were made for all SBT glasses as a function of frequency 100 Hz to 3 MHz. The true bulk conductivity of pure sample at room temperature (\(\sigma\_b=2.24 \times 10^{-4} \) S/cm) was found to be enhanced with increase in mol % of TeO\textsubscript{2} and found to be maximum 1.92 \times 10^{-3} S/cm at 503 K for 0.4 mol% of TeO\textsubscript{2}. Both DC & AC conductivities were found to increase and activation energies decreased with increasing the concentration of TeO\textsubscript{2}. The variation of conductivity with the TeO\textsubscript{2} content in the SBT system is explained using the diffusion path model, whereas the variation of conductivity with the frequency is analyzed by correlating the microscopic nature of the ionic conduction process in the SBT system.

\textbf{Key words:} Silver glasses, XRD, DC, AC conductivity.

1. Introduction
Fast ion conducting (FIC) glassy materials with exceptionally high ionic conductivity at ambient temperatures have potential applications in ionic devices, such as, solid state batteries, memory devices, capacitors, sensors, timers, fuel cells, electro chronic displays, etc.,[1,2]. Studies on silver based superionic conducting glasses have been increasingly interesting and important in the field of solid state ionicics, since they exhibit high conductivity, high stability, etc., at ambient temperatures. The present investigation deals with the preparation of varying formers compositions of fast ionic conducting 55AgI-22Ag\textsubscript{2}O-23[(1-x) B\textsubscript{2}O\textsubscript{3}-xTeO\textsubscript{2}] where x=0 to 0.4 in steps of 0.1 mol% glassy compounds by melt quenching technique. In this system B\textsubscript{2}O\textsubscript{3}, TeO\textsubscript{2} are glass formers, Ag\textsubscript{2}O is modifier and AgI is dopant salt. Also, deals with the XRD, DC and Impedance measurements respectively to study the nature, structure and electrical conductivity of all prepared SBT samples.

Tellurium oxide is also a good network former and a large number of binary and ternary tellurite systems easily form glasses. The structure of tellurite glasses has been examined by many authors [5-7] using various techniques. Tellurium oxide based glasses are mainly studied for their optical properties. The investigations of electrical conductivity on AgI–Ag\textsubscript{2}O–B\textsubscript{2}O\textsubscript{3}–TeO\textsubscript{2} glass systems have been studied recently. They also exhibit high ionic conductivity on suitable modifications of the network [8-10]. In addition to all these properties, tellurite glasses exhibit less hygroscopic in nature (compared to phosphate and other oxide glasses).

The present study aims to investigate the glasses containing two glass formers (B\textsubscript{2}O\textsubscript{3} and TeO\textsubscript{2}) with varying concentrations along with the fixed concentrations of high conducting electrolyte materials such as AgI and Ag\textsubscript{2}O. Silver oxides has been chosen as a network modifying oxide, since silver ions possess high ionic conductivity compared to alkali modifying cations such as Li\textsuperscript{+} ion. Keeping a constant molecular ratio of the network former, an increase of the ionic conductivity has been observed by mixing two different network modifiers. AC conductivity is one of the common methods to characterize the bulk resistance of glasses. In the present investigation complex impedance measurements are used to study AC conductivity. The frequency dependence of conductivity and dielectric relaxation has also been examined and an attempt is made to explain the conduction mechanism of
these systems.

2. Experimental

(a) Glass Preparation:

The glasses used for the present study are prepared by the melt quenching techniques. The starting materials used for the preparation of present series of glasses were Sigma Aldrich AR grade 99.9% pure reagents (AgI, Ag₂O, B₂O₃, TeO₂); the appropriate amounts of these compounds were thoroughly mixed in an agate mortar and melted in a porcelain crucible. In the present study, 55%AgI-22%Ag₂O-23%[(1-x)B₂O₃-xTeO₂] were prepared by varying the values of ‘x’ from 0 to 0.4 with step 0.1 and are labelled as SBT0, SBT1, SBT2, SBT3, SBT4 respectively.

The furnace used was a PID temperature controlled furnace. The powder was melted in the temperature range 700-750°C for half an hour till a bubble free liquid was formed. The glass samples were obtained by pouring the melt into a brass mould of different shapes. The samples were subsequently annealed at lower temperatures and then sliced and polished. The approximate final dimensions of the glasses used for various studies were 1cm x 1cm x 0.2cm. For dielectric measurements thin coating of silver paint was applied on either side of the glasses to serve as electrodes.

(b) X–Ray Diffraction

X-ray diffraction pattern are recorded in reflection mode for all compositions of SBT samples by Panalytical X-ray Diffractometer.

(e) AC Conductivity

AC conductivity studies are carried on Wayne kerr 6440B Precision Component Analyzer. This analyzer provides 4-terminal measurement of passive components over the frequency range 20Hz to 3MHz. The complex impedance spectroscopy measurements of AC conductivity is made on all the SBT samples by observing real and imaginary components of impedance (Z) over frequency range of 100Hz-3MHz, and temperature range of 300-503K, analyzing them in complex impedance plane. A complex impedance measurement gives information about electrical characteristics of materials and their interface with electrodes. Such studies would help in understanding dielectric nature, conduction processes and dielectric relaxations present in the material. Analysis of the complex impedance data is done by Non Least Square fit method (NLSF).

3. Results and discussion

(a) XRD

The absence of sharp peaks in Fig-1 of XRD clearly indicate the amorphous nature of these materials i.e., long-range atomic order is absent as desired. After confirming the formation of glassy material, the samples are studied for other characteristic properties.

(b) Physical Parameters

Table 1 represents the physical properties of SBT glasses. From the table 1 it can be observed that the density, average molecular weight, molar volume, oxygen packing density (OPD), polaron radius, tellurium ion concentration and interionic distance of tellurium ions increased with the increase in tellurium ion concentration.

The glass structure consist of three coordinated trigonal [BO₃²⁻]³ and four connected tetrahedral [BO₄²⁻]⁻ boron atoms and these [BO₄²⁻]⁻ atoms are produced by the modification at the expense of [BO₃²⁻]³ units [3, 4]. The trigonal and tetragonal conversion and formation of oxygen bridges by the oxide ion from the modifier reaches a maximum at the diborate composition. When the modifier concentration is increased further, the percentage of tetragonal boron decreases indicating a structural stability of tetrahedra in the presence of higher modifier oxide concentrations [5–7] and the notable feature is that there is no non-bridging oxygen (NBO) in the coordination of tetrahedral boron. Tellurium oxide is also a good network former and when the environment is more ionic, the addition of modifier seems to favour the formation of trigonal pyramidal, [TeO₃²⁻]³ (tp) units at the expense of trigonal bipyramidal, [TeO₄²⁻]⁴ (tbp) units [11–13].
Table 1 Physical property of SBT glasses

<table>
<thead>
<tr>
<th>Parameter(± error limits)</th>
<th>SBT0</th>
<th>SBT1</th>
<th>SBT2</th>
<th>SBT3</th>
<th>SBT4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>8.8</td>
<td>8.8</td>
<td>8.8</td>
<td>8.8</td>
<td>8.8</td>
</tr>
<tr>
<td>Avg.molecular weight (g)</td>
<td>196.1</td>
<td>198.1</td>
<td>200.2</td>
<td>202.3</td>
<td>204.3</td>
</tr>
<tr>
<td>Molar Volume (V_m)</td>
<td>22.2</td>
<td>22.4</td>
<td>22.5</td>
<td>22.8</td>
<td>22.9</td>
</tr>
<tr>
<td>OPD, O (g/atm l)</td>
<td>40.8</td>
<td>39.5</td>
<td>38.1</td>
<td>36.8</td>
<td>35.5</td>
</tr>
<tr>
<td>Poloron radius, R_p (Å)</td>
<td>-</td>
<td>0.01</td>
<td>0.008</td>
<td>0.005</td>
<td>0.003</td>
</tr>
<tr>
<td>Te ion conc. Ni, (10^21/cc)</td>
<td>-</td>
<td>2.4</td>
<td>4.8</td>
<td>7.2</td>
<td>9.6</td>
</tr>
<tr>
<td>R_i of Te ions, R_i (Å)</td>
<td>-</td>
<td>0.1</td>
<td>0.06</td>
<td>0.04</td>
<td>0.03</td>
</tr>
</tbody>
</table>

(c) DC Conductivity

Usually DC conductivity is measured to determine the conduction mechanism in these systems. DC conductivity of the samples at room temperature ranges between 10^-6 to 10^-5 S/cm. From table 2 it is observed that conductivity value increases up to 10^-2 S/cm with temperature and also increases with Tellurium ion concentration. The increase in conductivity with temperature is understood in terms of hopping of charges between the coordinating sites, local structural relaxation and segmental motion of polymer. The simultaneous addition of two network formers (B_2O_3 and TeO_2) might have formed a highly disordered network in the glass system facilitating the easy flow of charge carriers. This in turn enhanced the mobility and the conductivity increased to this particular sample.

From the graph plotted between log conductivity and 10^3/T (K^-1) (Fig-2 (a)), DC activation energies are calculated for all the samples using the Arrhenius equation and are tabulated in table 2.

\[ \sigma = \sigma_0 \exp \left( \frac{-E}{KT} \right) \]  (2)

where K- Boltzmann constant, E-Activation energy and \( \sigma_0 \)- preexponantial factor.

SBT0 glass sample (pure) has high activation energy (0.162 eV). SBT4 glass sample has lowest activation energy (0.142 eV). The graph between tellurium ion mol% and activation energy is shown in Fig 2 (b). It is obvious from this figure that the activation energy decreased with increase of the TeO_2 concentration. This clearly indicates that addition of TeO_2 favours the conduction in SBT glasses. This behaviour is typical of ionic conductors. So we can conclude that the samples prepared are ionic conductors.

![Fig.2](a) DC Conductivity versus temperature (b) E_ac versus mol% of TeO_2

Table 2 Values of conductivity and activation energies

<table>
<thead>
<tr>
<th>Sample</th>
<th>Conductivity at</th>
<th>E_ac(eV)</th>
<th>E_pc(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>303K</td>
<td>503K</td>
<td></td>
</tr>
<tr>
<td>SBT0</td>
<td>2.24x10^-6</td>
<td>3.4 x10^-3</td>
<td>0.162</td>
</tr>
<tr>
<td>SBT1</td>
<td>8.14x10^-6</td>
<td>4.7 x10^-3</td>
<td>0.158</td>
</tr>
<tr>
<td>SBT2</td>
<td>1.54x10^-3</td>
<td>7.2 x10^-3</td>
<td>0.155</td>
</tr>
<tr>
<td>SBT3</td>
<td>3.73x10^-3</td>
<td>9.4x10^-3</td>
<td>0.147</td>
</tr>
<tr>
<td>SBT4</td>
<td>5.17x10^-3</td>
<td>1.1x10^-2</td>
<td>0.142</td>
</tr>
</tbody>
</table>
(d) AC Conductivity

AC conductivities are calculated from impedance data. Fig 3(a) represents variation of AC conductivity with temperature of all SBT samples. AC conductivity values are found to vary between $10^{-6}$ to $10^{-5}$ (S/cm) at room temperature. It is observed that conductivity increases with increase in temperature. AC conductivity increases with increasing TeO$_2$ concentration indicating that addition of TeO$_2$ favours the conduction in SBT glasses. The increase in conductivity with temperature is understood in terms of hopping of charges between the coordinating sites, local structural relaxation and segmental motion of polymer [15].

Activation energies are calculated from Arrhenius equation. AC activation energy variation with mol% of TeO$_2$ is also represented in Fig 3(b). AC activation energy decreases with increasing TeO$_2$ concentration from 0.134eV to 0.107eV indicating that addition of TeO$_2$...
enhanced the conduction in SBT glasses.

Variation of real impedance with frequency at different temperatures of SBT1, SBT4 samples are represented in Fig-4(a, b). It is observed that real impedance decrease with the increase frequency, and they merged around 300 kHz. At higher temperatures energy distribution in the network become more uniform and the variation of impedances at higher frequencies become less. This makes real and imaginary impedances to converge at higher frequencies indicating that at higher frequencies conductivity and impedance become independent of temperature.

Variation of Imaginary impedance with frequency at different temperatures of SBT1, SBT4 samples is represented in Fig-4(c, d). A peak is found at lower frequency region, as the temperature increases the peak shift towards higher frequency region.

![Fig-5 (a, b) Cole-Cole plots for SBT1, SBT4 samples at different temperatures](image)

**Table 3** Relaxation frequencies in KHz.

<table>
<thead>
<tr>
<th>Temp(°C)</th>
<th>SBT0</th>
<th>SBT1</th>
<th>SBT2</th>
<th>SBT3</th>
<th>SBT4</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>6.2</td>
<td>6.2</td>
<td>6.2</td>
<td>314</td>
<td>37.6</td>
</tr>
<tr>
<td>50</td>
<td>6.2</td>
<td>188</td>
<td>628</td>
<td>75</td>
<td>37</td>
</tr>
<tr>
<td>100</td>
<td>6.2</td>
<td>157</td>
<td>251</td>
<td>314</td>
<td>188</td>
</tr>
<tr>
<td>150</td>
<td>12.5</td>
<td>502</td>
<td>188</td>
<td>251</td>
<td>502</td>
</tr>
<tr>
<td>200</td>
<td>251</td>
<td>942</td>
<td>125</td>
<td>251</td>
<td>125</td>
</tr>
</tbody>
</table>

The popular forms of data presentation are complex impedance plots ($Z'$ versus $Z''$). Sample data for SBT1, SBT4 samples at different temperatures is represented in Fig-5(a, b). The observed peaks within the range studied depend on the strength of dielectric relaxation. In addition to semi-circle, careful examination of the graph reveals a spike at low frequencies, which is the characteristic of a double layer capacitance ($C_d$). The spike is attributed due to the diffusion limited Warburg impedance, which is present at low frequencies and these clearly indicate the presence of space charge polarization. It is observed that the intercept of the semicircle with the real axis shifts towards the low resistance region with an increase in temperature. The intercept of the inclined straight line with the real axis gives the DC resistance for each composition and at each temperature. DC resistance decreases with increase in temperature.

For all samples from complex impedance plots, relaxation frequencies are calculated at different temperatures and tabulated in table 3. Any specific trend is not observed in the relaxation frequencies. The migration of mobile ions is described by the relaxation times. The existence of distribution of relaxation times in disorder solids is commonly reported [14].

**4. Conclusions**

Conductivity increased with increase in temperature, this reflects ionic conducting property of the samples. Impedance spectroscopy shows the presence of relaxation by showing semi-circle in mid frequency range. This also reflects the involvement of conducting ions. In all the samples DC values is lower than AC values. In all the samples the impedances are observed to decrease not only with increase in temperature, but also with increase in concentration of TeO$_2$.

The fast ion conducting glasses are characterized by greater freedom of movement of Ag$^+$ ions because these ions are not held in the lattice sites or anion cages firmly. Hence addition of network modifier such as TeO$_2$ introduces ionic bonds usually associating non-bridging oxygen ions with modifying cations.

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**References**

11. Ionics 76:297

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