Electrical and Dielectric Properties of Agi-Ag₂O-Bi₂O₃-B₂O₃ Ionic Glassy System

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Abstract: The effect of composition in the ionic glassy system AgI-Ag₂O-Bi₂O₃-B₂O₃ on the electrical properties was investigated. The glasses have been prepared by melt quenching technique. The synthesized materials with up to 40 mol% AgI were formed in amorphous form. Above this value, the materials were only partially amorphous and contained crystalline inclusions, which were identified as β/γ AgI. The electrical conductivity (σ), dielectric constant (ε') and dielectric loss (ε'') studies of the samples have been carried out at different temperatures and frequencies.

The conductivity of the glasses increased with the increase in the AgI content and attains a highest ionic conductivity value with a composition of (AgI)₀.₃(Ag₂O)₀.₂(Bi₂O₃)₀.₂₅(B₂O₃)₀.₂₅. The electrical data are discussed on the basis of Ag⁺ diffusion in the glassy structure, which plays a significant role in both conduction and dielectric relaxation processes in the glass matrix.

Key words: Ionic conductivity; dielectric constant; Bismuth glasses; Borate glasses.

I. Introduction

Super ionic conducting glasses have attracted considerable interest for the last several years [1–10]. Investigation of ionic conductivity in vitreous materials is interesting from both academic and practical points of view. Speaking from a practical aspect, results from their use as key materials for solid state electrochemical devices. The academic interest arises from the fact that the mechanism of ion transport and ion dynamics in glasses remain poorly understood. Recently, a number of fast ion conducting glasses have been reported and investigated through a number of experimental techniques [4]. Generally, it was found that structural consideration plays a more important role for ion migration either in the cluster or tissue of ionic glasses [4]. The present of two glass formers increases glass transition temperature (Tg), thermal stability and electrical conductivity as compared to those of single former glasses [11,12]. Despite the large number of studies that have been done, no theory of ion conduction in glasses has yet received general acceptance. Silver ion conductive glasses of the systems AgI–Ag₂O–M₂O₃ (M₂O₃ = B₂O₃, P₂O₅, MoO₃, etc.) exhibit high electrical conductivity (up to 5 × 10⁻³ S·cm⁻¹ at room temperature) [10–25] of purely ionic character. Glasses with Bi₂O₃ were found to participate in forming stable glasses with high Bi₂O₃ content [24–28]. This is attributed to the ability of the Bi₂O₃ to form conditional glass forming units (distorted BiO₆ (octahedral)) [29]. In borate glasses the boron coordination changes from BO₃ triangle to BO₄ tetrahedral dependent on the type and the ratio of the component oxides in the glass [30].

The high conductivity values of these oxide glasses are interesting to their use as potential solid electrolytes in all-solid power sources for electronic devices operating at room temperature. In view of these facts, an attempt is being made to prepare oxysalt system used as solid electrolyte system with low cost and appreciably high conductivity. The present study deals with the preparation, structural analysis and measurement of ac-conductivity of ionic silver oxysalt system Ag₂O–Bi₂O₃–B₂O₃ with AgI dopant to have a better solid electrolyte system with low cost and appreciably high conductivity.

II. Experimental

Glasses from the quaternary system AgI-Ag₂O-Bi₂O₃–B₂O₃ with the compositions listed in Table (1) were prepared using chemically pure raw materials AgI, AgNO₃, Bi₂O₃ and B₂O₃. The batches of raw materials were homogenized mechanically in an agate mortar with acetone. The mixture were melted in quartz crucible at 1180 K. Melting was continued for 15 min after the last traces of the batch constituents had disappeared and the melts were stirred to achieve homogeneity. The melts were quenched rapidly in stainless steel mould and transferred to a muffle furnace at about 600 K for annealing. The muffle was left to cool to room temperature at a rate of 40 K/h.

The X-ray diffraction technique was used to test the amorphous nature of the sample using a Schimadzu XD-3 diffractometer provided with a Cu-target and Ni filter. The thermal behavior was investigated using thermal analyzer, Schimadzu model 30; at a heating rate of 10 K/min.
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Electrical measurements were performed on pellet samples (1x7 mm) annealed for 15 min at a temperature 10 K below the glass transformation temperature. The surface of the pellet was painted with graphite paste to obtain equipotential surfaces and a double layer capacity which does not influence measurements. The electrical properties of the prepared glasses were measured using a programmable automatic RLC Phillips bridge model SRS 72 in the frequency range 0-10$^6$ Hz and at temperatures between room temperature to 10 K below $T_g$.

For the separation of the ionic from electronic conductivity, Wagner’s polarization method was employed [30], where a polarization cell is made of a pellet placed between two silver plates and applied a constant dc potential of 50 mV across the cell with polarity(-)(Ag+electrolyte)/electrolyte/carbon(+). The current was measured using a Keithly electrometer model 610C till the current becomes constant indicating the fully depleted condition of the blocking electrode.

III. Results and Discussion

XRD show amorphous character for all the samples investigated except the one containing 40 mol% AgI which shows some lines attributed to the presence of $\beta/\gamma$-AgI crystalline phases in the amorphous matrix, Fig.1.

![Figure 1](image-url)

**Fig.1.** XRD patterns: sample (1) containing 40% AgI, and samples 2-7 for glasses with composition have shown in Table (1).

Thermal analysis investigation, Fig.2 show endo- and exo- thermic peaks corresponding to glass transition temperature ($T_g$) and crystallization temperature ($T_c$) for each sample investigated. The data obtained are summarized in Table 1. Both $T_g$ and $T_c$ decreased with increasing AgI and Bi$_2$O$_3$ content in the samples. For the glass with 40 mol% AgI the DTA thermogram shows two exothermic peaks at 430 and at 540 K. The first is attributed to a phase transition from $\beta/\gamma$-AgI to $\alpha$-AgI and the second one due to liquid temperature [31]. The decrease in $T_g$ with increasing AgI content could be attributed to the presence of AgI micro domains which decrease the rigidity of the glass structure.
3.1 dc conductivity:

By applying the Wagner’s polarization technique, the time dependence of electric current showed the same behavior for all investigated samples, Fig.3. It can be seen that the initial current ($I_t$) decreases with time due to the depletion of the ionic species in the electrolyte and becomes constant ($I_e$) in the fully depleted situation. The ionic transport number, in our case is $t_{Ag^+}$ ($t_{Ag^+}$) and electronic transport number ($t_e$) of the samples were determined by using the relation:

$$t_{Ag^+} = \frac{I_{ion}}{I_t}, \quad t_e = \frac{I_e}{I_t}$$

Where $I_{ion}$ is the current due to the mobile $Ag^+$ ion and $I_e$ is the electron current, where

The transport numbers are given in Table 1. It can be seen that $t_{Ag^+}$ is higher than 0.990 indicating that the $Ag^+$ ion is the main charge carrier in our samples.

The temperature dependence of dc conductivity for the glasses investigated, Fig.4, shows an Arrhenius behavior of the form:

$$\sigma_{ion} T = A^\circ \exp \left( -\frac{E_\sigma}{kT} \right)$$

Where $A^\circ$ is the pre-exponential factor, $k$ is the Boltzmann constant, $T$ is the absolute temperature and $E_\sigma$ is the activation energy which is equal to the energy required to overcome the electrostatic force and energy barriers during the jump. The figure shows an increase in the conductivity with temperature, which is a typical characteristic of semi-conducting oxide glasses with thermally activated hopping mechanism. The activation energy for different compositions is obtained from the least square straight-line fitting and listed with the conductivity data in Table 1. It can be seen that the increase in $\sigma$ value is accompanied by a decrease in $E_\sigma$. Moreover, it is noted that by keeping the amount of $Ag_2O$ as well as the ratio between $Bi_2O_3$ and $B_2O_3$ constant, the conductivity was found to increase with increasing $AgI$ content in the sample till up a concentration of 30 mol% $AgI$ (samples 2-4). The increase in conductivity with increasing dopant salt ($AgI$) content in the glassy
matrix can be explained on the basis of the increase occurring in the mobility and the concentration of charge carriers [32]. For the sample containing 40 mol% AgI (sample 1), the conductivity is less than that of all other samples. This is due to the presence of small crystallites of α-AgI embedded in the glass matrix [33-36], as shown by XRD.

![Graph showing ln σ vs. 10^3/T for samples with different compositions (Samples No. 1, 2 and 7).](image)

**Fig. 4.** The plots of ln σ vs. 10^3/T for samples with different compositions (Samples No. 1, 2 and 7).

It is interesting to point out that the influence of Ag₂O content on E_τ is the same as that observed for AgI. The addition of Ag₂O with keeping AgI as well as the ratio between Bi₂O₃ and B₂O₃ constant (samples 4, 5), causes a decrease in E_τ. This suggests that E_τ values are some kind of average of activation energy attributed mainly to the diffusion paths of different kinds of silver ions. Ag⁺ migration paths would, therefore, involve sites other than those near I⁻ ions, for example those near non-bridging oxygen. Generally, in our system there are three kinds of silver ions can participate in the conduction process: (i) Ag⁺ which interacts with non-bridging oxygen atoms (ii) Ag⁺ interacts mainly with I⁻ (iii) Ag⁺ interacting with BO₄ BiO₆⁻ groups.

**Table 1: Thermal and electrical properties data for the investigated system.**

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Sample composition</th>
<th>T_g K</th>
<th>T_c K</th>
<th>σ x10⁶ S cm⁻¹</th>
<th>E_σ eV</th>
<th>t_τ s⁻¹</th>
<th>τ_τ x10¹² s</th>
<th>E_τ eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(AgI)₀.₄(Ag₂O)₀.₆(Bi₂O₃)₀.₀₂</td>
<td>r</td>
<td>380</td>
<td>0.20</td>
<td>0.72</td>
<td>0.991</td>
<td>10.3</td>
<td>0.68</td>
</tr>
<tr>
<td>2</td>
<td>(AgI)₀.₆(Ag₂O)₀.₄(Bi₂O₃)₀.₀₂</td>
<td>590</td>
<td>669</td>
<td>50.11</td>
<td>0.31</td>
<td>0.986</td>
<td>0.36</td>
<td>0.33</td>
</tr>
<tr>
<td>3</td>
<td>(AgI)₀.₆(Ag₂O)₀.₄(Bi₂O₃)₀.₀₂</td>
<td>605</td>
<td>686</td>
<td>15.61</td>
<td>0.46</td>
<td>0.994</td>
<td>0.71</td>
<td>0.44</td>
</tr>
<tr>
<td>4</td>
<td>(AgI)₀.₆(Ag₂O)₀.₄(Bi₂O₃)₀.₀₂</td>
<td>613</td>
<td>695</td>
<td>1.21</td>
<td>0.59</td>
<td>0.991</td>
<td>6.17</td>
<td>0.61</td>
</tr>
<tr>
<td>5</td>
<td>(AgI)₀.₆(Ag₂O)₀.₄(Bi₂O₃)₀.₀₂</td>
<td>620</td>
<td>704</td>
<td>4.34</td>
<td>0.51</td>
<td>0.992</td>
<td>1.36</td>
<td>0.52</td>
</tr>
<tr>
<td>6</td>
<td>(AgI)₀.₆(Ag₂O)₀.₄(Bi₂O₃)₀.₀₂</td>
<td>614</td>
<td>697</td>
<td>7.23</td>
<td>0.48</td>
<td>0.994</td>
<td>0.99</td>
<td>0.50</td>
</tr>
<tr>
<td>7</td>
<td>(AgI)₀.₆(Ag₂O)₀.₄(Bi₂O₃)₀.₀₂</td>
<td>621</td>
<td>707</td>
<td>3.02</td>
<td>0.53</td>
<td>0.992</td>
<td>2.73</td>
<td>0.55</td>
</tr>
</tbody>
</table>

σ is the ionic conductivity at room temperature.

### 3.2 Dielectric and ac conductivity studies:

The frequency dependence of ac conductivity (σ_ac) at room temperature for the glassy samples investigated is shown in Fig 5. It shows two distinct regions; an almost frequency independent plateau region at low frequencies and a dispersion at high frequencies. This is a typical common feature of the ac conductivity in ion conducting glasses [7,37,38]. It is quite reasonable to assume that in ionic conductors the mobile-ion motion is responsible for the ionic conductivity σ_ac as well as for the dispersive ac behavior at higher frequencies [41]. This implies that the interaction among the mobile ions play an important role and may become more evident with increasing ion concentration.

The ionic conduction of glasses is always accompanied by dielectric relaxation. Such dielectric relaxation arising from the different ionic motions in glasses. The first is the rotation of ions around their negative sites. The second is the hopping of the ions from sites with low free-energy barriers to sites with high free-energy barriers in the electric field direction in dc or low-frequency electric field or oscillate between the sites with high free-energy barriers in an ac electric field [42,43]. Both the first and second motions make a contribution to the dielectric constant ε' of glasses.
Fig. 5. The frequency dependence of ac conductivity ($\sigma_{ac}$), at room temperature for the glassy samples investigated.

The temperature and composition dependence of dielectric constant $\varepsilon'$ for the samples investigated is shown in Fig. 6. It shows an increase in $\varepsilon'$ with increasing the conducting ion density (Ag$^+$) in the glass matrix. And when the Ag$^+$ content kept constant $\varepsilon'$ is found to increase with the increase in Bi$_2$O$_3$ content in the sample (samples 5-7). Increasing Bi$_2$O$_3$ lead to an increase in each of the electronic and the ionic polarization. The dielectric constant $\varepsilon'$ is found to increase with increasing temperature. This is more pronounced at low frequencies, since the ions have more time to participate in the motion. The magnitude of dispersion ($\Delta\varepsilon'$) decreases with the increase in the temperature. This is because when the temperature increases, the glassy network relaxes. In addition to that, more and more ions can dissociate from their sites and get over high free-energy barriers to take part in the conduction which leads to the increase in the dielectric constant.

Fig. 6 The temperature dependence of dielectric constant $\varepsilon'$ at 1 kHz for all the samples investigated.

The ionic motion for the ions present in sites with higher energy states conduct electricity and cause the dielectric loss ($\varepsilon''$). The temperature dependence of the dielectric loss ($\varepsilon''$) for each sample investigated, showed a peak in the dielectric loss which shifts towards higher temperature with increasing the frequency, typical plots are given in Fig.7. The shift is consistent with a Debye model \cite{44} for dielectric relaxation characterized by relaxation time ($\tau$) at which the dielectric loss ($\varepsilon''$) is proportional to the term ($\omega\tau / (1 + (\omega\tau)^2)$).

A peak in the dielectric loss occurs when $\omega\tau=1$ and $\tau$ usually found to decrease with temperature according to the relation:

$$\tau = \tau_0 \exp \left( \frac{E_\tau}{kT} \right)$$

(2)
Fig. 7. Temperature dependence of the dielectric loss ($\varepsilon''$) for $(\text{AgI})_{0.2}(\text{Ag}_2\text{O})_{0.2}(\text{Bi}_2\text{O}_3)_{0.1}(\text{B}_2\text{O}_3)_{0.5}$ at different frequencies.

The plot of $\ln \tau$ vs. $1/T$ showed straight line, typical plot is given in Fig. 8. The activation energy values for relaxation process $E_\tau$ were calculated using least square fitting and listed in Table 1. The table shows that $E_\tau$ values change with the composition of glass network refers to the contribution of the glass former in conduction process.

Fig. 8. Plot of $\log \tau$ versus $10^3/T$ for $(\text{AgI})_{0.2}(\text{Ag}_2\text{O})_{0.2}(\text{Bi}_2\text{O}_3)_{0.1}(\text{B}_2\text{O}_3)_{0.5}$.

**Conclusion**

1. In the quaternary system AgI-Ag$_2$O-Bi$_2$O$_3$-B$_2$O$_3$ glasses with composition up to 40% AgI are formed. For sample containing 40 mol% AgI, a glass matrix containing $\beta/\gamma$-AgI crystalline phases is obtained.
2. The prepared samples behave as high silver ion conducting glassy materials.
3. The increase of both AgI and Ag$_2$O content causes an increase in the electrical conductivity $\sigma$, and a decrease in the glass transition temperature, $T_g$. The increase of $\sigma$ is primarily due to increase the concentration of migration of Ag$^+$ ion and to the decrease of the activation energy for conduction, $E_\sigma$.
4. The dielectric constant and the dielectric loss were found to depend on the glass composition and obey Debye relaxation model. The activation energy for the relaxation process is nearly the same as that for conduction, indicating same process.

**References**

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