Electrical studies of D%AgI-(100-D)%[0.667Ag₂O-0.333{(0.4)B₂O₃-(0.6)TeO₂}] fast ion conducting glasses

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Abstract. Super ion conducting glasses of composition D%AgI-(100-D)%[MAg₂O-F{(F1)B₂O₃-(F2)TeO₂}]; D=10.0 to 60.0 in steps of 10.0 for a fixed values of F1 (0.4), F2 (0.6) which are glass network formers, fixed values of modifier M(0.667), F (0.333) and D is dopant salt which was varied. These glasses were prepared by melt quenching technique. XRD spectra taken for all the samples. Electrical characterization was done in terms of AC and DC conductivities. DC and AC conductivities at room temperature increased from 10⁻⁵ to 10⁻¹ scm⁻¹ and DC activation energy (E_{dc}) found to decrease from 0.36 to 0.19eV with increase in D% ratio. Measurements are performed over the frequency range 1 kHz to 3 MHz at different temperatures. From the impedance spectroscopy real and imaginary parts of impedances (Z', Z''), conductivities were calculated and plotted, and equivalent R-C circuit parameters were obtained from Cole-Cole plots. With the increase in D%, AC conductivity is observed to increase whereas the AC activation energy (E_{ac}) is observed to decrease from 0.23 to 0.14 eV. The quantitative analysis of these results indicates that the electrical conductivity of silver borate glasses is enhanced with increase in D% ratio. Based on conductivity values these glasses are ionic conductors, in which conduction is by hopping mechanism. An attempt is made to understand the charge transportation process.

1. Introduction
Several electrical studies on glassy materials revealed that glasses under certain circumstances can be super ionic conductors [1–3]. These glassy materials are of technological interest in view of their applications such as biosensors, storage batteries and fuel cells etc.. The conductivity depends on the nature and content of the modifier oxide and also glass former compositions [4, 5]. The incorporation of alkali halides or metal halides into the mixed glass formers [6, 7] is considered to be predominant factor playing the role of enhancing the conductivity of the conventional glasses to reach the values of super ionic materials. The nature of the interaction between metal ions (Ag⁺) and amorphous molecules is usually studied by different techniques. The structure and the electrical properties of silver ion-conducting borate-based glasses are reported in the literature [8, 9]. Borate glasses exhibit well-known and unique structural features. The fast ion conducting glasses are characterized by greater freedom of movement of Ag⁺ ions. The mobility of Ag⁺ ions associated with an iodide environment is considered to be higher and based on the fact that increase in the percentage of AgI in the glass gives rise to higher conductivities [10-12].
One of the most widely used glass formers for the synthesis of super ionic conducting glass is B₂O₃. It is reported in literature that in many cases the conductivity is enhanced by mixing two different glass formers [10-15] with different coordination polyhedrons. But such mixtures have a strong tendency to form phase separation at low modifier oxide molar ratio. Therefore, the complete substitution of one network former by another one has not always been possible [11].

Tellurium oxide is also a good network former and a large number of binary and ternary tellurite systems easily form glasses [16, 17]. The structure of tellurite glasses has been examined by many authors [18-20] using various techniques. Electrical conductivity investigation on AgI–Ag₂O–B₂O₃–TeO₂ glass systems have been started recently. They also exhibit high ionic conductivity on suitable modifications of the network [21-23]. Correlation between structural properties and electrical behavior and electrical transport mechanisms is scanty in literature. So an attempt is made to fill this gap. As tellurite glasses exhibit low glass transition temperature, high thermal expansion coefficient and are less hygroscopic in nature compared to phosphate and other oxide glasses. So tellurite glasses are preferred over other glasses. The present study aims to investigate the conductivity of the glasses containing high conducting electrolyte materials such as AgI, Ag₂O and by changing the concentrations of glass formers B₂O₃ and TeO₂. Silver oxide is chosen as a network modifying oxide, since silver ions possess high ionic conductivity compared to alkali modifying cations such as Li⁺ ion. Keeping a constant molecular ratio of the network modifiers, an increase of the ionic conductivity has been observed by mixing two different network formers. The DC and AC conductivity studies at room temperature and at higher temperatures provide significant information on the transport mechanism of the materials, which in turn are aimed to correlate with the battery characteristics in future. 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 at room temperature and at higher temperatures is also examined and an attempt is made to explain the conduction mechanism of these systems.

2. Experimental

Silver borate tellurite [SBT] glasses of various compositions are prepared as per the equation D%AgI-(100-D)%[MAg₂O·F₁B₂O₃·(F₂)TeO₂]; D=10 to 60 in steps of 10 for a fixed values of F₁ (0.4), F₂ (0.6) which are glass network formers, fixed values of modifier M(0.667), F (0.333) and D is dopant salt by melt quenching method. Sample with D=10 is termed as SBT1 and sample with D=20 is termed as SBT2 and so on. AgI, Ag₂O, B₂O₃ and TeO₂ are taken according to their molecular weight percentage (mol.wt.%) and mixed thoroughly in a porcelain crucible. The powder form of pellets was characterized by using X-ray diffraction (XRD) and electrical studies. In the present investigation, XRD measurements were carried out using Philips X’pert pro diffractometer with Cu Kα-radiation of wavelength λ =1.5418Å between 10° and 80° of 2θ. Electrical characterization is done from room temperature to 423K by impedance spectroscopy over a frequency range of 1 kHz to 3 MHz. For AC characterization pellets of all the glass samples (dia=1cm, thickness=1.5 mm approximately) are painted both sides with silver for better electrode contact are used. Impedance measurements were carried out by Wayne kerr LCR-6440B impedance analyzer from 1 kHz to 3MHz over the temperature range of 303K to 423K for all SBT samples. Impedance data were analyzed using Zview equivalent circuit software, evaluated bulk resistance for all compositions of SBT glasses and from those curves AC conductivity, activation energy, the equivalent R-C circuit values and relaxation values were calculated. Ionic transport number measurements were also calculated by dc wagner’s polarization technique which is helpful in preparation of solid state batteries. A polarization cell is made in the form of a pellet with a non-blocking
electrode (a mixture of silver metal powder and electrolyte) on one side and a blocking electrode (carbon) on other side of the pellet.

3. Results and discussions

3.1. XRD
From Fig. 1 we can conclude that these all SBT samples are amorphous in nature because of missing of sharp peak in given below structure.

![Figure 1. XRD spectrum of SBT system.](image)

3.2. DC Electrical Conductivity
DC volt-ampere characteristics are obtained at various temperatures. DC and AC conductivity of the samples ranges between $10^{-5}$ (SBT1) to $10^{-2}$ scm$^{-1}$ (SBT6) at room temperature. Table 1 reveals that, the conductivity value increases not only with temperature and also with AgI mol% concentration. This in turn enhanced the mobility and there by conductivity of the samples [24].

![Figure 2. (a) Log conductivity vs. temperature; (b) DC activation energy vs. mol% of AgI.](image)
Table 1. DC, AC conductivities and activation energies for all samples at room temperature.

| S.No. | Sample | $\sigma_{dc}$ (Scm$^{-1}$) RT(303K) | $E_{dc}$ (eV) | $\sigma_{ac}$ (Scm$^{-1}$) RT(303K) | $E_{ac}$ (eV) |
|-------|--------|-----------------------------------|--------------|------------------------------------|--------------|
| 1     | SBT1   | $5.70 \times 10^{-5}$             | 0.44         | $1.50 \times 10^{-5}$             | 0.33         |
| 2     | SBT2   | $8.82 \times 10^{-4}$             | 0.38         | $2.20 \times 10^{-4}$             | 0.28         |
| 3     | SBT3   | $2.61 \times 10^{-3}$             | 0.31         | $2.18 \times 10^{-3}$             | 0.24         |
| 4     | SBT4   | $9.29 \times 10^{-3}$             | 0.25         | $8.17 \times 10^{-3}$             | 0.21         |
| 5     | SBT5   | $3.74 \times 10^{-2}$             | 0.20         | $5.75 \times 10^{-2}$             | 0.18         |
| 6     | SBT6   | $9.83 \times 10^{-2}$             | 0.16         | $7.62 \times 10^{-2}$             | 0.12         |

The graph Fig. 2(a) is log conductivity and $10^3/ T(K-1)$ and it reveals that the conductivity increases with concentration of AgI and with temperature. DC activation energies are calculated for all the samples by using the Arrhenius equation from log conductivity graph, and is shown in Fig. 2(b). The SBT1 glass sample has highest DC activation energy (0.44eV). The SBT6 glass sample has lowest DC activation energy (0.16eV). It is obvious that the DC activation energy decreases with increasing the AgI concentration. Variation of increasing conductivity with increasing temperature is characteristic of ionic conductors [24].

3.3. AC Conductivity

Variation of real part of impedance ($Z'$) with imaginary part of impedance ($Z''$) at different temperatures for SBT1, SBT6 samples is represented in Fig. 3(a) & (b) respectively. From these plots it is observed that with the increase in temperature the intercept of the semi-circle with the real axis at lower frequency shifts towards the higher frequency. The intercept of the semi-circle is equivalent dc resistance (bulk resistance-$R_b$) for each composition and at each temperature. DC resistance decreases with increase in temperature [24].

Figure 3(a), (b). Cole-Cole plots of conductivity.
Fig. 3 (c) & (d) represents the variation of real part of impedance ($Z'$) with frequency at different temperatures for SBT1, SBT6 samples respectively. It is observed that real part of impedance ($Z'$) is both frequency and temperature independent up to about 300 kHz. Fig. 3(e) & (f) represents variations of imaginary impedance ($Z''$) with frequency at different temperatures for SBT1, SBT6 samples respectively. It is observed that imaginary part of conductivity increases with the increasing the temperature at higher frequency region, and merged at lower frequencies for all temperatures [24].

![Figure 3(c), (d). Real part of Z vs. frequency.](image)

![Figure 3(e), (f). Imaginary part of Z vs. frequency.](image)

It is observed from Fig. 3 (g) the AC conductivity increases with increase of temperature and also with increasing AgI mol\% concentration, hence this favor the conduction in SBT glasses. Higher temperatures favor the conduction in SBT glasses. Activation energies are calculated from Arrhenius equation and these values are decreasing from 0.33 to 0.12eV with increasing AgI mol\% concentration, plotted in Fig. 3 (h) and tabulated in Table 2.
AC activation energy decrease depends on increase in temperature at selected frequency. This behavior is a characteristic of conductors with hopping charge carriers. Nonlinear least square fit of complex impedance plots gives equivalent R-C circuit. The present glass samples can be approximated to a parallel combination of bulk resistance ($R_b$), bulk capacitance ($C_b$) and from these values relaxation times calculated and tabulated in table 2. The migration of mobile ions is described by the relaxation times and relaxation time decreases with increase in temperature means that the relaxation frequencies are increasing [24].

| Temperature (K) | SBT1 | SBT6 |
|-----------------|------|------|
|                 | $R_b$(ohm) | $C_b$(nf) | $\tau$(ms) | $R_b$(ohm) | $C_b$(nf) | $\tau$(ms) |
| 303             | 20849 | 0.589 | 0.012 | 1624 | 3.98 | 0.064 |
| 323             | 17374 | 0.718 | 0.012 | 1275 | 5.67 | 0.072 |
| 373             | 8686 | 1.264 | 0.011 | 893 | 9.44 | 0.084 |
| 423             | 3847 | 1.983 | 0.007 | 346 | 12.45 | 0.043 |

3.4. Ionic Transport number
The ionic transport number ($t_i$) and electronic transport number ($t_e$) of the sample were obtained by using the relation $t_i = I_i / I_T$, $t_e = I_e / I_T$

Where $I_i$ is the current due to the mobile ions, $I_e$ is the electron current and $I_T$ is the total current due to all the mobile species, i.e., ions and electrons. The initial total current $I_T$ is equal to sum of current due to the mobile ion $I_i$ and electronic current $I_e$.

The transport number due to ionic ($t_i$) and electronic ($t_e$) obtained from conductivity studies for all of SBT glasses are presented in table 3. The values of ionic transport number ($t_i$) and electronic transport number ($t_e$) for the lowest SBT1 and SBT6 are 0.9883, 0.0117 and 0.9995, 0.0005 respectively. Since the
ionic transport number is much greater than electronic transport number, it can be easily attributed that the present glass system is an ionic conductor. It reveals that the transport number of Ag ions is showing the increasing trend with the increase in AgI and found to be nearly unity.

The \( t_i \) and \( t_e \) are found to decrease with increase in concentration of AgI. These results suggest that the SBT glasses are mixed conductors ionic transport number (\( t_i \)) increases and electronic transport number (\( t_e \)) decreases, this shows that all the SBT glasses are ionic conductors, which are supports for battery characterizations.

### Table 3. Transport numbers, electronic numbers of SBT glass system.

| S.No. | Sample | \( t_i \) (ion) | \( t_e \) (ele) |
|-------|--------|----------------|----------------|
| 1     | SBT1   | 0.9883         | 0.0117         |
| 2     | SBT2   | 0.9892         | 0.0108         |
| 3     | SBT3   | 0.9892         | 0.0108         |
| 4     | SBT4   | 0.9912         | 0.0088         |
| 5     | SBT5   | 0.9945         | 0.0055         |
| 6     | SBT6   | 0.9995         | 0.0005         |

### 4. Conclusions

Absence of sharp peak in XRD confirms that these prepared samples are glassy in nature. It is observed that the conductivity of all the glassy samples increases with increasing frequencies, with temperature and with increase in dopant concentration also. It has been found that \( \sigma \) value for 10%AgI doped glass is minimum and 60%AgI doped glass is maximum. The highest doped glass exhibit lower activation energy in comparison to the lowest doped glass indicating the loosening of the glassy network on the addition of the dopant which facilitates easy migration of mobile ions responsible for higher conductivities in the doped glasses. The increase in conductivity with increase in temperature could attribute to an increase in the mobility of Ag\(^+\) ions because of the formation of non-bridging oxygen’s at higher temperatures.

On the basis of the ionic transport studies reported above, it can be concluded that all synthesized glasses are principally ionic conductors with negligibly electronic conductivity in them. Ionic (\( t_i \)) transport number is found to increase and electronic (\( t_e \)) transport number decreases, with increase AgI concentration. Hence, these glasses are supported for preparation of solid state batteries.

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