

**9th International Symposium on New Materials and Nano-Materials for  
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**Electrical Transport Studies of the Solid Electrolyte System  $x\text{AgI}-(95-x)[2\text{Ag}_2\text{O}-\text{B}_2\text{O}_3]-5\text{TeO}_2$ , where  $45 \leq x \leq 65$**

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**ABSTRACT**

Superionic conducting glassy electrolyte materials with high ionic conductivity are of technological interest due to their potential applications in solid state batteries, capacitors, sensors, memory devices etc. An interesting class of superionic conductors is AgI doped silver borate glasses, which can accommodate AgI in a disordered phase without any evidence of crystallization. In this work, quaternary silverborotellurite glasses of the composition  $x\text{AgI}-(95-x)[2\text{Ag}_2\text{O}-\text{B}_2\text{O}_3]-5\text{TeO}_2$ , where  $45 \leq x \leq 65$  in steps of 5 were synthesized by melt quenching technique. The synthesized samples were characterized by X-ray diffraction and Differential Scanning Calorimetry, to confirm the amorphous nature and glass transition. Ac conductivity measurements were carried out in the frequency range 1Hz to 32MHz by using Solartron 1260 impedance analyzer in the temperature range 303-473K. The present work explains the effect of AgI addition on the silver borotellurite glass and the obtained dc conductivity is found to increase with the addition of AgI and maximum conductivity is obtained for  $x=65$  mole%. The frequency dependence of conductivity is found to obey Jonscher's Universal law. Impedance and dielectric analysis indicated the ionic motion in the system is responsible for the conductivity and relaxation effect. The cooperative motion due to strong coupling between the mobile  $\text{Ag}^+$  ions are assumed to give rise to non-Debye type of relaxation.

**Keywords:** Glass, electrolyte, conductivity, dielectric

## **1. Introduction**

Superionic conducting glassy electrolyte materials with high ionic conductivity are of technological interest due to their potential applications in solid state batteries, capacitors, sensors, memory devices etc [1]. Several studies on these materials have revealed that glasses need not necessarily be insulators, but can be super ionic conductors under certain circumstances [2]. These glasses have more advantages over crystalline materials because of their isotropic properties, ease of glass formation and change in composition. Considerable effort has been taken to the development of new  $\text{Ag}^+$  ion conducting glasses, since the discovery of high ionic conductivity in  $\text{RbAg}_4\text{I}_5$  system. Among the super ion conducting systems studied,  $\text{AgI}$  doped glasses are frequently investigated because it is easy to form glassy specimens having high ionic conductivity at room temperature. To optimize the transport properties of these systems various compositional variations of glass formers and modifiers were studied with the incorporation of alkali halides and metal halides as dopants, which is considered to be a predominant factor playing the role of enhancing the conductivity of conventional glasses to achieve the values of super ionic conductors. The introduction of glass modifier such as  $\text{Ag}_2\text{O}$  introduces ionic bonds usually associated with non-bridging oxygens (NBOs) along with modifying cations. The glass modifier  $\text{Ag}_2\text{O}$  leaves its oxygen and negative charges to the glass network and becomes rich in  $\text{Ag}^+$  ions, and gains the capability to act as solvent for metal halide salts. Hence the mobility of  $\text{Ag}^+$  ions in the iodide environment is considered to be higher and based on the fact that increase in the percentage of  $\text{AgI}$  in glass gives rise to higher conductivities.

Many studies have shown that the conductivities can be enhanced by mixing two different glass formers with different coordination polyhedrons [3]. However, such as mixture of glass formers has a tendency of phase separation at low modifier ratio; therefore the complete substitution of one network former by another is always possible. The most widely studied glass former for super ionic conducting glass is  $\text{B}_2\text{O}_3$  and the structure and electrical properties of silver ion conducting borate based glass have been reported in the literature [4]. The glass structure consist of three co-ordinated trigonal  $\text{BO}_3$  and four connected tetrahedral  $\text{BO}_4$  boron atoms and these  $\text{BO}_4$  atoms are produced by the modification at the expense of  $\text{BO}_3$  units. The trigonal and tetrahedral 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. Tellurium oxide is also a good network former and the interesting aspect of its structure is that when the environment is more ionic, the addition of modifier seems to favor the formation of trigonal pyramidal,  $\text{TeO}_3$  (tp) units at the expense of trigonal bipyramidal  $\text{TeO}_4$  (tbp) units. Tellurium appears to prefer these coordinations; tp units form chains while tbp units show three dimensional networks. Also when  $\text{TeO}_2$  added to the borate group, for example diborate which is quite ionic,  $\text{TeO}_2$  prefers to form chains which interpenetrate the borate network. Tellurium oxide based glasses exhibit high dielectric constant and ionic conductivity with suitable modifications of the network and exhibit low glass

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transition temperature, high thermal expansion co-efficient and are less hygroscopic in nature compared to phosphate and other oxide glasses which makes them suitable for many applications [5].

The ac conductivity measurements have been considered as an important tool for studying the ionic transport properties of these materials. Impedance spectroscopy is used widely to study the ionic conduction in solids and to avoid the polarization effects during the dc conductivity measurements. From the ac conductivity studies, the low frequency measurements gives useful insight into mobile ion diffusion and high frequency conductivity data helps us to study the short time phenomena due to local motion of mobile ions. The passage of electric current through a solid electrolyte is the result of several processes like ion movement through the bulk of the electrolyte, charge transfer across the electrode-electrolyte interface etc. Each of these processes usually has widely different relaxation times and therefore responds to the applied electric field at different frequency ranges. In the present study, we aim to investigate the glasses containing two glass formers  $B_2O_3$  and  $TeO_2$ , by keeping the amount of  $TeO_2$  as constant. In order to see the effect of dopant AgI on silver borotellurite glasses, we synthesized the composition  $xAgI-(95-x)[2Ag_2O-B_2O_3]-5TeO_2$ , where  $45 \leq x \leq 65$  in steps of 5 by melt quenching technique.

## 2. Experimental

The glass samples of composition  $xAgI-(95-x)[2Ag_2O-B_2O_3]-5TeO_2$ , where  $45 \leq x \leq 65$  in steps of 5 were synthesized using the reagent grade chemicals AgI,  $Ag_2O$ ,  $H_3BO_3$  and  $TeO_2$  by melt quenching technique. The chemicals were weighed according to their molecular weight percentage and mixed thoroughly in an agate mortar and pestle by wet grinding method and the mixtures of these materials were kept in an alumina crucible heated to a temperature range 800-1000K for 4 h. The resultant melt obtained was then quenched by pouring the melt immediately on a copper block kept at room temperature and pressed by another copper block. The glass nature of the samples was confirmed by X-ray diffraction and differential scanning calorimetric methods. The glass transition temperature of the amorphous sample was measured by differential scanning calorimeter at a heating rate of 10K/min, by TA instruments (Model MBSE-2910). The electrical conductivity measurements of the glasses were carried out from room temperature up to the glass transition temperature by complex impedance method by using Impedance Analyzer (Solartron 1260) in the frequency range of 10Hz to 32MHz. The samples of the appropriate shape (1mm thickness) were cut and coated with silver paint to serve as electrodes of the configuration Ag/electrolyte/Ag. The samples were kept in contact with two polished, cleaned and spring loaded copper electrodes.

## 3. Results and Discussion

The glassy nature of the synthesized samples was confirmed by XRD and DSC analysis. Figure 1 show the X-ray diffraction patterns for the composition  $45 AgI - (50-x)[2Ag_2O-B_2O_3]-2TeO_2$ . It show a broad hallow thus suggesting their highly disordered nature. The diffractogram of all the samples of the series shows X-ray amorphous. In order to show that all these compositions were indeed glasses, they were analyzed by DSC technique.



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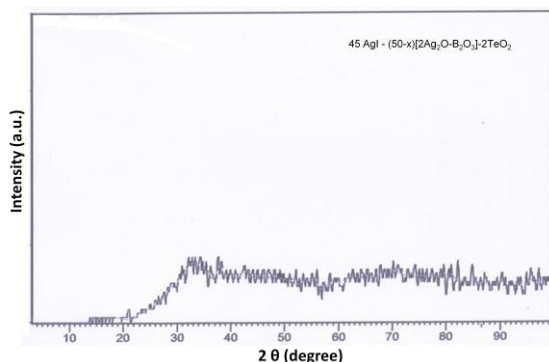


Figure 1. XRD pattern for the glass system 45 AgI - (50-x)[2Ag<sub>2</sub>O-B<sub>2</sub>O<sub>3</sub>]-2TeO<sub>2</sub>

and DSC spectra of all the compositions exhibit a glass transition temperature. Figure 2 shows the DSC spectra for the glass system with x=60 mole%. It shows an endothermic baseline shift corresponding to glass transition followed by exothermic peak due to crystallization of the glassy phase.

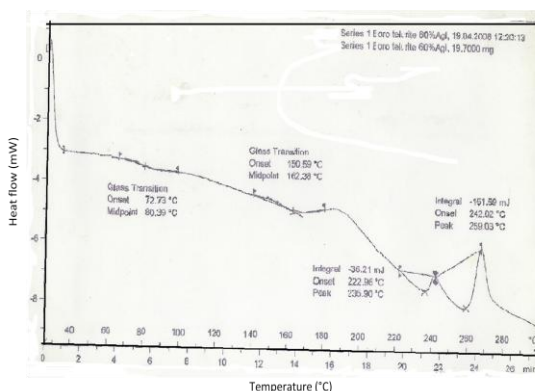


Figure 2. DSC scan for the sample with x=60 mole%

Complex impedance measurements were carried out to determine the electrical properties of glasses over a range of temperature and frequencies. Figure 3 shows the impedance plot obtained for x=50 mole% of AgI doped composition at different temperatures. Figure shows a depressed semicircle and with the increase in temperature, the intersection of the impedance plot on the real axis shifted towards the origin. That means the bulk resistance of the sample decreases with the increase in temperature which indicates a thermally activated conduction mechanism. The depressed semicircle arises from the distributed bulk relaxation due to ion migration in the glassy matrix. Bulk resistance values were determined from the real axis intercept at the low frequency side. The depressed semicircle in the impedance plot is characteristic of the parallel combination of capacitor and resistor respectively, which are the bulk capacitance  $C_b$  and bulk resistance  $R_b$  of the material.

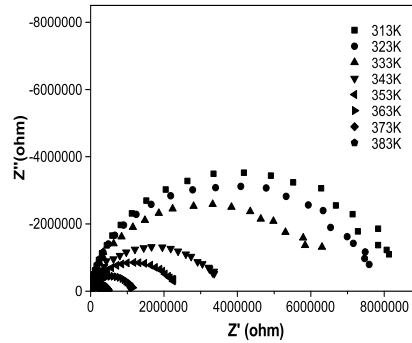


Figure 3. Complex impedance plot for the sample with x=30 mole% at different temperatures.

The real part of the ac conductivity is determined from the complex impedance data by using the relation

$$\sigma' = (t / A)(Z' / (Z'^2 + Z''^2)) \quad (1)$$

where  $Z'$  and  $Z''$  are the real and imaginary part of the impedance respectively,  $t$  is the sample thickness and  $A$  is the area of the sample. Figure 4 shows the frequency dependence of conductivity at different temperatures for the sample with x=50mole% of AgI. It is observed from the figure that the conductivity increases gradually as the frequency increases. The frequency dependent behavior of conductivity is analyzed by the power law exponent.

$$\sigma'_{(\omega)} = \sigma_{dc} + A\omega^n \quad (2)$$

Where  $\sigma_{(\omega)}$  is the conductivity at a particular frequency,  $\sigma_{dc}$  is the dc conductivity of the sample or the conductivity at zero frequency,  $A$  is a constant at a particular temperature,  $\omega$  ( $=2\pi f$ ) is the angular frequency of the applied field and  $n$  is the power law exponent in the range  $0 < n < 1$ . According to Jonscher [6], a non-zero  $n$  in the dispersive region of conductivity is due to the energy stored in the short range collective motion of ions. The power law of ac behavior is observed in a wide range of system, Jonscher called it Universal behavior, since equation (2) is accepted universally for finding the sample dc conductivity, hopping rate, frequency dependence of conductivity etc. The frequency dependent conductivity plots at various temperatures show two distinct regions; an almost frequency independent plateau region at low frequencies and a dispersion at high frequencies. The frequency dependent of conductivity is the sum of dc conductivity due to the movement of free charges and the polarization conductivity due to the movement of the bound charges. The low conductivity value at low frequencies is related to the accumulation of the ions due to the slow periodic reversal of the electric field. In the high frequency region, the power law nature ( $\sigma'_{(\omega)} \propto \omega^n$ ) is observed and the conductivity sharply increases with the frequency. The power law variation has been widely investigated and the strong dispersion at low temperature in the high frequency region is attributed to many body effects [7].

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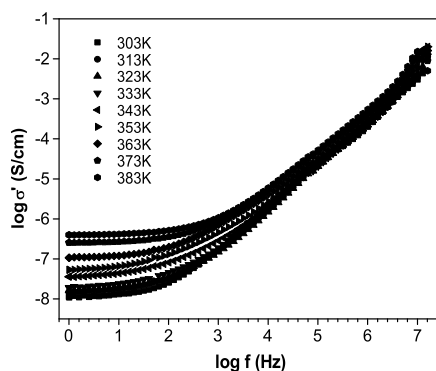


Figure 4. Frequency dependent conductivity at different temperatures for the composition  $x=50$  mole%.

Figure 5 shows the plot of  $\log \sigma$  versus  $10^3/T$  for different compositions. The temperature variation of conductivity is found to obey the Arrhenius behavior.

$$\sigma_{dc} = \sigma_0 \exp(-E_a / kT) \quad (3)$$

Where  $\sigma_0$  is the conductivity pre-exponential factor,  $E_a$  is the activation energy,  $k$  is the Boltzmann's constant and  $T$  is the absolute temperature. The dc conductivity ( $\sigma_{dc}$ ) is found to increase with temperature as well as with the concentration of AgI. The increase in conductivity with the dopant salt is mainly due to the increase in mobile ion concentration. The activation energy of conduction are measured from the slope of  $\log \sigma_{dc}$  versus  $10^3/T$ .

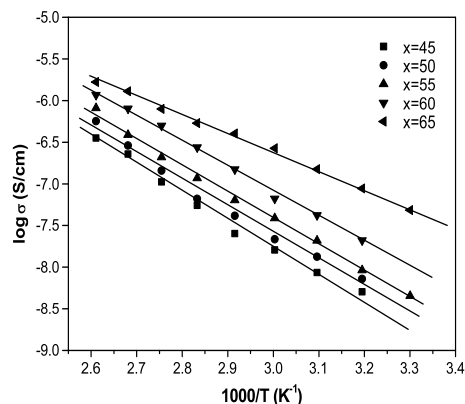


Figure 5. Arrhenius plot of dc conductivity as a function of the inverse of temperature for different compositions.



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The observed variation of conductivity with the increase in AgI amount is due to the silver ions attached to  $\Gamma$  ions in the AgI clusters instead of  $\text{Ag}^+$  attached to the borotellurite structural units which are more tightly bound. Figure 6 shows the dc conductivity and activation energy for all the samples of the present study. The dc conductivity is found to increase with the increase of AgI concentration and activation energy decreases the same.

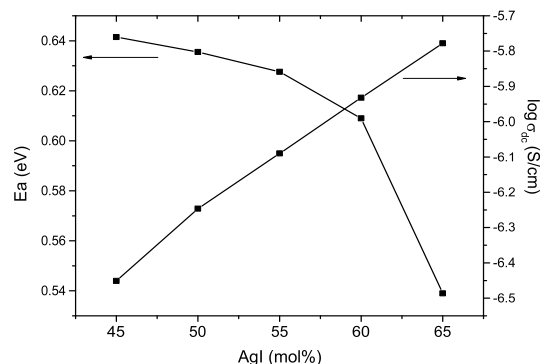


Figure 6. Variation of dc conductivity and activation energy with AgI content

Complex permittivity is related to the impedance data as,  $\epsilon^* = 1/j\omega C_0 Z^* = \epsilon' + j\epsilon''$ , where  $Z^*$  is the complex impedance,  $\omega = 2\pi f$  is the angular frequency and  $C_0$  is the vacuum capacitance of the cell. Frequency dependence of the real part of the permittivity (dielectric constant  $\epsilon'$ ) for  $x=65$  mole% of AgI is shown in figure 7 at different temperatures. The observed high value of  $\epsilon'$  at low frequency is due to the presence of large capacitance at the electrode electrolyte interface. The value of  $\epsilon'$  is found to decrease with increase in frequency and saturates at higher frequencies. Dielectric constant  $\epsilon'$  exhibits a dispersion which shifts to higher frequencies with increase in temperature. This is because at high temperature the jump frequency of mobile ion is large and it resonates with the frequency of the applied electric field. Since the conductivity in the solid electrolyte is visualized as a series of jumps by ions along the lattice sites. If all the sites are equivalent, the ions spend equal amount of time at each site during the conduction process. This is not the case when the sites are not equal. Thus, the charge carriers tend to pile up at high free energy barriers resulting in an increase of capacitance at low frequency. Thus, the variation of  $\epsilon$  at lower frequencies is due to the long range diffusion of  $\text{Ag}^+$  ions involving series of jumps over barriers of varying height. At higher frequencies, the periodic reversal of field takes place so rapidly that there are no excess ionic jumps in the field direction. The capacitive effect at the high free energy barrier site disappears at high frequencies and results in the low value of dielectric constant as shown in figure 7.

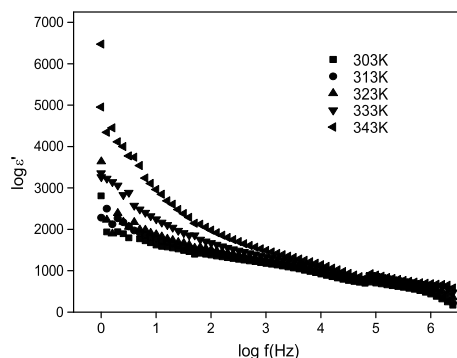


Figure 7. Frequency dependence of dielectric constant for the sample with  $x=65$  mole % at different temperatures.

Many studies on AgI based super ionic conductors agree with the conclusion that the insertion of metallic oxide  $\text{Ag}_2\text{O}$  as modifier disrupts the glassy network leading to the different structural arrangements of  $\text{B}_2\text{O}_3$ - $\text{TeO}_2$  glass network [8]. This change results in the formation of non-bridging oxygen and O-Ag partial co-valent bonding. The  $\text{Ag}^+$  ions bonded to the NBOs have less freedom to move and are expected to be less mobile compared to  $\text{Ag}^+$  ions in an iodine environment. Many structural studies revealed that the glass network is not strongly modified by the introduction of halide salt (AgI). Hence in the present system the increase of conductivity is explained by diffusion path model given by Minami [9]. According to the diffusion path model, a wide and shallow potential is formed by the interaction of  $\text{Ag}^+$  ions with iodide ions while a narrow deep one is formed due to their interaction with oxide ions in the glassy structure. It is also suggested that the diffusion path is more easily formed in disordered structures than on an ordered one. In the present system,  $x\text{AgI}-(95-x)[2\text{Ag}_2\text{O}-\text{B}_2\text{O}_3]-5\text{TeO}_2$  the concentration of AgI increases with the increase in dopant  $x$ , and the increase of conductivity can be explained in accordance with the conductivity expression,  $\sigma = ne\mu$ , where  $n$  is the number of charge carriers,  $e$  is the charge and  $\mu$  is the mobility. Therefore, the increase in the number and mobility of charge carriers ( $\text{Ag}^+$ ) with increase in dopant  $x$  in the present system follows the diffusion path model, where the increase of conductivity with dopant salt content in the glassy matrix is interpreted due to the increase of the concentration of the charge carriers  $\text{Ag}^+$  attached to AgI and their mobility [10].

#### 4. Conclusions

The present study deals with the synthesis of the glass system  $x\text{AgI}-(95-x)[2\text{Ag}_2\text{O}-\text{B}_2\text{O}_3]-5\text{TeO}_2$  where  $45 \leq x \leq 65$  in steps of 5 by melt quenching technique and its electrical characterization. The composition with 65 mole% of AgI is found to exhibit the highest electrical conductivity. Frequency dependent conductivity study shows that the present system obeys Jonschers Universal response and the high frequency dispersion is attributed to many body interactions



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between the conducting species. The variation of dielectric constant with frequency is attributed to ion diffusion and polarization occurring in the glass system.

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