

# Investigation of the silver ion dynamics in a tellurite glass matrix

Soumyajyoti Kabi<sup>1</sup>

<sup>1</sup>Department of Physics, Hijli College, Hijli Cooperative Society  
Kharagpur 721306, West Bengal, India

## Abstract

Silver ion conducting tellurite glass has been synthesized by melt quenching technique. The structure of the glass has been investigated by x-ray diffraction and scanning electron microscopy. It has been observed that the glass is amorphous in nature with few nanoparticles dispersed in the glass matrix. The charge carrier dynamics of the glass has been investigated by employing conductivity spectroscopy. It has been observed that the temperature dependence of the dc conductivity and crossover frequency does not follow the same traits in contradiction to the so called BNN relation. The temperature and frequency dependent conductivity data have been analyzed in the context of Almond West formalism and Jump relaxation model.

**Keywords:** glass, fast ion conducting glass, impedance spectroscopy, ion dynamics

## 1. Introduction

Solid materials can be classified into two classes such as crystalline and amorphous solids based on the periodicity of the atomic arrangement. Glassy materials are examples of amorphous solids which exhibit glass transition temperature [Kabi S. et. al, 2012]. Glassy materials have enormous use in our daily life. We can find its application in our furniture, building materials, spectacles, kitchen-ware, cook-ware, lab-ware, display of electronic gadgets, and so on. These are conventional usages of the glass known by common people. Other scientific applications are found in lasers, fibre optics, sola cell, sensor, smart windows, etc. Depending on the charge conduction species glasses can be divided into two classes namely, ion conducting glass and electron conducting glass. In ion conducting glass, ions are the charge carrier and electrons take part in bond formation in the glass matrix. Such types of glasses find application in electrolytes of solid state batteries [Minami T., 1985]. The conductivity of some of the ion conducting glasses may be as high as  $\sim 10^{-3} \Omega^{-1}\text{cm}^{-1}$  [Minami T, 1985]. These glasses are

known as fast ion conducting glasses or superionic glasses [Minami T., 1985]. Due to the lack of understanding about the detailed structural information of the glassy materials, the mechanism of ion conduction in glassy medium is not properly understood. Several models have been proposed so far to explain the ion dynamics [Sidebottom D. L., 2009, Dyre J. C. et. al, 2000, Funke K., 1993]. However, still there is no widely accepted model of ion dynamics.

It has been observed that tellurite glasses can be used as a matrix for fast ion conduction [Dutta D. et. al, 2004, Dutta D. et. al, 2008]. Tellurite network consists of  $\text{TeO}_4$  tetragonal bipyramid and  $\text{TeO}_3$  trigonal pyramid units. With addition of alkali oxides such as  $\text{Ag}_2\text{O}$  into the glass matrix, the  $\text{TeO}_4$  units are converted to  $\text{TeO}_3$  units with formation of non-bridging oxygen in the glass network. These non-bridging oxygen sites act as charge compensating sites of silver ions and the ions hop from one site to another upon application of the electric field. The conductivity of tellurite glass can be increased significantly with addition of AgI into the glass matrix. It has been observed that the glass network structure is unaffected with incorporation of AgI [Swenson S. et. al, 2001]. However, the free volume of the glass is increased and the I<sup>-</sup> ion of AgI forms a preferential path for the conduction of silver ions leading to the significant enhancement of the conductivity [Swenson S. et. al, 2001].

The ion dynamics of charge carriers in AgI- $\text{Ag}_2\text{O}$ - $\text{TeO}_2$  system has been reported earlier [Dutta D. et. al, 2004, Dutta D. et. al, 2008]. It has been shown that the conductivity of such type of glasses can be increased by increasing the concentration of AgI or  $\text{Ag}_2\text{O}$ . The conductivity spectra in such glasses follow the conventional power law model. The temperature dependence of the dc conductivity and crossover frequency bears the same traits obeying the so called BNN relation [Dutta D. et. al, 2004, Dutta D. et. al, 2008]. However, in the present report a

glass has been prepared with higher AgI content compared to that in previous reports [Dutta D. et. al, 2004, Dutta D. et. al, 2008]. It has been observed that the ion dynamics has been changed with incorporation of high AgI content. It has been observed that the temperature dependence of the dc conductivity and crossover frequency show different types of behaviour violating the BNN relation. The ion conduction mechanism has been explained in the context of well-established jump relaxation model proposed by Funke [Funke K., 1993], apart from the conventional power law model.

## 2. Materials and Methods

A glass composition of the formula  $0.50\text{AgI}-0.50(0.45\text{Ag}_2\text{O}-0.55\text{TeO}_2)$  has been synthesized by conventional melt quenching technique. The appropriate amount of the chemicals AgI,  $\text{AgNO}_3$  and  $\text{TeO}_2$  have been properly weighed in a digital balance as per required stoichiometry. The raw chemicals were mixed properly in an agate mortar and transferred to an alumina crucible. The mixture was calcined at  $400^\circ\text{C}$  for two hours in a high temperature muffle furnace in air atmosphere and finally melted at  $730^\circ\text{C}$  and kept for 30 minutes at this temperature to obtain better homogeneity. The melt was rapidly quenched between two highly polished aluminium plates kept at room temperature. The glass flakes of thickness  $\sim 0.7$  mm were produced. The x-ray diffraction pattern of the powdered glass sample was recorded in an X-ray diffractometer, model Rigaku miniflex 600 from  $2\theta = 10^\circ$  to  $80^\circ$  in step of  $0.02^\circ$ . The high resolution SEM micrographs of the sample were taken using FESEM (Model no.- JSM-6700F, JEOL). Differential scanning calorimetric measurements were performed in a NETZSCH DSC 214 differential scanning calorimeter (DSC) under nitrogen atmosphere. For electrical characterisation; both polished surfaces of the sample were coated with highly conducting silver paste to serve as electrodes. Frequency dependent conductivity measurement was performed using a high precision automatic LCR meter (Hioki make, model IM3536), over a frequency range from 42 Hz to 8 MHz and a temperature range of 103K– 303K in a closed-cycle liquid nitrogen filled cryostat chamber. Eurotherm temperature controller was used to control the temperature with temperature constancy of  $\pm 0.1^\circ\text{C}$ .

## 3. Results and Discussion

Fig. 1 exhibits the x-ray diffraction (XRD) pattern of the glass sample. The sample shows an amorphous hump which confirms the amorphous character of the

prepared sample. There are no prominent diffraction peaks in the spectrum which rules out the presence of significant amount of crystalline volume fraction embedded in the glass matrix. The temperature dependence of the heat flow obtained from differential scanning calorimetry measurement is shown in Fig. 2. The sample shows a baseline shift in heat flow curve. The value of the glass transition temperature ( $T_g$ ) is  $205^\circ\text{C}$  which was obtained from the baseline shift of heat flow curve. The crystallization temperature is  $259^\circ\text{C}$ .

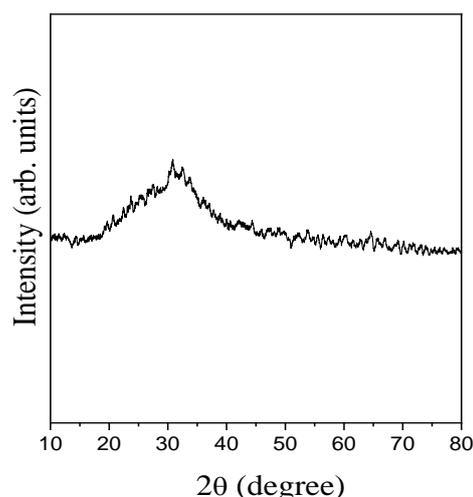


Fig. 1: The XRD pattern of the sample

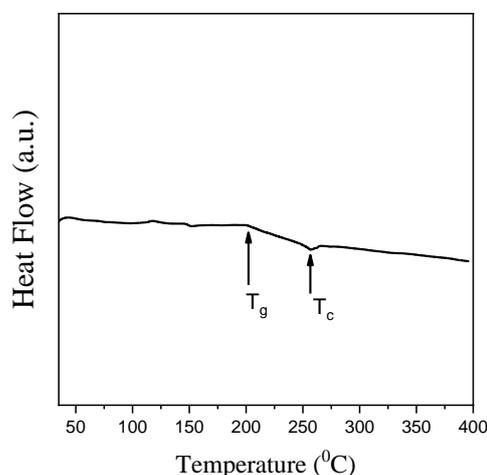


Fig. 2: DSC curve of the sample is shown

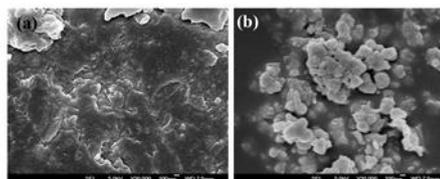


Fig. 3: SEM micrograph of the glass

Fig. 3 depicts the SEM micrographs of the glass sample. Fig. 3(a) reveals the amorphous surface morphology of the sample which is in accord to the result obtained from x-ray diffraction. The image of Fig. 3(b) has been taken from a particular zone of the sample. It is observed that some crystalline grains in nanometer dimension are embedded in the glass matrix. These grains may be produced due to heavy doping of the glass matrix by AgI resulting in some un-reacted AgI dispersed in the matrix [Kabi S. et. al, 2012]. It should be mentioned that such types of grains are very few which were observed in the sample. It may be noted that the x-ray diffraction pattern of the sample does not show any diffraction peak despite the presence of such crystalline grains. This is due to the fact that the volume fraction of these crystalline grains is too low to produce any sharp diffraction peak in the spectrum.

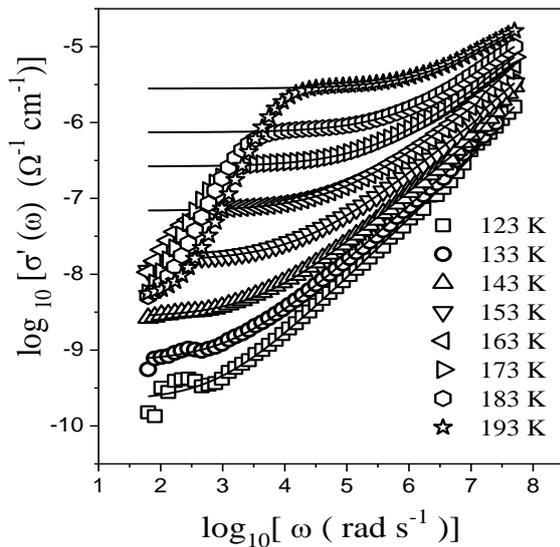


Fig. 4: Real part of the conductivity spectra as a function of frequency at different temperatures. The solid lines are fit to the Eq. 1.

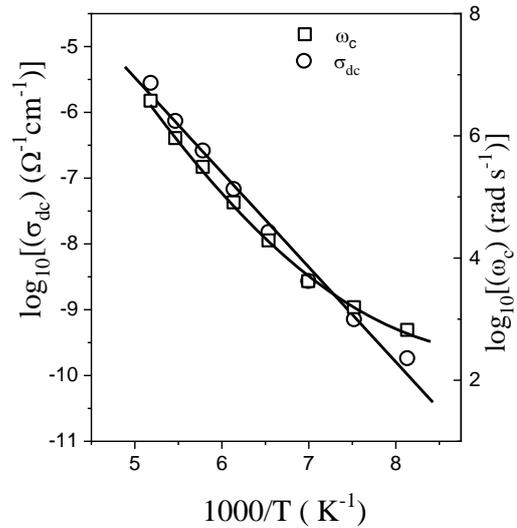


Fig. 5: Reciprocal temperature dependence of the dc conductivity and the crossover frequency is shown. Solid line is least square straight line fit to the experimental data whereas curve line is guide to the eye only.

Fig. 4 shows the real part of the conductivity spectra as a function of frequency of the applied electric field at different temperatures. The spectra are almost similar to those observed for other ion or electron conducting glasses [Sidebottom D. L., 2009]. It has been observed that the shape of the real part of the conductivity spectra of different types of ion conducting disordered materials is almost universal in nature [Sidebottom D. L., 2009]. It is observed from Fig. 4 that there is a levelling off of the conductivity in the lower end of the frequency zone which evolves due to the presence of metallic silver electrode that blocks the silver ions in the glass sample that intends to flow in the external circuit [Sidebottom D. L., 2009]. As a result, a pile up of positive ions occurs in one side of the glass electrode interface, whereas in the opposite side of that interface a depletion zone containing negative charge is formed. This effect is known as electrode polarisation effect. This phenomenon arises solely due to electrode sample interface effect and it does not depend on the type of the sample [Sidebottom D. L., 2009]. However, it is noted from the Fig. 4 that this effect increases with increase of temperature. It is observed that just after the polarisation part of the conductivity spectra, the conductivity remains almost constant up to a certain frequency value. This part of the conductivity spectra is known as frequency independent conductivity or dc conductivity. After a particular value of the frequency the conductivity increases with increase in frequency. This part of the conductivity corresponds to the dispersive conductivity or ac conductivity. There is a crossover frequency, at which the dispersion in the

conductivity starts. The crossover frequency shifts towards higher values with increase of temperature.

It may be mentioned that frequency dependent conductivity of almost all types of ion conducting glasses or polymers follow Jonscher type of power law below a few MHz frequency and moderate temperature range well below to the glass transition temperature [Sidebottom D. L., 2009]. The equation describing this power law is given below [Almond D. P., 1983]

$$\sigma'(\omega) = \sigma_{dc} \left( 1 + \left( \frac{\omega}{\omega_c} \right)^n \right) \quad (1)$$

Here,  $\sigma'(\omega)$  is the real part of the total conductivity,  $\sigma_{dc}$  is the dc conductivity,  $\omega_c$  denotes the crossover frequency from dc to the dispersive conductivity and  $n$  denotes the frequency exponent of the dispersive conductivity. The real part of the conductivity of the sample at several temperatures was fitted to Eq. 1, excluding the polarization part. The values of the fitting parameters such as  $\sigma_{dc}$ ,  $\omega_c$ , and  $n$  were estimated at different temperatures for the sample. The resulting nonlinear fit to the data performed in Origin software is described by the solid lines in Fig. 4.

Fig. 5 describes the reciprocal temperature dependence of the dc conductivity and crossover frequency. Generally, the temperature dependence of the dc conductivity follows Arrhenius relation [Sidebottom D. L., 2009]

$$\sigma_{dc} = \sigma_0 \exp\left(-\frac{E_{dc}}{k_B T}\right) \quad (2)$$

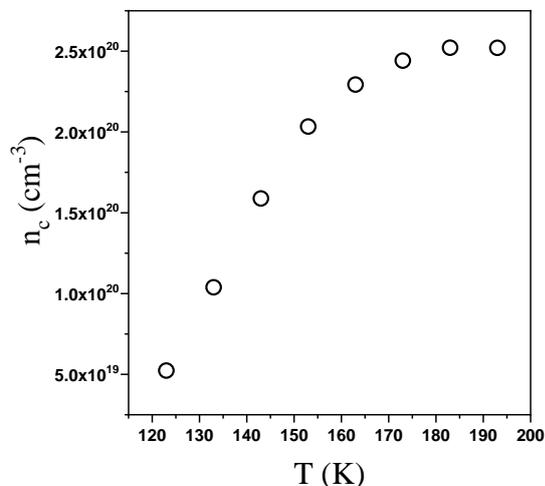


Fig. 6: Mobile ion concentration as a function of temperature for the sample is shown.

It is observed that the dc conductivity for the sample is thermally activated in nature with activation energy of 0.29 eV which was obtained by linear fit to the data according to Eq. 2 as shown by solid straight line in Fig. 5. However, the crossover frequency shows non-Arrhenius behavior described by the curved line in Fig. 5. The BNN relation [Sidebottom D. L., 2009] predicts that

$$\sigma_{dc} = (1/2H_R)\epsilon_0\Delta\epsilon\omega_c \quad (3)$$

Therefore, it is worthy to mention that the temperature dependence of the dc conductivity and crossover frequency should follow the same traits if  $\Delta\epsilon$  remains constant with temperature (other parameters in Eq. 3 are constants). Thus, in the present sample BNN relation is not obeyed in contradiction to that observed in similar kind of samples [Dutta D. et. al, 2004, Dutta D. et. al, 2008]. However, the parameter  $\Delta\epsilon$  also depends on some factors such as the mobile ion concentration and average jump distance of the ions [Sidebottom D. L., 2009]. Therefore, violation of BNN relation may be aroused if mobile ion concentration and average jump distance of the ions change in such a way with respect to temperature so that  $\Delta\epsilon$  remains no more constant with temperature. In fact, it has been observed that the mobile ion concentration ( $n_c$ ) estimated from Nernst-Einstein relation [Ghosh A. et. al, 2009] increases in a non-linear fashion with increase of temperature (Fig. 6). It has also been noted that some crystalline grains have been formed inside the glass matrix. The grains hinder the motion of mobile silver ions [Kabi S. et. al, 2011]. Thus, mobility of the silver ions may be affected with increase of temperatures. Ion-ion interaction may be increased due to high AgI content in the sample. Therefore, multiple effects such as, number density of charge carriers, grain boundary and ion-ion interaction may lead to non-uniform variation in  $\Delta\epsilon$  with respect to temperature resulting in the violation of BNN relation. It has been observed that the value of the frequency exponent  $n$  for the sample is 0.69 ( $\pm 0.03$ ). The value of  $n$  does not vary significantly with respect to temperature.

Jonscher's power law model is an empirical model for the analysis of frequency dependent conductivity data. However, there is no solid theoretical basis for this model and mechanism of ion conduction can not be understood. Funke proposed a model for ion conduction based on jump relaxation theory [Funke K., 1993]. In this model, it has been proposed that a moving ion resides in between an ion cloud formed by the neighboring mobile ions. Each of the ions feels Coulomb repulsion from the neighboring ions. The ions try to stay in minimum Coulomb potential.

When an ion is displaced from position A to position B, two competing relaxation phenomena can occur. In one case, the ion may move backward to its initial position A, passing a low energy barrier. Here correlated backward-forward hopping sequence is formed. It may be noted that in dc conductivity regime the hopping sequence is uncorrelated and random. In another case, the ion cloud will be relaxed in such a way that the new position of the ion i.e. B will be the new potential minimum for the ion. Therefore, the hop becomes successful leading to nonzero conductivity. The temperature dependence of the real part of the conductivity in this model can be expressed by the following relation [Funke K., 1993]

$$\sigma'(\omega)T = A_{dc}e^{-\frac{E_{dc}}{kT}} + A_{ac}\omega^{0.67}e^{-\frac{E_{ac}}{kT}} \quad (4)$$

Fig. 7 describes the reciprocal temperature dependence of the conductivity at different frequencies. It is observed that at low frequency ( $100 \text{ rad s}^{-1}$ ) the conductivity shows single activation energy. However, at higher frequencies two distinct activation energies are observed. Therefore, two different kinds of relaxation mechanism are present at high and low temperatures [Funke K., 1993]. The temperature dependent conductivity data at  $\omega = 10^6 \text{ rad s}^{-1}$  and  $\omega = 10^7 \text{ rad s}^{-1}$  has been fitted to the Eq. 4. Similarly, the frequency dependent conductivity data were also fitted to the Eq. 4 as shown in Fig. 8. The solid curve lines in Fig. 7 and 8, respectively indicates the theoretical lines according to Eq. 4. The values of the parameters such as  $E_{dc}$ ,  $E_{ac}$ ,  $A_{dc}$  and  $A_{ac}$  were estimated from non-linear curve fitting to the experimental data performed by Origin software. The high temperature activation energy i.e.  $E_{dc}$  slightly depends on frequency and temperature. It is caused by the jump relaxation mechanism with a Vogel-Tammann-Fulcher type temperature dependence. It has been observed that the value of  $E_{dc}$  obtained at  $\omega = 10^6 \text{ rad s}^{-1}$  is  $0.26 \text{ eV}$  which reduced to  $0.21 \text{ eV}$  at  $\omega = 10^7 \text{ rad s}^{-1}$ . However, the value of  $E_{dc}$  was  $0.25 (\pm 0.02) \text{ eV}$  in experimental temperature range. On the other hand, the value of low temperature activation energy  $E_{ac}$  was almost independent of frequency and temperature with a value of  $0.06 (\pm 0.01) \text{ eV}$ . The value of  $A_{dc}$  was  $1.25 \times 10^3 (\pm 0.5 \times 10^3) \Omega^{-1} \text{ cm}^{-1} \text{ K}$  and the value of  $A_{ac}$  was  $2.52 \times 10^{-7} (\pm 0.5 \times 10^{-7}) \Omega^{-1} \text{ cm}^{-1} \text{ K}$ .

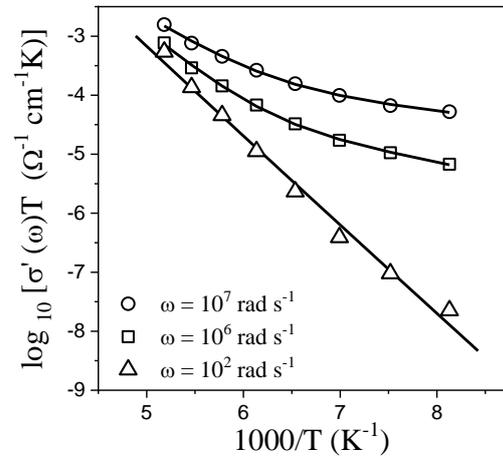


Fig. 7: Reciprocal temperature dependence of the conductivity at three selected frequencies. Curved solid lines are fit to the experimental data according to Eq. 4. Solid straight line is least square straight line fit.

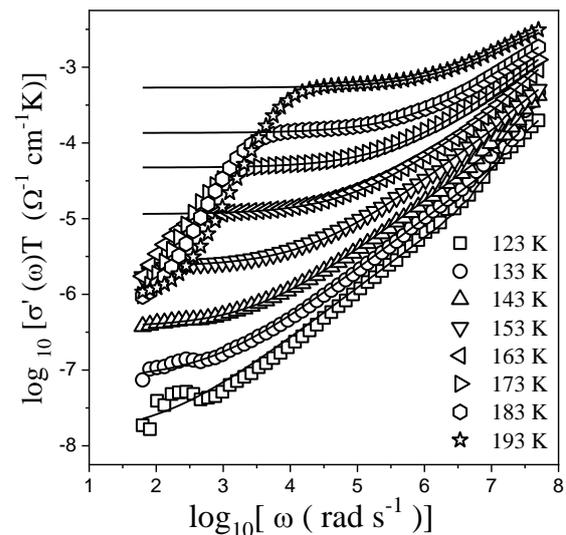


Fig. 8: Fitting of frequency dependent conductivity data according to jump relaxation model (Eq. 4). The solid lines indicate the fit to the data.

### 3. Conclusions

The silver tellurite glass matrix is amorphous but some crystalline grains have been formed due to heavy doping of AgI into the glass matrix. The heavy doping in glass results in the increase of ion-ion interaction. The dc conductivity of the glass increases with temperature in Arrhenius fashion. However, the temperature dependence of crossover frequency shows non-Arrhenius behavior. The BNN relation is not hold for the present sample. Formation of crystalline grains, increase of ion-ion interaction and increase of charge carrier density with temperature are responsible for such type of behavior. The ion dynamics has been explained in the context

of Jump relaxation theory. Presence of two distinct activation energies indicates that two separate relaxation processes are involved in high and low temperatures.

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