Understanding the Composition Dependence of the Fragility of AgI-Ag$_2$O-M$_x$O$_y$ Glassy Systems

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Abstract. It has been reported that the fragility in the AgI-Ag$_2$O-M$_x$O$_y$ (M = B, Ge, P, Mo) system is determined by Ag$_2$O-M$_x$O$_y$ and does not depend on the amount of AgI. This is an interesting result and provides a hint to understand the nature of the glassy state of these materials. However, the origin of such behavior has not been sufficiently discussed. In the present report a model for the above behavior is presented. According to the model, the behavior arises from the solid like nature of the network formed by Ag$_2$O-M$_x$O$_y$ and the liquid like AgI which flow between the networks. The model is consistent with the structural model of superionic glasses proposed previously.

1. Introduction

Superionic conducting glasses have attracted considerable interest for the last several years. Investigation of ionic conductivity in vitreous materials is interesting from both academic and practical points of view. The 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 in glasses remains poorly understood. The topic covered in the present report is also one of the subjects not well understood.

The temperature dependence of the viscosity or relaxation time for various glass forming materials can be characterized by using the concept of fragility, which quantifies the degree of deviation from the Arrhenius behavior [1]. The concept of fragility has been used widely and has played a fundamental role in understanding the relaxation behavior of supercooled liquids. Concerning the fragility of superionic glass forming system and related materials, some studies have been reported [2-4]. Among these, the most interesting behavior is the composition dependence of the fragility exhibited by AgI-Ag$_2$O-M$_x$O$_y$ (M = B, Ge, P, Mo) system. Contrary to the naive expectation that the fragility in these systems will increase with the concentration of AgI due to the enhancement of the ionic conductivity, the measured data do not depend on the concentration of AgI [2,3]. This behavior is proving a clue to understand the nature of the glassy state of superionic glasses. However, as far as the author is informed, studies aimed to understand the behavior from a fundamental point of view have not been performed.

In the present report, a model to explain the composition dependence of the fragility in AgI-Ag$_2$O-M$_x$O$_y$ system is presented. According to the model, the fragility is determined by the solid like nature of the network formed by Ag$_2$O-M$_x$O$_y$. The degree of the fragility is described in terms of the parameters defined by the Bond Strength –Coordination Number Fluctuation (BSCNF) model of

the viscosity [5]. The notion gained from the analysis of the composition dependence of the fragility of AgI-Ag$_2$O-M$_x$O$_y$ system is in harmony with the model of superionic glasses proposed by some researchers [6,7] and with the correlation between ionic conduction and medium range structure of glasses found by the author [8].

2. Structural Model of Superionic Glasses

It has been shown some years ago that the ionic conductivity and the activation energy of ion transport in AgI-Ag$_2$O-M$_x$O$_y$ glasses increases and decreases respectively, with the decrease of the First Shatp Diffraction Peak (FSDP) wave number [8]. The behavior has been explained by using a structural model whose activation energy profile is illustrated in figure 1. The key point of this model was the recognition that in AgI-Ag$_2$O-M$_x$O$_y$ glasses, the Ag atoms form at least three types of bonds. The Ag-I bond dominant in the doped salt, the Ag-O bond dominant in the network, and the I-Ag-O bond that abound in the boundary sites between doped salt and network. According to the bond fluctuation model of superionic conductors [9] the I-Ag-O bonded Ag ions are more mobile, because these Ag ions feel an asymmetric field of forces which result in the local atomic site instability. The high ionic conductivity results from the percolation of these sites [8]. Since the concentration of these sites increases and the FSDP wave number decreases with the concentration of AgI, the correlation between FSDP wave number and ionic conductivity mentioned above is explained straightforwardly [8]. The model of AgI-Ag$_2$O-M$_x$O$_y$ glasses illustrated in figure 1 is consistent with the network expansion that occurs by adding AgI in Ag$_2$O-M$_x$O$_y$ glasses [6,7].
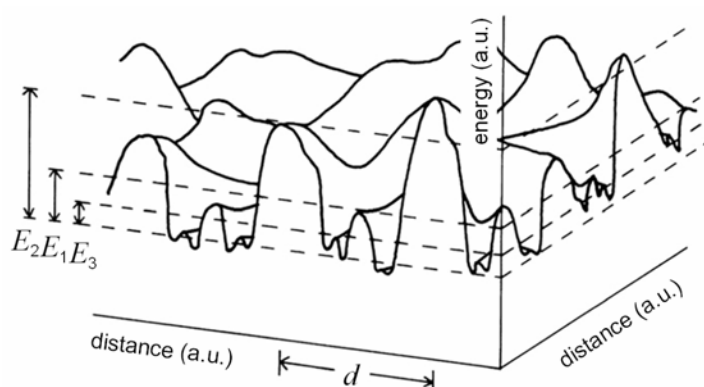
Figure 1. A schematic representation of the energy barrier profile in superionic glasses. E_1 and E_2 are the average values of the activation energies in the doped salt and in the network, respectively. E_3 is the activation energy of the highly conducting sites. d is a distance that characterizes the medium range structure. The FSDP wave number is given by 2 /d.

3. Model for the Fragility

The BSCNF model of the viscosity has been proved to be a very useful model in the analysis of the fragility of many kind of materials [5,10]. According to this model, the fragility is determined by the relaxation of structural units that form the melt. In terms of the parameters of the model, the fragility is given by

$$F = \frac{R}{T_g}\left(\frac{\partial \ln \eta}{\partial (1/T)}\right)_{T_g} = \frac{B - C + 2[\ln(\eta_{T_g}/\eta_0) + 0.5\ln(1-B)]}{1-B}R \,, \tag{1}$$

where

$$C = \frac{Z_0 E_0}{RT_g} \quad \text{and} \quad B = \frac{(\Delta Z)^2 (\Delta E_0)^2}{R^2 T_g^2} \,.$$

Here, E_0 and Z_0 denote the average values of the binding energy and coordination number of the structural units, and ΔE and ΔZ are their fluctuations, respectively. R is the gas constant and T_g is the glass transition temperature. η_{Tg} and η_0 are the viscosities at the glass transition temperature and at the high temperature limit, respectively. The parameter C gives the total bond strength between the structural units and B gives its fluctuation.

In a previous study, it has been shown that the typical value of the parameters B and C in AgI-Ag$_2$O-M$_x$O$_y$ glass forming systems are $C \approx 10\text{-}20$ and $B \approx 0.4\text{-}0.5$ [11]. Form the analysis of this value, it been shown that bond breaking of about 10 structural units are necessary for the occurrence of viscous flow. The analytical expression that describes this quantity is given by [12]

$$N_{\mathrm{B}} = \frac{B - C + 2[\ln(\eta_{Tg}/\eta_0) + 0.5\ln(1-B)]}{(1-B)C} \, . \tag{2}$$

The above quantity carries information on the cooperative motion between the structural units. Its relation with other theories of glasses is given elsewhere [12].

4. Composition Dependence of the Fragility in AgI-Ag$_2$O-M$_x$O$_y$

As illustrated in figure 1, the glassy network in AgI-Ag$_2$O-M$_x$O$_y$ is determined by Ag$_2$O-M$_x$O$_y$. The network forming ability can be evaluated for instance, by using the average electronegativity. According to this scale, the network forming ability of Ag$_2$O-M$_x$O$_y$ is much higher than that of AgI [13]. The same conclusion could be obtained by applying other scales of glass formation. The network starts to develop in the liquid phase and freezes at T_g. On the other hand, the AgI component is dispersed between the networks as evidenced from the neutron scattering data [7]. The AgI is the main source for the Ag$^+$ ions that diffuses through the sites denoted by E_3 in figure 1. By lowering the temperature below T_g, the mobile Ag$^+$ ions are also frozen as detected by thermal analysis [14]. The above observations indicate that in the liquid phase of AgI-Ag$_2$O-M$_x$O$_y$ close to the glass transition temperature, the Ag$_2$O-M$_x$O$_y$ tend to solidify whereas AgI remains liquid like. In other words, for the occurrence of viscous flow, the structural units must overcome the energy barrier determined by the network forming Ag$_2$O-M$_x$O$_y$ component. This situation can be formulated in a simple way as

$$E_\eta(T) = [1 - V(T)]E_1 + V(T)E_s \tag{3}$$

where E_η, E_1 and E_s are the activation energies for viscous flow of the system, the liquid like and the solid like components, respectively. $V(T)$ is the volume fraction of the solid like component which depends on temperature T. In addition to the inequality $E_1 < E_s$, $V(T)$ approaches 1 at temperature close to T_g. Thus, for the materials type in considerations we have

$$E_\eta \approx E_s \, . \tag{4}$$

According to the definition of the fragility given by the first equality of equation (1) we have

$$F = E_\eta / T_g \, . \tag{5}$$

From equations (4) and (5), we recognize that the fragility of the AgI-Ag$_2$O-M$_x$O$_y$ system is determined by the solid like network forming component. This explains the origin of why the fragilities in AgI-Ag$_2$O-M$_x$O$_y$ systems do not depend on the concentration of AgI [2,3]. It should be noted that the present model puts in harmony many properties of AgI-Ag$_2$O-M$_x$O$_y$ system reported till

now.

The degree of the fragility can be evaluated from equation (1) and its application to AgI-Ag$_2$O-M$_x$O$_y$ system has been described briefly in section 3. By comparing the values of B and C mentioned there with the values determined for other systems, we note that the fragility of the system in consideration takes an intermediate value. It is not strong as in SiO$_2$, nor fragile as in ZBLA [10]. This is an important point that should be noted, because it indicates that the existence of certain degree of rigidity in the network is favorable for the fast ion transport. This observation is also consistent with the prediction of the bond fluctuation model of superionic conductors, which requires the presence of certain degree of bond bending force constant to originate the correlated ion dynamics [9].

In a previous study related to the topic described in section 2, it has been predicted that there must be an optimal value of the FSDP wave number for an efficient ion transport processes. This prediction linked with the present model suggests that at the composition where the FSDP wave number is expected to exhibit a minimum, the fragility of the system will start to increase due to the disruption of the network. However, experimental studies done till now were not successful into synthesize glasses with large amount of AgI due to the crystallization. A possible candidate material to observe the predicted behavior could be AgI-alkylammonium which exhibits a FSDP at relatively low wave number.

5. Conclusion

The fragility of the AgI-Ag$_2$O-M$_x$O$_y$ system is determined by Ag$_2$O-M$_x$O$_y$ and does not depend on the composition of AgI. In the present study, a model to explain such a behavior has been proposed. According to the model, the network forming tendency of Ag$_2$O-M$_x$O$_y$ determines the fragility and the AgI is dispersed in the spaces formed between the networks. The result is in harmony with the model of superionic glasses proposed by some researchers and with the result of the correlation between ionic conduction and medium range structure of glasses found by the author.

Acknowledgment

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