

Structural characterization of the ac conductivity in Ag ion conducting glasses

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Abstract The material trends in various silver ion conducting glasses have been studied recently by focusing on the relationship between the first sharp diffraction peak (FSDP) wave number Q , and the fitting parameters of the ac conductivity, precisely the ratio $(\log A)/n$, where A and n represent the pre-exponential factor and the power law exponent of Jonscher's law, respectively. In the present paper, a model for the FSDP wave number dependence of the ratio $(\log A)/n$ has been proposed and a good agreement has been found with the experiments. By using the concept of bond fluctuation in superionic conductors, the results have been successfully explained, leading to the conclusion that the universal aspect of the power law reflects the universal pattern of the potential barrier at intermediate length scales. The result reconfirms that the ion transport in glasses is intimately related with the FSDP wave number.

Introduction

Amorphous solid electrolytes form a class of materials currently under intensive investigations for their possible applications in a variety of devices including batteries, fuel cells, sensors, electrochromic displays, etc. [1]. The conductivity of best ionic conducting glasses may reach up to 10^{-2} S/cm at room temperature. Although the details

depend on the glass in consideration, most glasses exhibit several advantages over crystalline electrolytes such as physical isotropy, absence of grain boundaries, continuously variable composition, and good workability [2]. Materials such as ceramics, ionic or electronic conducting polymers, ionic conducting glasses, amorphous semiconductors, metal cluster compounds, transition metal oxides, etc. share a common frequency dependent conductivity which is characterized by a low frequency region of constant conductivity known as dc conductivity, followed by a gradual transition at higher frequencies to a frequency dependent conductivity [1–9]. A large number of studies have been done to better understand this universality, but to date, no theory has yet received a non-controversial acceptance [10]. Recently, Papathanassiou [11] reported that for the glassy system $[(\text{Li}_2\text{O})_x(\text{Na}_2\text{O})_{1-x}]_{0.3}(\text{B}_2\text{O}_3)_{0.7}$, the ratio $(\log A)/n$ with $n > 1$, is composition independent up to the THz frequencies, where A and n represent the pre-exponential factor and the exponent of the power law. This behavior is related to the mixed alkali effect of A and n reported by Cramer et al. [12]. That is, the minimum in $\log A$ is accompanied with a maximum in n , which implies that the ratio $(\log A)/n$ does not depend on the composition. Motivated by this finding, the composition dependence of the ratio $(\log A)/n$ has been investigated for some AgI and Ag_2S based superionic glasses. The results have ascertained that the ratio varies with respect to the nature of the glass and on the composition as shown in Fig. 1. Therefore, the constancy of $(\log A)/n$ reported in [11] is not observed for the glassy systems considered here. Data of pre-exponential factor A , power law exponent n , and composition x have been taken from references [13–17] for the glassy systems $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$, $(\text{AgI})_x(0.5\text{Ag}_2\text{O}-0.5\text{MoO}_3)_{1-x}$, $(\text{Ag}_2\text{O})_x(\text{MoO}_3)_{1-x}$, $(\text{Ag}_2\text{S})_x(\text{AgPO}_3)_{1-x}$, and $(\text{Ag}_2\text{S})_x(\text{Ag}_4\text{Te}_3\text{O}_8)_{1-x}$, respectively.

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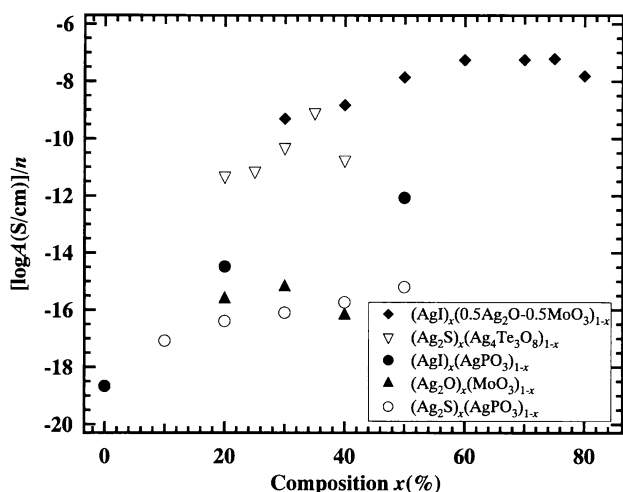


Fig. 1 The composition dependence of the ratio $(\log A)/n$ for different systems of superionic glasses

Recently, based on the previous works [10], further investigations have been made to better understand the subject by studying the relationship between the FSDP wave number and the ratio $(\log A)/n$ for the glassy systems $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$, $(\text{Ag}_2\text{O})_x(\text{B}_2\text{O}_3)_{1-x}$, $(\text{AgI})_x(\text{Ag}_2\text{O}-2\text{B}_2\text{O}_3)_{1-x}$, $(\text{Ag}_2\text{S})_x(\text{AgPO}_3)_{1-x}$, and $(\text{AgI})_x(\text{Ag}_2\text{O})_{0.6}(\text{V}_2\text{O}_5)_{0.4}{}_{1-x}$. It has been found that the ratio $(\log A)/n$ is intimately related to the FSDP wave number [18]. In the present paper, the study is extended to other systems and a model for the FSDP wave number dependence of the ratio $(\log A)/n$ is proposed. It will be shown that the prediction of the model shows a good agreement with the experimental results.

The ac electrical response of disordered materials

Concerning the electrical ac response, there is abundant experimental evidence showing almost identical characteristics irrespective of the conductor material type. In addition, a variety of other phenomena such as dipolar dielectric relaxation, hopping electron ac conductivity, viscoelasticity, mechanical relaxation, NMR relaxation associated with hopping ions, etc. exhibit similar and seemingly related characteristics. Jonscher [4] has suggested that there is a “universal relaxation law” based on the indisputable common property of all condensed matter: the many body interactions between their constituent parts. A large number of theoretical models such as random potential energy model [19], jump relaxation model [20], vacancy model [21], symmetric hopping model [5], etc. have been proposed in order to explain this “universality”, but to date no consensus has been obtained. These models can be classified into three groups: network models, Debye

relaxation models with distributions of relaxation times (DRT), and models employing fundamentally modified atomic level relaxation processes [22].

The ac conductivity $\sigma(\omega)$ in glasses is described as [4]

$$\sigma(\omega) = \sigma(0) + A\omega^n, \quad (1)$$

where $\sigma(0)$ is the dc conductivity (low frequency) corresponding to the frequency independent part of $\sigma(\omega)$, n is the power law exponent varying roughly between 0.6 and 0.7 at room and higher temperatures but is found universally to rise to 1.0 at low temperatures [22], and A is a constant given by

$$A = \omega_c^{-n} \cdot \sigma(0), \quad (2)$$

where ω_c represents the onset frequency of the dispersive behavior.

Nowick et al. [23] have shown that in the region between constant loss regime ($n = 1$) and Jonscher regime ($n \approx 0.6$), it is possible to treat the data as a superposition of both regimes. In other words,

$$\sigma(\omega) = \sigma(0) + A\omega^n + B\omega. \quad (3)$$

The exponent value of 0.6 in Jonscher regime is considered to arise by the ion–ion interactions. During the process of the hopping of the ions, even separate hopping events may have a broad distribution of relaxation times, and this effect can manifest as stretching of the relaxation times. Thus, the term $A\omega^n$ exhibits activated temperature dependence in contrary to the term $B\omega$ which exhibits only weak temperature dependence. The exact origin of the last term is unclear. However, some authors believe that it may be the result of low energy distortions occurring in the network [24]. In the Jonscher regime, the estimated value of $(\log A)/n$ can be deduced from (2) as

$$(\log A)/n = (\log \sigma(0))/n - \log \omega_c. \quad (4)$$

Medium range structure and ion dynamics in superionic glasses

The structural correlations that exist in glasses on a length scale typically of the order of 1 nm (larger than atomic bond lengths, typically 0.1–0.3 nm but smaller than the scale of inhomogeneities when they exist, normally ≥ 5 nm) are referred to as “intermediate range order” [25]. Their existence is demonstrated through characteristic signatures in various properties, such as neutron and X-ray diffraction patterns and Raman spectra, and they are unquestionably related to the peculiar dynamics of glasses and to ionic transport through the network. Intermediate range order exists in different forms in molecular glasses, pure and modified network glasses, and fast ion conducting glasses [25]. The most general and persistent evidence of

intermediate range order is the first sharp diffraction peak (FSDP), the feature observed at low wave vector in the structure factor $S(Q)$ of many systems, including oxides and complex liquids [26]. The distance that characterizes the medium range structure, d , is related to the FSDP wave number Q by

$$d = 2\pi/Q. \tag{5}$$

The role of intermediate range structure on the ion transport properties has been studied by one of the authors [27]. There, the concept of bond fluctuation model of superionic conductors has been used to interpret the results. The bond fluctuation model suggests that in superionic conductors, the change of bonding that occurs locally and fluctuates in time is playing an important role. The local fluctuation of the bonding creates a field of forces to move the ions, which in turn, triggers new bond fluctuations. According to this model, materials become superionic when the number of bond fluctuating sites increase to a certain extent [28].

Modelisation of the ionic conductivity, the activation energy, and the power law exponent

In order to extract information about the influence of the glassy structure on the ionic transport, the relationship between the ionic conductivity and the wave number where the first sharp diffraction peak is observed has been studied [29]. As shown in Fig. 2, it is observed that the ionic conductivity $\sigma(0)$ increases as the FSDP wave number Q decreases. Figure 2 indicates that the trend can be approximated as

$$\log \sigma(0) = \alpha Q + \beta, \tag{6}$$

where α and β are constants. Data of ionic conductivity and FSDP wave number have been taken from references [30–34] and [30, 33, 35–37], respectively.

It has also been observed that the activation energy of the ionic conductivity depends strongly on the FSDP wave number [27]. This is a strange result because the activation energy is expected to be determined mainly by short-range interatomic interactions. Such a behavior has been explained by using the energy barrier profile suggested by the bond fluctuation model. The model predicts that the activation energy for ion transport initially decreases by doping salt, reaches a minimum at certain concentration, and increases by further doping, whereas in this course the FSDP wave number decreases monotonically [27]. In the range of FSDP wave number shown in Fig. 3, the relationship between the activation energy and the FSDP wave number can be approximated as

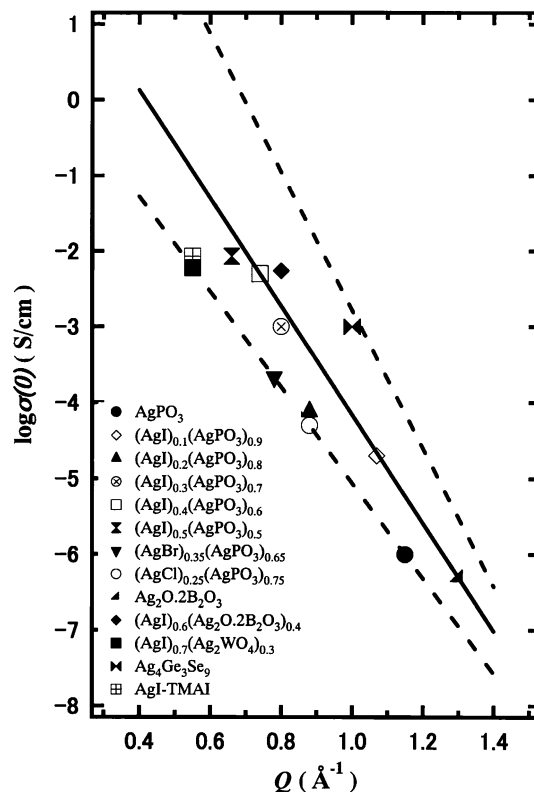


Fig. 2 Relationship between the ionic conductivity of glasses at room temperature and the FSDP wave number. The full line is given by (6) with $\alpha = -7.142$ and $\beta = 2.984$. Broken lines indicate the scatter regions of the data

$$E_a = \gamma Q + \delta, \tag{7}$$

where γ and δ are constants. Data of activation energy of ion transport and FSDP wave number have been taken from references [30–34] and [30, 33, 35–37], respectively.

The onset frequency of the dispersive behavior ω_c can be approximated as

$$\omega_c = \omega_0 \exp[-E_a/k_B T], \tag{8}$$

where the symbols have usual meanings. For the value of ω_0 we have adopted a typical value of atomic vibration in solids, $\omega = 10^{12}$ rad/s. By substituting (7) into (8), we have

$$\omega_c = 10^{12} \exp[-(\gamma Q + \delta)/k_B T]. \tag{9}$$

The relationship between the FSDP wave number and the power law exponent n of the ac conductivity dispersion has been studied for many glasses. It has been observed that the FSDP wave number decreases and the power law exponent increases with the increase in the concentration of the salt [10]. From such a relationship it has been suggested that the universality of the power law reflects the universal pattern of the energy barrier profile at intermediate length scales. The relationship between the FSDP wave number

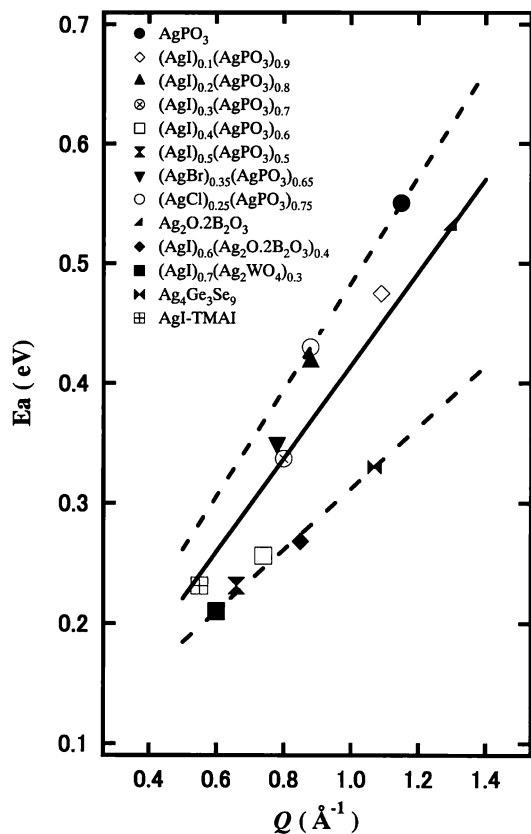


Fig. 3 Relationship between the activation energy of the ionic conductivity of glasses at room temperature and the FSDP wave number. The full line is given by (7) with $\gamma = 0.388$ and $\delta = 0.026$. Broken lines indicate the scatter regions of the data

and the power law exponent of the ac conductivity shown in Fig. 4 can be approximated as

$$n = \lambda Q + \mu, \quad (10)$$

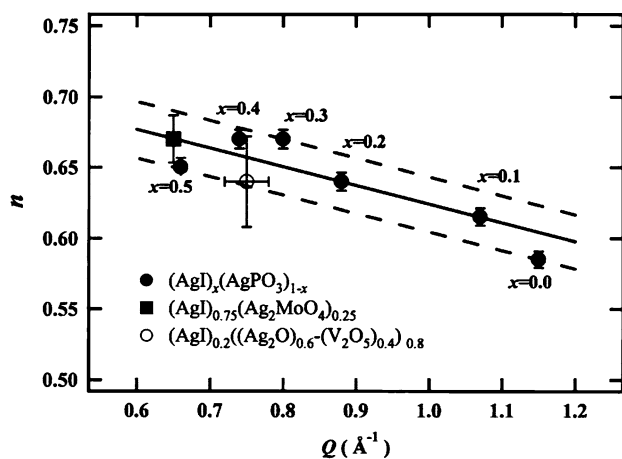


Fig. 4 Relationship between the power law exponent of the ac conductivity of glasses at room temperature and the FSDP wave number. The full line is given by (10) with $\lambda = -0.131$ and $\mu = 0.755$. Broken lines indicate the scatter regions of the data

where λ and μ are constants. Data of power law exponent and FSDP wave number have been taken from references [1, 14, 38] and [30, 36, 39], respectively.

Application of the model and discussion

Based on the interrelations between the FSDP wave number and the ion transport properties given above, the FSDP dependence of the ratio $(\log A)/n$ can be predicted. From (4), we obtain

$$(\log A)/n = \frac{\alpha Q + \beta}{\lambda Q + \mu} - \log\{10^{12} \exp[-(\gamma Q + \delta)/k_B T]\}. \quad (11)$$

Despite experimental data to verify directly the above expression is very scarce, the workability of the model has been checked. The result is shown in Fig. 5. Data of pre-exponential factor A , power law exponent n , and FSDP wave number Q have been taken from the references [1, 14, 30, 36, 38, 39, 40, 41] for the glassy systems $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$, $(\text{Ag}_2\text{O})_x(\text{TeO}_2)_{1-x}$, $(\text{AgI})_{0.75}(\text{Ag}_2\text{MoO}_4)_{0.25}$, and $(\text{AgI})_{0.2}((\text{Ag}_2\text{O})_{0.6}-(\text{V}_2\text{O}_5)_{0.4})_{0.8}$, respectively.

The model shows a good agreement with the experimental data. Figure 5 confirms that the ion transport in glasses is intimately related to the FSDP wave number. The agreement supports the view that the universal aspect of the power law reflects the universal pattern of the potential barrier at intermediate length scales [10].

The relationship between the FSDP wave number and the ion transport properties in superionic conductors shown in Figs. 2, 3, and 4, can be explained by using the concept of

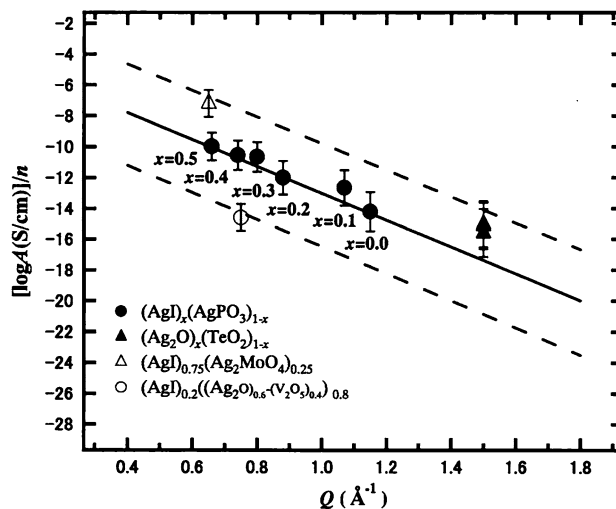


Fig. 5 Comparison between the calculated and the measured values of the ratio $(\log A)/n$ at room temperature for some glasses. The full line is calculated by (11) with the constants given in the previous figures. Broken lines indicate the scatter regions of the data

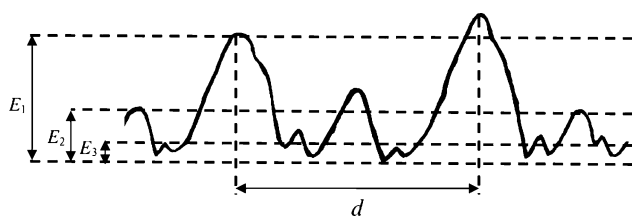


Fig. 6 A schematic representation of the energy barrier profile. E_1 and E_2 are the average values of the activation energies in the network and in the doped salt, respectively. E_3 is the activation energy in the highly conducting sites whose existence is predicted by the bond fluctuation model

the bond fluctuation model of superionic conductors proposed by one of the authors [28]. Glasses are prepared by rapidly cooling the melt, before the system reaches its thermal equilibrium. Therefore, at the microscopic level, inhomogeneities of the local structure and local chemical composition remain. From the chemical bond point of view, if we focus on $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$ glasses for instance, we can distinguish at least three types of Ag^+ ions. The Ag^+ ions in the doped salt which are bonded with I^- , the Ag^+ ions in the network which are bonded with O^{2-} , and the Ag^+ ions located in the boundary between network and doped salt which are bonded with I^- and O^{2-} . According to the bond fluctuation model, the third type of Ag^+ ions are more mobile than others, because the Ag^+ ions surrounded by different atoms feels an asymmetric field of forces which results in the anharmonic atomic vibration and large atomic migration. In the schematic representation of the energy barrier profile shown in Fig. 6, such processes occur mainly in the highly conducting sites which have small average activation energy, denoted as E_3 [10]. From this figure it is easy to understand the increase of the characteristic distance d and the decrease of the FSDP wave number Q by the increase in the composition of AgI .

It is worth to note here that the various models of ionic and electronic ac conductivity that have been proposed in the past [2, 5–9] share in part the notions gained in the present study. In most of these models, random distributions of potential barriers or energy levels that reflect the structure of the material are assumed. In the case of ionic conduction, the quantities that characterize the transport phenomena A and n will depend on the hopping probability of the ions across the random potential barriers. In the case of electronic conduction, A and n will depend on the magnitude of the tunneling or hopping of the electrons between the random distribution of energy levels.

Conclusion

The ratio $(\log A)/n$ has been estimated for many superionic glasses and it has been found that there is a good agreement

with experiments. The composition dependence of the FSDP wave number has been used to predict the composition dependence of the ratio, independently on the nature of the glass. The concept of bond fluctuation has been successfully used to explain the results which suggest that the universal aspect of the power law reflects the universal pattern of the potential barrier at intermediate length scales. Further experimental studies are needed to verify the prediction of the model.

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