

# Medium range structure and power-law conductivity dispersion in superionic glasses

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## **Abstract**

The relationship between the exponent of the power law behavior in the ac conductivity and the wave number of first sharp diffraction peak (FSDP) in superionic glasses has been studied. For the case of  $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$  glasses, it is shown that the exponent of the power law increases with the decrease of the FSDP wave number. Other superionic glasses such as  $(\text{AgI})_{0.2}(\text{0.6Ag}_2\text{O-0.4V}_2\text{O}_5)_{0.8}$  and  $(\text{AgI})_{0.75}(\text{Ag}_2\text{MoO}_4)_{0.25}$  follow this trend. The relationship found is explained by using the energy barrier profile for the mobile ions in a disordered structure. The local energy barrier for the ion movement is determined by the local structure and bonding, and the ions flow through the low energy barrier sites. According to the model, the exponent of the power law contains information about the degree of connectivity of these low energy sites that extend at the intermediate length scale. The result suggests also that the universal aspect of the power law reflects the universal pattern of the potential barrier at intermediate length scales.

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## 1. Introduction

Superionic conducting glasses have attracted considerable interest for the last several years [1-35]. Investigation of ionic conductivity in vitreous materials is interesting from both academic and practical points of view. Speaking from a practical aspect, results from their use as key materials for solid state electrochemical devices has raised interest. The academic interest arises from the fact that the mechanism of ion transport and ion dynamics in glasses remain poorly understood. Despite the large number of studies that have been done, no theory of ion conduction in glasses has yet received general acceptance.

Most existing models of superionic glasses such as the diffusion path model [1], cluster model [6], cluster bypass model [2], etc., relate the ion transport to some specific structural features. However, there is a lack of investigation concerning the role of medium range structure on the ionic conduction in glasses. In order to fill this gap, the interrelations between ionic conductivity, network expansion by salt doping, medium range order, and average electronegativity in AgI containing oxide glasses have been studied [7,8]. There it was shown that salt doping in glassy matrix results in the decrease of the average electronegativity, increase of the ionic conductivity, and decrease of the wave number of first sharp diffraction peak (FSDP). In contrast, in Li ion conducting oxide glasses and Ag or Cu ion conducting chalcogenide glasses, the FSDP wave number decreases with the increase of average electronegativity [9]. Such difference has been interpreted in terms of the tendency of network formation and dissociation, which is quantified by the average electronegativity [9].

On the other hand, large numbers of studies have been done concerning the ac conductivity dispersion in glasses [10-25]. The most fascinating aspect of the ac conductivities is that they are quite similar irrespective of whether they are glasses, polycrystalline semiconductors, polymers, transition metal oxides, organic-inorganic composites, etc. [10]. These facts indicate the existence of a universality in the ac conductivity which transcends the difference in conduction mechanisms.

In view of the above situations, it is of considerable interest to investigate the role of the medium range structure in the ac conductivity dispersion. In the present contribution, the relationship between the exponent of the power law in the ac conductivity and the FSDP wave number in the superionic glass  $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$  is studied. For the sake of comparison, data of other glasses such as  $(\text{AgI})_{0.2}(\text{0.6Ag}_2\text{O}-\text{0.4V}_2\text{O}_5)_{0.8}$  and  $(\text{AgI})_{0.75}(\text{Ag}_2\text{MoO}_4)_{0.25}$  have been also considered.

## 2. Conductivity dispersion

Studies of ac conductivities in superionic glasses up to far-infrared frequencies provide a valuable tool for understanding the ion dynamics in these materials. A common feature of the ac conductivity in ion conducting glasses and other materials is that it is composed of a plateau at low frequencies, and of a frequency dependent dispersion part at high frequencies [10-27]. The frequency independent plateau



part corresponds to the dc conductivity,  $\sigma(0)$ . It is known that the ac conductivity can be well described as

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

where  $A$ ,  $B$  and  $n$  are constants. The term  $A\omega^n$  exhibits activated temperature dependence and it is due to the ionic transport. Experimentally, it is known that the exponent  $n$  of ion conducting glasses take values that vary roughly between 0.5 and 0.7. On the other hand, the term  $B\omega$  exhibits only weak temperature dependence. Concerning the origin of this term, its exact origin is unclear. However, some authors believe that it may be the result of low energy distortions occurring in the network [20]. In the following, we will concentrate on the conductivity dispersion related to the first process. That is, on the processes related to the ion transport.

Concerning the conductivity dispersion of ion conducting materials, Sidebottom has found an interesting behavior [20]. He showed that the power law exponent  $n$  decreases with the decrease of the dimensionality of the ion conduction pathways. For instance, in alkali- oxide, thiosilicate, and thioborate glasses which form homogeneous disordered networks and have three dimensional ionic pathways, the exponent takes a value of  $n \approx 0.67$ . On the other hand, in  $\beta$ -aluminas, which have two dimensional pathways, the exponent is  $n \approx 0.60$ . For the one dimensional ionic conductors priderites and hollandites, the exponent takes the value that lies between 0.22 and 0.40.

The measurements of the ac ionic conductivities in  $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$  glasses have revealed that the exponent  $n$  increases with the content of AgI, and the increase in the expansion of the network [21]. On the other hand, in alkali metal metaphosphate glasses,  $\text{MPO}_3$ , where  $\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Rb}$  or  $\text{Cs}$ ,  $n$  decreases with the network expansion. When  $n$  is considered as a function of the “constriction” of the cation ( i.e., the cation size relative to the chain separation ), the exponent  $n$  behaves similarly for both  $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$  and  $\text{MPO}_3$ , glass systems. That is,  $n$  decreases with the increase in the constriction of the cations [21]. Such a result has been interpreted as a result from a reduction in the coordination of the cation’s local conduction space caused by increased constriction. This observation of the ionic conduction pathway dimensionality dependence of the exponent  $n$  motivated the investigation into the relationship between  $n$  and the medium range structure of the glasses presented in this paper. Concerning the composition dependence of  $n$  in  $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$  glasses, it will be fair to mention that there is also a report that does not observe the composition dependence [22]. Based on experimental results reported in many glasses, in the present report, it is considered that  $n$  depends on composition.

### 3. Medium range structure and ionic conductivity

Various structural studies in glasses have shown the presence of a characteristic peak at low values of momentum transfer [36,37]. This peak, which is called first sharp diffraction peak (FSDP), has been



interpreted to arise from some kind of intermediate range ordering within the glass. There has been a lot of debate about the origin of FSDP. The specific interatomic correlations that originate the observed FSDP depend on the glass system under consideration. For the superionic glasses considered in this report, there is convincing evidence that the FSDP arise from the density fluctuations in the glass forming network such as  $\text{AgPO}_3$  [29].

The relationship between the ion transport properties and the FSDP wave number in  $\text{AgI-Ag}_2\text{O-M}_x\text{O}_y$  glasses ( $\text{M}_x\text{O}_y = \text{P}_2\text{O}_5, \text{B}_2\text{O}_3, \text{GeO}_2, \text{MoO}_3$ , etc.), has been studied [7,8]. There, it has been found that the ionic conductivity increases and the activation energy decreases with the decrease of the FSDP wave number.

The relationship between the FSDP wave number and the ion transport properties has been explained by using the concepts of bond fluctuations in superionic conductors [38] as summarized below. 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. A schematic energy barrier profile representing this situation is shown in Fig. 1. For instance, in  $\text{AgI-AgPO}_3$  glasses, the network is formed by  $\text{AgPO}_3$  and  $\text{AgI}$  is the doped salt. The distance that characterizes the medium range structure is denoted by  $d$ . The medium range structure is given by  $Q = 2\pi / d$ .

If we focus on the  $\text{Ag}^+$  ions, we can distinguish at least three types of ions. The  $\text{Ag}^+$  ions in the doped salt which are bonded with  $\text{I}^-$ , the  $\text{Ag}^+$  ions in the network which are bonded with  $\text{O}^{2-}$ , and the  $\text{Ag}^+$  ions located in the boundary between network and doped salt which are bonded with  $\text{I}^-$  and  $\text{O}^{2-}$ . According to the bond fluctuation model [38], the third type of  $\text{Ag}^+$  ions are more mobile than the others, because the  $\text{Ag}^+$  ion surrounded by different atoms feels an asymmetric field of forces which results in the anharmonic atomic vibration and large atomic migration. This situation is denoted in Fig. 1 as highly conducting regions, and it is described by the average activation energy  $E_3$ .

The relationship between the FSDP wave number and ion transport properties [7,8] is understood by using the model represented in Fig. 1. By doping the network with salts, the characteristic distance  $d$  increases ( decrease of the FSDP wave number ). This is the network expansion reported by some authors [28,29]. By doping salts, the amount of highly conducting regions, or the sites with low activation energies increase, which results in the increase of the ionic conductivity. Beside reproducing the observed FSDP – ion transport property relationship, 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 [8]. It is gratifying to note that the evolution of the ionic conductivity predicted by the model has also been obtained by using percolation concepts in the analysis of composition dependence of diffusion in ion conducting glasses [35].



#### 4. Relationship between the FSDP wave number and the exponent of the power law

The relationship between the FSDP wave number and ion transport properties presented in Sec. 3 was for dc conductivity. The low frequency conductivity explores a wide pathway in the energy profile as illustrated schematically in Fig. 2. More specifically, the potential barrier profile denoted  $E_3$  in Fig. 1 are explored in a large space extent. As the frequency of the applied field increases, the spatial extent of the energy profile explored by the mobile ions diminishes. That is, the information that could be extracted from the ac conductivity becomes more local.

The above views of ion dynamics in superionic glasses prompt us to study the relationship between medium range structure and the ac conductivity dispersion. The relationship between the FSDP wave number and the exponent  $n$  in the conductivity dispersion obtained for the case of  $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$  glasses is shown in Fig. 3. We can see that the FSDP wave number decreases and the exponent  $n$  increases with the increase of the concentration of AgI. The figure indicates that there is a relationship between the FSDP wave number and the exponent  $n$ . Concerning the origin of  $n$ , no consensus exists among the researchers. Some authors attribute it to some kind of interactions involving the mobile ions [18,19]. Others connect it to some kind of geometric factors [20]. The result shown in Fig. 3 indicates that  $n$  is related to the intermediate range structure of the glass. That is, the figure suggests that the universal aspect of the power law reflects the universal pattern of the potential barrier at intermediate length scales. This finding is new, not previously reported by any author. It must be mentioned however, that some related works have been reported recently [39,40]. For instance, the onset frequency of the ac conductivity in ion conducting glasses has been related to the fraction of high energy barriers that connect the clusters of fast ion conducting sites [39]. Such a model also indicates that the characteristic length scale determining the ionic conductivity is about 7 Å. It is interesting to note that this value is close to the characteristic length considered in the present paper,  $d = 2\pi / Q$ .

The behavior shown in Fig. 3 can be understood as follows. When the amount of doped AgI is small, most of the  $\text{Ag}^+$  ions arise from  $\text{AgPO}_3$  that form the network, and are bonded mainly to  $\text{O}^{2-}$  ions. Therefore, the highly conducting regions referred to in Fig. 1 do not extend over long distances. They are restricted in a limited region as indicated schematically by the spread regions around the network skeleton in Fig. 4a. By increasing the amount of AgI, the number of  $\text{Ag}^+$  ions bonded to I and  $\text{O}^{2-}$  ions increase, which results in the increase of the highly conducting regions ( or sites with low activation energies ). At the same time, such regions connect to a large extent, which leads to an efficient ion transport over long distances. For this case, note also that many channels for ion transport open, accompanying the increase of the highly conducting region as illustrated in Fig. 4b. The figure also shows the network expansion by salt doping which results in the decrease of the FSDP wave number [7,28,29]. According to this model, the increase of the value of  $n$  is related to the increase of



the number of channels available for ion transport. Such a result is in harmony with the finding of Sidebottom [20] that relates  $n$  to the dimensionality of ion transport pathways.

The model of the present paper which is illustrated in Fig. 1 predicts that the connectivity of the highly conducting regions will exhibit a maximum at certain values of salt doping [8]. Therefore, further doping salt over this particular concentration will result in the decrease of the connectivity of the highly conducting region as illustrated in Fig. 4c. According to the relationship found in this paper, this situation will lead to the decrease of the exponent  $n$ . It is tempting to relate this prediction to the small decrease of  $n$  observed for  $(\text{AgI})_{0.5}(\text{AgPO}_3)_{0.5}$ . It seems that the datum of AgI-alkylammonium iodide also favors this prediction. However, systematic studies in other glassy systems are necessary in order to verify with certainty the prediction.

In Fig. 3, data of glasses such as  $(\text{AgI})_{0.2}(\text{0.6Ag}_2\text{O-0.4V}_2\text{O}_5)_{0.8}$ ,  $(\text{AgI})_{0.75}(\text{Ag}_2\text{MoO}_4)_{0.25}$ , etc. have also been included for the sake of comparison. It is gratifying to note that although somewhat dispersed, this data follows the trend found for  $(\text{AgI})_{0.5}(\text{AgPO}_3)_{0.5}$  glasses. The inset of Fig. 3 shows the behavior of alkali metaphosphate glasses. We see the effect of mixed alkalis and recognize that the trend is different with that found for silver metaphosphate glasses. This difference is understandable, because in Ag containing oxide glasses such as AgI-AgPO<sub>3</sub>, the network expands without breaking the network connectivity by adding AgI. On the other hand, in glasses that contain alkali, the network tends to fragment [9,28]. Such difference arises from the difference in chemical bonding between Ag and alkali as discussed previously [9].

## 5. Conclusion

The ion transport properties in superionic glasses are intimately related with the medium range structure which is reflected in the FSDP. Specially, it is known that in Ag ion conducting oxide glasses, the dc ionic conductivity increases with the decrease of the FSDP wave number. In the present contribution, it is shown that the exponent of the power law in the ac conductivity of superionic glass  $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$  is related to the FSDP wave number. More specifically, it is shown that the FSDP wave number decreases and the power law exponent increases with the increase of the concentration of AgI. Data of other glasses such as  $(\text{AgI})_{0.2}(\text{0.6Ag}_2\text{O-0.4V}_2\text{O}_5)_{0.8}$ ,  $(\text{AgI})_{0.75}(\text{Ag}_2\text{MoO}_4)_{0.25}$ , etc. support the existence of this trend. The relationship found has been interpreted by using a model of glasses derived from the bond fluctuation model of superionic conductors. According to the model, the local energy barrier for the ion movement is determined by the local structure and bonding, and the ions flow through the low energy barrier sites. Therefore, the trends found imply that the exponent of the power law contains information about the degree of connectivity of these low energy sites that extend at the intermediate length scale. The result suggests also that the universal aspect of the power law reflects the universal pattern of the potential barrier at intermediate length scales. As far as the



author is informed, the relationship between the power law exponent and the intermediate range ordering found in this paper is new, which provides an alternative viewpoint to the nature of the power law behavior.

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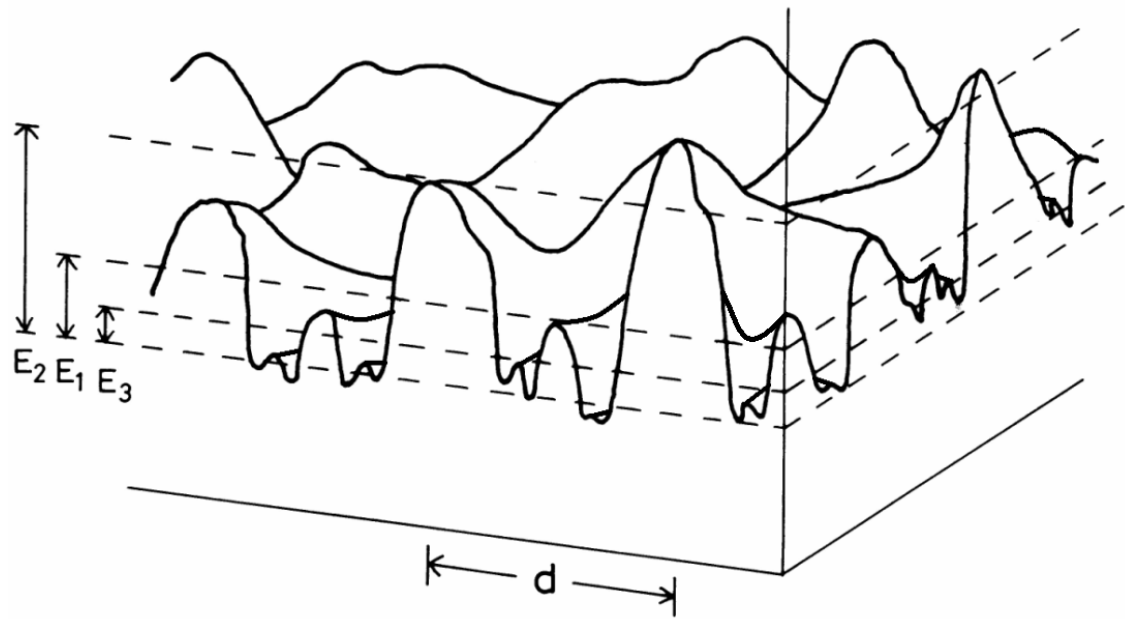
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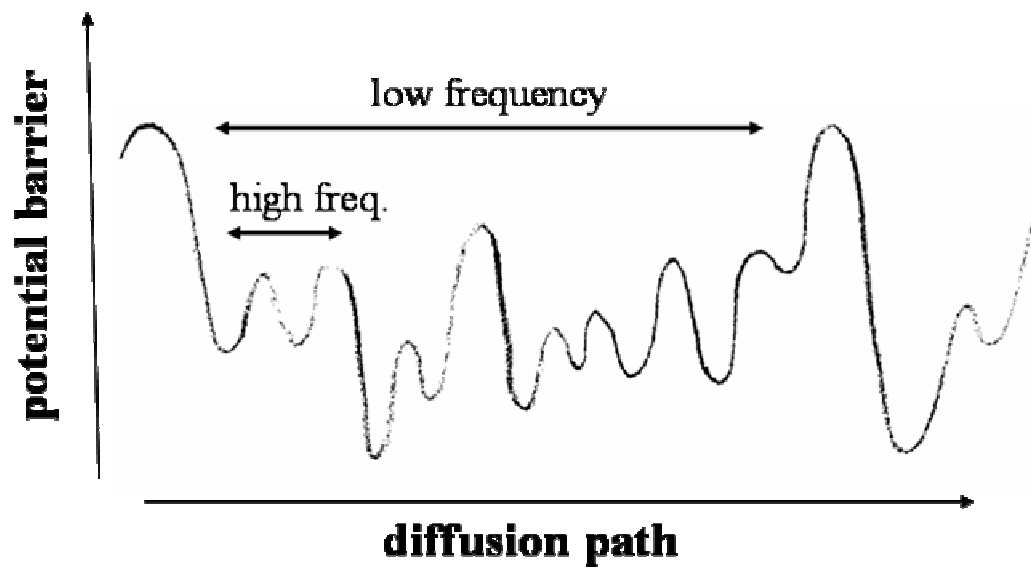
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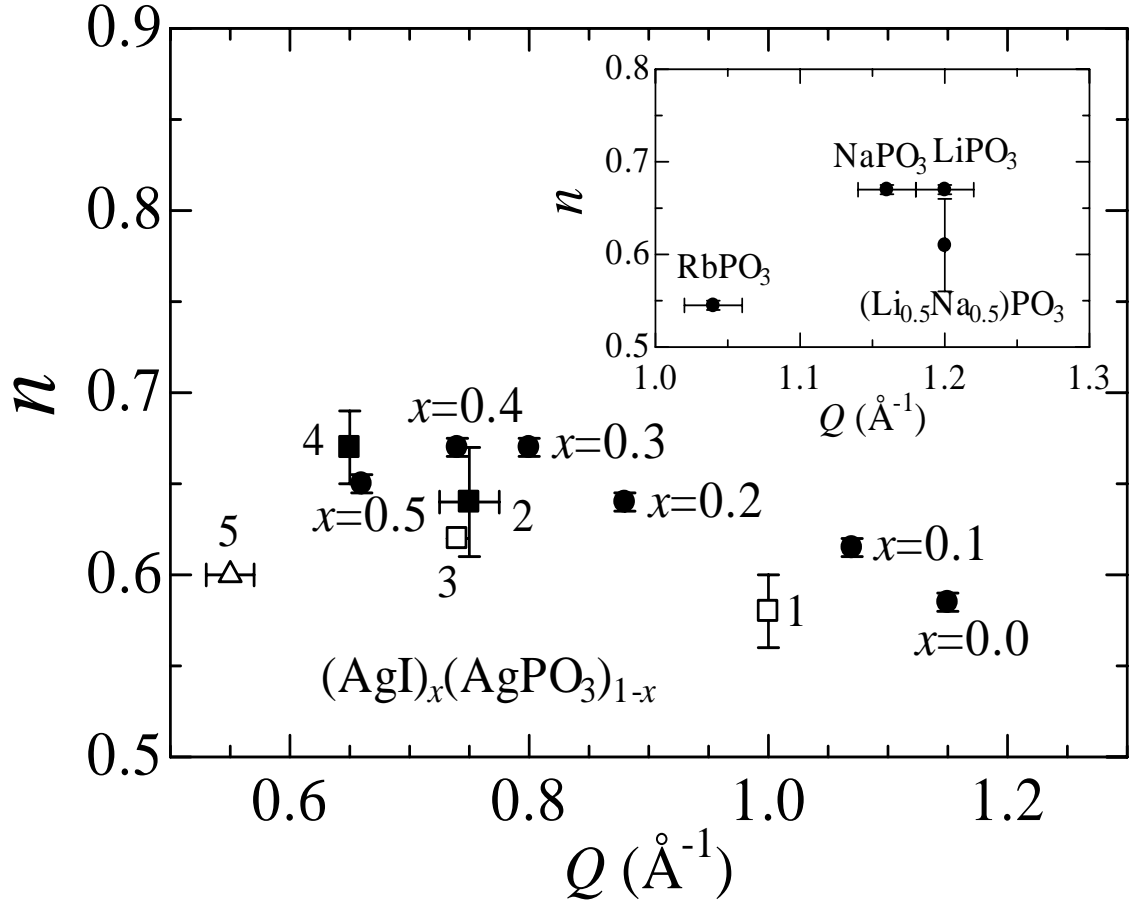
**Fig. 1.** A schematic representation of the energy barrier profile in superionic glasses.  $E_1$  and  $E_2$  are the average values of the activation energies in the doped salt and in the network, respectively.  $E_3$  is the activation energy of the highly conducting region.  $d$  is a characteristic distance that defines the medium range structure.





**Fig. 2.** At low frequencies, the mobile ion explores a large space in the potential barrier profile, whereas at high frequencies, it explores a local barrier profile.





**Fig. 3.** Relationship between the FSDP wave number and the exponent  $n$  of the ac conductivity dispersion. For the  $(\text{AgI})_x(\text{AgPO}_3)_{1-x}$  glasses, data of the FSDP and  $n$  are taken from [6] and [21], respectively. The numbers denote the following glasses: (1)  $(\text{Ag}_2\text{S})_{0.3}(\text{GeS}_2)_{0.7}$  [23,30], (2)  $(\text{AgI})_{0.2}(0.6\text{Ag}_2\text{O}-0.4\text{V}_2\text{O}_5)_{0.8}$  [24,31], (3)  $(\text{AgI})_{0.48}(\text{Ag}_2\text{SeO}_4)_{0.52}$  [25,32], (4)  $(\text{AgI})_{0.75}(\text{AgMoO}_4)_{0.25}$  [26,33], (5) AgI-alkylammonium iodide [27,34]. The inset shows the behavior for alkali metaphosphate glasses [21,41,42].



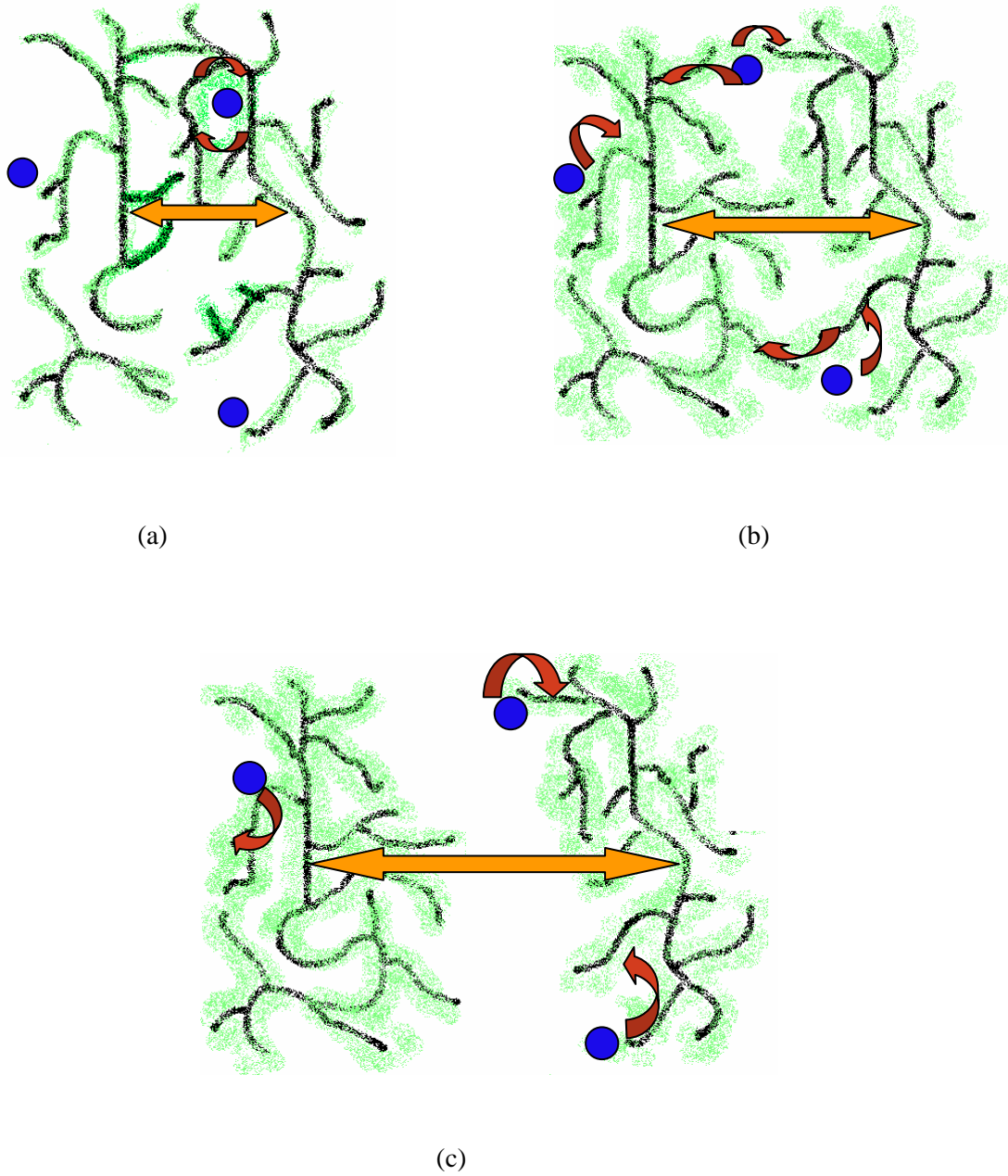


Fig. 4. A schematic representation showing how the connectivity of the highly conducting regions, or the low activation energy sites ( illustrated as spreads around the network skeleton ) vary with the concentration of doped salts ( not explicitly shown for clearness ). The doped salt concentration increases from (a) to (c) and expands the network separation.