Correlation between Free Volume and Ionic Conductivity in Fast Ion Conducting Glasses

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It is well known that fast ionic conductivity can be obtained by doping modified oxide glasses with a metal-halide salt. The role of the dopant salt, apart from providing additional charge carriers, for the ionic conductivity has been a much debated issue. Using conductivity and density data for different host glasses mixed with various metal-halide salts, we find a remarkable common cubic scaling relation between the conductivity enhancement and the expansion of the network forming units induced by salt doping. This suggests that the glass network expansion, which is related to the available free volume, is a key parameter determining the increase of the high ionic conductivity in this type of fast ion conducting glasses. [S0031-9007(96)01369-5]

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High room temperature ionic conductivity in solid materials is technologically interesting for various solid state electrochemical devices, e.g., batteries, "smart windows". Apart from some exotic crystalline materials such as Rb_4AgI_5, the highest ionic conductivity at room temperature has been observed in some salt doped oxide, sulfur, and halide glasses. The salt doped oxide glasses are particularly interesting for applications because of their ease of preparation, their stability, and the large available composition ranges, and have also become model materials for investigations of diffusion in disordered solids.

Since the discovery of fast ionic conductivity in glasses, there has been a large interest in explaining the diffusion mechanism. With this knowledge one may be able to design new glasses with optimized properties for various applications. It is well known that the ionic conductivity increases rapidly when a network glassformer such as B_2O_3, P_2O_5, or SiO_2 is modified by the addition of a metal oxide. Even more dramatic is the increase when a modified glass is doped by a metal halide salt and conductivity of more than 10^{-2} S/cm can be obtained at room temperature [1]. The transport properties show several peculiarities that deviate from purely random motion of the mobile ions, e.g., a universal frequency dispersion of the conductivity from a low frequency dc plateau up to phonon frequencies is observed and the relaxation function shows strong deviations from exponential behavior. For highly doped glasses deviations from Arrhenius temperature dependence is also observed [2]. Despite a considerable experimental and theoretical effort, there is currently no consensus regarding the diffusion mechanism [3]. Several models have been proposed; they range from thermodynamic models with roots in models for liquid electrolytes, such as the weak electrolyte model [4,5], to models based on solid state concepts such as the jump diffusion model [6], the strong electrolyte model [7], and the microscopic dynamic structure model [8–10]. In these models the dopant salt is assumed to be homogeneously dissolved in the glass matrix. There are also models in which the ionic conductivity occurs in a structurally inhomogeneous glass matrix, e.g., in and between microclusters of the dopant salt [11–14] or alternatively in connected pathways of low activation barriers built up by charged groups of the network and the anions [15–17]. Others propose that the dopant salt simply expands the glass network, resulting in a more open structure suitable for ion conduction [18]. Nevertheless, a few empirical rules of thumb for high ionic conductivity have been established: the anion should be large and highly polarizable, the cation should be relatively small and also polarizable, and a mixture of glassformers (e.g., borophosphate glasses) is favorable for ionic conduction [19]. Furthermore, it is well known that a mixing of alkali ions is detrimental for the conductivity (mixed mobile ion effect) [17]. The most straightforward explanation of the mixed mobile ion effect is provided by the dynamic structure model [8–10], where the authors propose that the two kinds of mobile ions creating and maintaining their own distinctive environments, i.e., a site memory effect, leading to percolation limited diffusion of the different ionic species.

Experimentally, considerable effort has been made to try to establish a link between the microscopic structure and fast ion conductivity in glasses. Spectroscopic and structural studies show that the dopant ions in general do not participate directly in the network formation of the glass. Rather the ions are introduced into voids of the structure [20–23] and are decoupled from the network. However, the way the salt ions are introduced in voids has been a matter of controversy [4–14,24–29]. The models for ionic conduction, mentioned above, are usually based on completely different spatial distributions of the dopant ions. The suggestions range from a homogenous distribution [4–10] to relatively large clusters of the dopant salts (of size >10 Å) [11–14].

In this paper we have taken a simple approach; we consider only the macroscopic conductivity and density in an attempt to evaluate ideas concerning the role of an open structure for ionic conductivity. We find a general relation between the ionic conductivity enhancement and the expansion of the network forming units which clearly shows that the salt-induced volume expansion of the glass network is a key parameter for high ionic conductivity. Thus, the results are in obvious general support of Tuller and Button's suggestion that an open structure is essential to promote ionic conductivity [18].

Density measurements of various fast ion conducting glasses indicate that the glass network expands considerably upon salt doping. For example, using the density data for the $(AgI)_x$-$(AgPO_3)_{1-x}$ system [30], one finds that the P-O network has to expand about 80% to accommodate the AgI salt for the $x = 0.5$ composition as compared to the undoped glass ($x = 0$). It appears from literature data [18,30,31] that similar expansions of the network structure occur for most salt doped glassy ionic conductors.

In order to investigate the possibility of a general relation between ionic conductivity and the volume occupied by the network skeleton, we have calculated the expansion $(V_d - V_m)/V_m$ of the network, where V_m and V_d are the volumes the network forming units (e.g., B_2O_3, P_2O_5, etc.) occupy in the undoped modified (e.g., Li_2O-$2B_2O_3$, $AgPO_3$, etc.) and doped (e.g., LiCl-Li_2O-$2B_2O_3$, AgI-$AgPO_3$, etc.) glasses, respectively. Thus, the introduced dopant salt (e.g., LiCl, AgI) increases the volume of the network skeleton with $V_d - V_m$. The calculated expansion has then been related to the change of the relative ionic conductivity σ/σ_0, where σ_0 is the ionic conductivity of the undoped glass ($x = 0$). We have used density [18,30,31] and conductivity [1,18–20,31] data reported in the literature for a variety of fast ion conducting glass systems, namely, $(AgI)_x$-$(Ag_2O$-$2B_2O_3)_{1-x}$ [19,30], $(AgI)_x$-$(Ag_2O$-$B_2O_3)_{1-x}$ [1,19,30], $(LiCl)_x$-$(Li_2O$-$2B_2O_3)_{1-x}$ [18], $(AgI)_x$-$(AgPO_3)_{1-x}$ [19,30], $(AgBr)_x$-$(AgPO_3)_{1-x}$ [1], $(AgCl)_x$-$(AgPO_3)_{1-x}$ [1], $(LiCl)_x$-$(2Li_2O$-B_2O_3-$P_2O_5)_{1-x}$ [31], $(AgI)_x$-$(Ag_2MoO_4)_{1-x}$ [1,30], $(AgCl)_x$-$(Ag_2O$-$2B_2O_3)_{1-x}$ [20], $(AgBr)_x$-$(Ag_2O$-$2B_2O_3)_{1-x}$ [20], and $(NaCl)_x$-$(Na_2O$-$2B_2O_3)_{1-x}$ [18]. We have complemented the existing density data with measurements of densities of the glasses $(AgBr)_{0.48}$-$(AgPO_3)_{0.52}$, $(AgCl)_{0.4}$-$(AgPO_3)_{0.6}$, AgBr-Ag_2O-$2B_2O_3$, and AgCl-Ag_2O-$2B_2O_3$, which were found to be 5.45, 5.00, 3.83, and 3.52 g/cm^3, respectively.

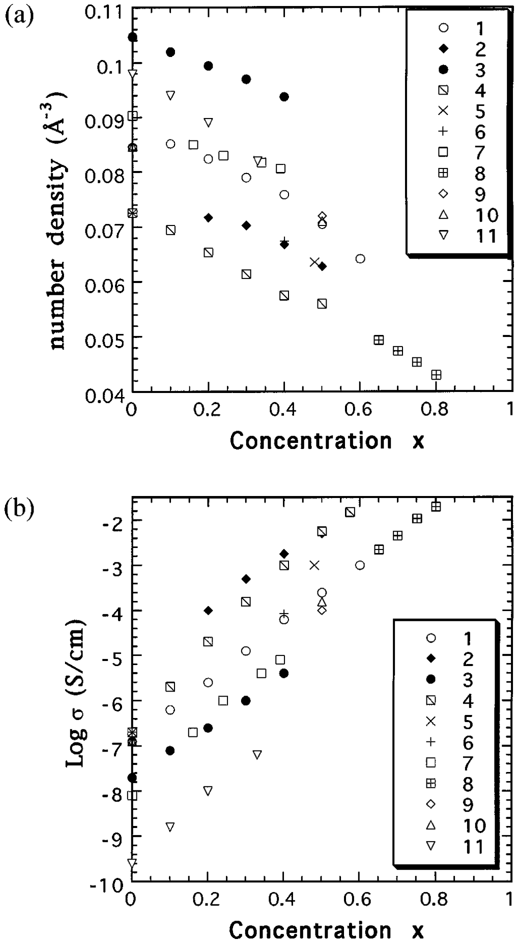

FIG. 1. (a) Number densities and (b) conductivities as a function of dopant salt concentrations for a number of different glass systems. The data points correspond to the following glass systems: (1) $(AgI)_x$-$(Ag_2O$-$2B_2O_3)_{1-x}$ [19,30], (2) $(AgI)_x$-$(Ag_2O$-$B_2O_3)_{1-x}$ [1,19,30], (3) $(LiCl)_x$-$(Li_2O$-$2B_2O_3)_{1-x}$ [18], (4) $(AgI)_x$-$(AgPO_3)_{1-x}$ [19,30], (5) $(AgBr)_x$-$(AgPO_3)_{1-x}$ [1], (6) $(AgCl)_x$-$(AgPO_3)_{1-x}$ [1], (7) $(LiCl)_x$-$(2Li_2O$-B_2O_3-$P_2O_5)_{1-x}$ [31], (8) $(AgI)_x$-$(Ag_2MoO_4)_{1-x}$ [1,30], (9) $(AgCl)_x$-$(Ag_2O$-$2B_2O_3)_{1-x}$ [20], (10) $(AgBr)_x$-$(Ag_2O$-$2B_2O_3)_{1-x}$ [20], and (11) $(NaCl)_x$-$(Na_2O$-$2B_2O_3)_{1-x}$ [18].

In Fig. 1(a) we show the number densities of all the included glasses as a function of the dopant salt concentration x. One can see that the total number density (i.e., including the dopant salt) usually decreases slightly with increasing salt concentration. Figure 1(b) shows the logarithm of the conductivity for the same glasses. The conductivity increases generally rapidly with increasing dopant concentration, although the rate varies between the various glass systems. In Fig. 2(a) we present the obtained relative conductivity $\log(\sigma/\sigma_0)$, where σ_0 is the ionic conductivity of the undoped glass ($x = 0$), vs the expansion of the network forming units for a wide variety of salt doped glassy ionic conductors. The systems $(AgI)_x$-$(Ag_2O$-$B_2O_3)_{1-x}$ and $(AgI)_x$-$(Ag_2MoO_4)_{1-x}$ have their undoped samples outside the glass formation region. In these cases we have extrapolated the data down to the undoped composition using data for glasses within the respective glass forming regions. The glass systems in Fig. 2(a) cover various glassformers (phosphates, borates, borophosphates, and molybdates) as well as a variety of dopant salts (AgI, AgBr, AgCl, LiCl, NaCl). A striking common relation between the relative conductivity and the expansion for all the investigated glassy systems is apparent from Fig. 2(a); i.e., for a given expansion all the different systems respond with the same increase of the relative conductivity regardless of chemical or microstructural details. Note that the data in Fig. 2(a) represent conductivity

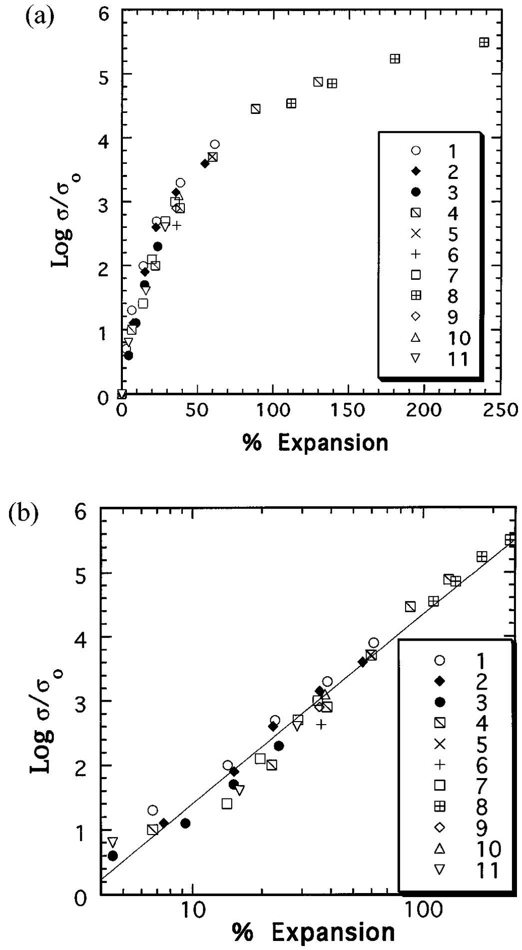

FIG. 2. Relative conductivity σ/σ_0, where σ_0 is the ionic conductivity of the undoped glass ($x = 0$), versus the expansion of the glass network forming units $(V_d - V_m)/V_m$ is plotted for various salt doped ionic glassy conductors. The expansion is plotted linearly in (a) and on a logarithmic scale in (b). The straight line with a slope of 3 in (b) indicates a power law $\sigma/\sigma_0 \sim [(V_d - V_m)/V_m]^3$. The symbols correspond to the same glass systems as in Fig. 1.

values that vary by 8 orders of magnitude [see Fig. 1(b)]. In Fig. 2(b) we plot the data in a log-log plot. The data follow a straight line with a slope of 3.0 ± 0.05 which indicates a power law $\sigma/\sigma_0 \sim [(V_d - V_m)/V_m]^3$. The origin of this cubic scaling relation is, at present, not clear. However, it is remarkable that such a general behavior is observed.

The common behavior of the conductivity increase on expansion of the network structure observed for the various glasses suggests that the excess volume introduced by the dopant salt is a key parameter that determines the conductivity properties. Thus, it appears that the details of the microscopic structure have no direct importance for the ionic conductivity in this kind of amorphous conductors. However, it should be noted that, in principle, it is the microscopic interactions that lead to variations of the degree of expansion. Hence, in order to explain the conducting properties and to increase the ionic conductivity, one should focus on the mechanism that promotes a large expansion of the network forming units.

It is of interest to try to understand the microscopic structural origin of the expansion and how it affects the ionic conductivity. In recent structural studies of metal halide doped oxide glasses using neutron and x-ray diffraction techniques combined with Reverse Monte Carlo simulations [25,28,29], it was shown that units or segments of the glassforming matrix are separated locally on salt doping. The ions are introduced in, and expand, the space between segments or units of the glassforming skeleton and form narrow (few atomic spacings) pathways that appear to be favorable for ionic conduction. The detailed local structure depends on the constituents involved. For example, AgI doping leads to a relatively well defined and homogeneous expansion of the space between the skeleton molecules, whereas for LiCl the separation between the segments shows a much wider distribution. The difference may be attributed to the differences in the covalent character of the ions involved. The relatively large degree of covalent character of Ag and I would lead to a higher degree of local ordering between the segments through crosslinking effects of the ions and also to a larger expansion of the glass skeleton due to a lower coordination number. The higher ionic conductivities of the AgI (as well as AgBr and AgCl) doped glasses is then simply because the silver and iodine ions expand the network more than other dopant salts.

It is interesting to note that the increase in ionic conductivity on salt doping is almost entirely due to the fact that the activation energy E_a required for a "cation jump" decreases (see Refs. [1,18,19,31]). Thus, the pre-exponential term in the Arrhenius law, $\sigma = \sigma_1 \exp(-E_a/k_B T)$, is largely unaffected upon the salt doping. The reason for the decrease of the activation energy with increasing doping concentration is, however, not clear. The expansion of the glass skeleton and the introduction of the dopant ions in voids in the structure forming narrow pathways would lead to two effects that lower the activation energy and thus promote the ionic conductivity. In terms of the strong electrolyte model, E_a may be written as a sum of two terms, which are denoted by the binding energy, E_b, and the strain energy, E_s [7]. E_b is the average energy a cation requires to leave its site, and E_s is the average kinetic energy a cation needs to structurally distort the environment to create a "doorway" through which it can diffuse of "jump" to a new site. The dopant salt induced expansion of the network skeleton would lead to a lowering of the strain energy part E_s of the activation energy, and the formation of pathways, in which the cations may coordinate both the oxygens of the network and the anions of the dopant salt, would also lead to a lowering of E_b. The present finding of the common scaling between the conductivity enhancement and the expansion suggests that it is the expansion of the glass skeleton and thus the strain energy part that mainly determines the conductivity properties in the salt doped fast ion conductors.

Although the reason for the present remarkable common relation is largely unknown, we note that, in a wider context, recent computer simulations on various simple liquids and a binary fast ion conductor show a universal scaling law between atomic diffusion rate and atomic structure [32]. The atomic diffusion rate in dense media is shown to be determined universally by the excess configurational entropy. At this stage we cannot make a direct quantitative comparison of the present observations with such a picture; however, a qualitative dependence may be inferred from the present study; the local expansion introduced by a halide salt leads to a large increase of the configurational entropy and thus also to a large increase of the diffusion. However, further investigations are needed to explore a connection of the present common relation for fast ion conduction in glasses with the diffusion model of Ref. [32].

In summary, a common simple relation between the relative conductivity increase and the expansion of the glass network skeleton is revealed for widely different salt doped glasses. This shows the extraordinary importance of an open structure, with excess free volume, for high ionic conductivity and shows that the precise microscopic interactions are of subordinated importance. The consequence of the present findings is that in order to optimize an ionic conductor of this type one should seek a dopant salt with the largest possible expansion capability of the glass network.

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