Non-Arrhenius Conductivity in Glass: Mobility and Conductivity Saturation Effects

Joseph Kincs* and Steve W. Martin[†]

Department of Materials Science & Engineering, Iowa State University,
Ames, Iowa 50011
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Extreme non-Arrhenius dependence of the ionic conductivity in optimized fast ion conducting glasses has been observed. When all the chemical factors controlling the ionic conductivity in glass have been optimized, the conductivity fails to reach the values expected, >0.1 $(\Omega \, \text{cm})^{-1}$ at 298 K. A new series of glasses $z\text{AgI} + (1 - z) \, [0.525\text{Ag}_2\text{S} + 0.475\text{B}_2\text{S}_3\text{:SiS}_2]$ have been measured for the first time and are found to exhibit a non-Arrhenius conductivity, the extent of which increases the greater the AgI content. Such behavior is believed to be a new feature of optimized fast ion conducting glasses and will be a critical obstacle to overcome if the conductivity of such systems is to ever reach the values needed for optimum device performance.

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Fast ion conduction (FIC) in glass has been studied for some time, and much effort has been directed at obtaining high conductivity in glass. Recent success in sulfide- and silver-doped glasses has pushed the maximum room temperature conductivity in glass up to 10^{-2} $(\Omega \, \text{cm})^{-1}$ [1]. Concomitant with this success has been the clarification of the structural and dynamic models used to understand FIC in these "superionic" glasses. Our work, for example, has clearly identified the wide composition dependence of the ionic conductivity with both structural and conduction energetics features of these glasses [2]. Other work has shown the intimate interplay between composition, structure, and the dynamics of the FIC in these glasses [3]. In all of this work, the question still remains of how high the ionic conductivity can be pushed in these glasses. For example, does the limit of 10^{-2} $(\Omega \, \text{cm})^{-1}$ represent a fundamental limit that will not be overcome, or do the calculations that have been made earlier [4], where a conductivity of 1 to 100 $(\Omega \, \text{cm})^{-1}$ at room temperature is predicted, still hold promise that more glass chemistry optimization must be done before the limit is reached?

In this Letter, we show that by using all the available knowledge that links ionic conductivity to glass chemistry and structure a new feature in the composition and temperature dependence of ionic conductivity in glass arises that may well limit the maximum conductivity that is obtainable in glass. When all the features of the glass chemistry and composition have been carefully optimized to obtain the highest conductivity in glass, the conductivity exhibits a strong non-Arrhenius temperature dependence that reduces the conductivity at room temperature some 1 to 2 orders of magnitude below that predicted from low temperature (subambient) conductivities. We believe this behavior to be an as yet undiscovered ubiquitous behavior of all superionic FIC glasses and points to another feature of ionic conduction in glass that must be fully understood in order to make any more progress in optimizing the conductivity in these glasses. Indeed, this behavior may

well point to a fundamental device limitation for these glasses.

The purpose of this paper is to report new measurements on a series of new silver iodide-doped silver thioborosilicate glasses that were specifically designed to yield optimum ionic conduction in glass.

Glasses of general composition $z\text{AgI} + (1 - z) \times [x\text{Ag}_2\text{S} + (1 - x)\text{B}_2\text{S}_3\text{:SiS}_2]$ were prepared by batch melting AgI with previously prepared $x\text{Ag}_2\text{S} + (1 - x)\text{B}_2\text{S}_3\text{:SiS}_2$ glasses in vitreous carbon crucibles in a high quality O_2- and H_2O-free glove box at $\sim$850 °C and quenching into 1–2 mm $\times$ 25 mm disks in stainless steel molds held near the T_g of the glass, $\sim$350 °C. The $x\text{Ag}_2\text{S} + (1 - x)\text{B}_2\text{S}_3\text{:SiS}_2$ glasses were prepared from reagent grade Ag_2S and SiS_2 (99.9%, Cerac, Inc.) and B_2S_3 prepared in this laboratory [5]. Conductivity measurements were made using a high quality impedance spectroscopy facility over the frequency range of 0.1 Hz to 32 MHz and from 100 to 600 K [4]. Complex plane analysis was used to determine the dc conductivity of these glasses. T_g's were determined using a PE-DSC 4 at 20 °C/min.

It has been widely shown that, due to their high electronic polarizability, silver cations always exhibit conductivities in glass some 1 to 4 orders of magnitude higher than any of the alkali ions [1]. Similarly, sulfide glasses, first discovered by Levasseur *et al.* [6], show conductivities some 3 to as many as 10 orders of magnitude higher than any corresponding oxide glass. More recently, the effect of doping FIC glasses with halide salts, especially AgI, can increase the conductivity some 2 to 3 orders of magnitude [1]. Finally, it has also been shown that mixing different glass formers such as SiO_2 and B_2O_3 produces nonlinear increases in the conductivity for reasons that are not completely understood, and this has been termed the mixed-glass former effect [1]. Using these observations, it follows that high ionic conductivity in glass, if not the highest yet reported, should be
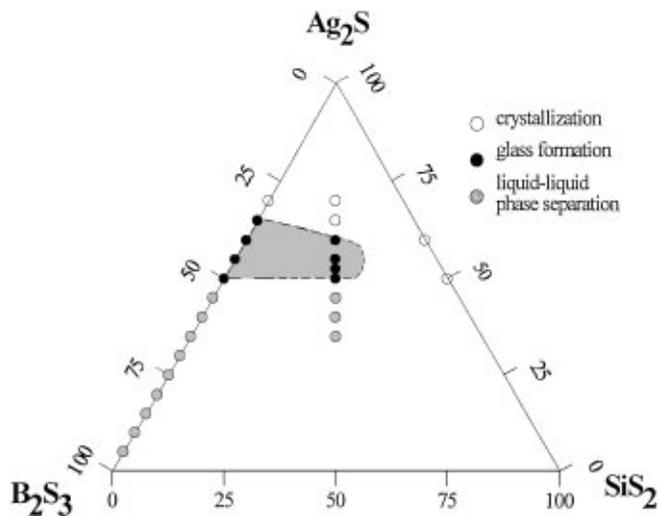

FIG. 1. Glass forming region for ternary $Ag_2S + SiS_2 + B_2S_3$ glasses. Glasses were quenched to room temperature in a stainless steel mold.
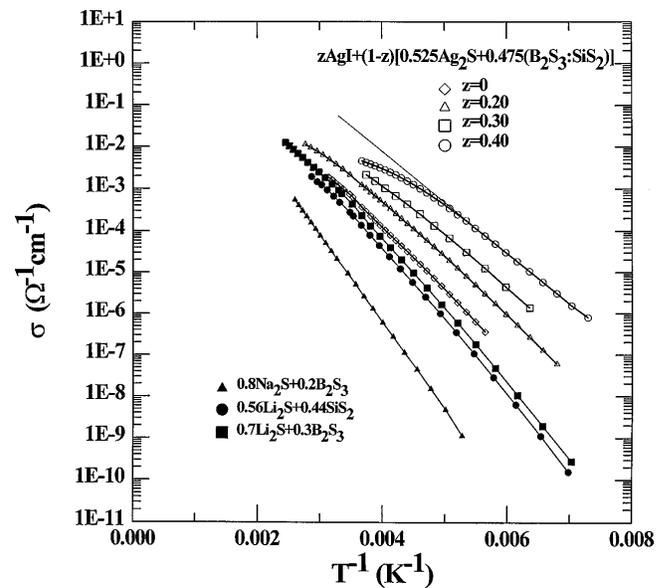

FIG. 2. Arrhenius plots of the ionic conductivity for glasses studied in this work and compared to those for other Li and Na conducting glasses. Notice that for the poorer conducting glasses, the Arrhenius plots have a straight slope, whereas the optimized Ag conducting FIC glasses have significant curvature at highest temperatures.

found among glass compositions chosen in the series $AgI + Ag_2S + SiS_2 + B_2S_3$.

Although wide compositions of glass formation were not found, Fig. 1 shows that glasses in the ternary $Ag_2S + SiS_2 + B_2S_3$ could be prepared. It was observed that at the $SiS_2:B_2S_3$ ratio of 1:1, and a Ag_2S fraction of 60 mole %, the strongest glass former was observed. This glass was then used as a host for the AgI doping and as in many other AgI-doped glasses [1], 40 mole % of AgI could be doped into the glass before devitrification was observed. The glasses reported in this paper therefore belong to the compositional series $yAgI + (1 - z)[xAg_2S + (1 - x)B_2S_3:SiS_2]$, where $0 \leq z \leq 0.4$ and $x = 0.525$. Other glasses were prepared and studied and will be reported on separately. The present series is the highest conducting and most strongly glass forming.

Figure 2 shows the Arrhenius plots of the conductivity for these glasses along with a few other glasses in both this family and others to show the level of conductivity increase that the current series exhibits. Figure 2 shows that these glasses do indeed exhibit the highest yet reported of all conductivities in glass at room temperature, a result quite surprising in itself, except that the glass chemistry was specifically designed to yield this result. Table I shows that the conductivity at room temperature reaches $\sim 4 \times 10^{-2}$ $(\Omega \text{ cm})^{-1}$ for $z = 0.4$ and is combined with a T_g of 501 K (± 5 K). The T_g's reported in Table I are the highest ever reported for a AgI-doped FIC glass and even though T_g decreases with z, they remain exceptionally high. These two features of high conductivity and T_g are combined with the property that these glasses are exceptionally stable in both air and water. Even though they comprise some 50 at. % of SiS_2 and B_2S_3, both of which are exceptionally chemically unstable, the resulting

glasses are very chemically durable. These three features make these glasses particularly attractive for device fabrication and use.

Most dramatic about these glasses, however, is the fact that Fig. 2 shows that their conductivities are exceptionally non-Arrhenius. A dashed line on the $z = 0.4$ glass data shows that the room temperature conductivity is some 2–3 orders of magnitude less than that predicted. This behavior has been reported before for other low T_g "oxysalt" FIC glasses, where the non-Arrhenius behavior was associated with the dynamic temperature dependent restructuring of the I^- anion "sublattice" [7]. Such restructuring was proposed to be associated with the low T_g's of these glasses, $<100\,°C$. By annealing the glasses and presumably densifying the glass to the point

TABLE I. Conductivity parameters for optimized $zAgI + (1 - z)[0.525Ag_2S + 0.475B_2S_3:SiS_2]$ glasses.

zAgI	T_g(K)	Low temperature activation energy (eV)	σ_{dc}(298 K) (extrapolated from low T) $[(\Omega \text{ cm})^{-1}]$	σ_{dc}(298 K) (actual) $[(\Omega \text{ cm})^{-1}]$
0	593	0.33	0.0014	0.0010
0.1	576	0.32	0.0020	0.002
0.2	548	0.31	0.0071	0.003
0.3	525	0.28	0.0116	0.004
0.4	501	0.25	0.0406	0.006

where the I^- anions could not restructure, Ingram, Vincent, and Wandless [7] observed that they could remove the non-Arrhenius temperature dependence. In the present glasses, where the T_g approaches 400 °C and Fig. 2 shows that the non-Arrhenius behavior persists even for glasses without AgI, it is clear that such a simple model may not be entirely correct. Indeed, Fig. 2 also shows this behavior for a lithium ion FIC glass. For these reasons, it is argued that the non-Arrhenius temperature dependence is a ubiquitous feature of all FIC glasses that have optimized ionic conductivities. We believe this to be a new feature for FIC glasses that must be fully understood before any more significant increases in the conductivity of FIC glasses can be obtained. In the following, we propose a simple hypothesis that may account for this behavior that does not depend upon any unique features of glass chemistry or structure as the previous models.

The specific aim to obtain a glass with a maximum conductivity implies that the activation energy for conduction must be minimized. In this case, at high temperature the concept of ion conduction in glass being the result of infrequent individual ion hops over large energy barriers may not be appropriate. At low temperatures, however, where kT is far below the activation energy, this is an appropriate picture of the conduction dynamics and the conductivity exhibits near but not completely Arrhenius temperature dependence. At higher temperatures and optimized glass compositions and minimized activation energies, it is very likely that a significant fraction, indeed, most if not all, of the ions in the glass will be dissociated from their anionic potential energy wells and able to conduct in the glass. For example, kT at 500 K is on the order of 0.04 eV, in the range, ~0.10 eV, observed for the activation energy for the most compositionally optimized glass studied here. In this case, the effect of temperature would no longer be to thermally create charge carriers for conduction but rather to increase the mobility of the carrier population. The hypothesis in this model would be that the conductivity has reached a mobile carrier concentration limit, and further increases in conductivity depend upon increasing the mobility of the carriers. Such behavior is observed and well studied in electronic semiconductors, where even lower activation energies are observed. In these cases, of course, the charge carrier is the quantum-effects controlled electron, and the comparison to the "classical-limit" behavior of the mass and charge carrying ion conductors cannot be taken too far, however. Nonetheless, the analogy is important and may lead to a better understanding of these glasses and their anomalous behavior.

Such a hypothesis is in agreement with the often cited notion that in glassy FICs, it is the carrier concentration that dominates the conductivity [8]. In the weak electrolyte model, this is seen as the dissociation energy required to create a mobile carrier. In the strong electrolyte Anderson-Stuart model, this is seen as the electrostatic
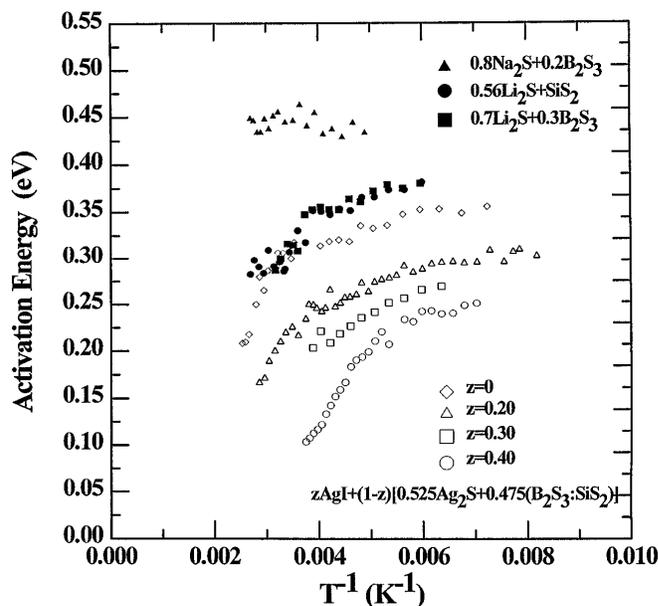

FIG. 3. Plot of the "apparent" activation energy for the glasses shown in Fig. 2. The apparent activation energy is simply taken as a running slope between adjacent temperature-conductivity points on Fig. 2. Notice that the higher activation energy and poorer conducting glasses have the normal behavior of a constant activation energy, where as the optimized FIC glasses of this study have rapidly decreasing activation energies as temperature increases.

binding (Coulombic) energy barrier to conduction [9]. In both cases, the dominant energy barrier is believed to be associated with the electrostatic (Coulombic) attraction between mobile cations and stationary anions in the glass. It is significant then that, as Fig. 3 shows, the "apparent" activation energy decreases as temperature increases. The low temperature limit of the activation energy may be associated with the total activation energy for conduction in the glass comprising both electrostatic and mobility activation energies. The high temperature limit of the activation energy may well only be associated with the mobility part of the activation where all ions are participating equally in the conduction events.

If such a model were correct for these glasses, it would seem that at some temperature, below T_g, ion-ion interaction and scattering should become major obstacles for conduction and the conductivity should begin to decrease with temperature in a manner seen in electronic band conductors. In the present case, the glasses appear to have not reached this limiting behavior. We are, however, using these base compositions to further optimize the glass chemistry to increase the T_g even further to observe whether such behavior occurs.

*Present address: Motorola Inc., Northbrook, IL.

[†]To whom correspondence should be addressed.

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