Structure and Ionic Conduction in $(\mathrm{AgI})_x(\mathrm{AgPO}_3)_{1-x}$ Glasses

J. D. Wicks,[1] L. Börjesson,[2] G. Bushnell-Wye,[3] W. S. Howells,[4] and R. L. McGreevy[5]

[1]*Department of Physics and Astronomy, University College, Gower Street, London WC1E 6BT, United Kingdom*
[2]*Department of Physics, Royal Institute of Technology, S-100 44 Stockholm, Sweden*
[3]*Synchrotron Radiation Source, Daresbury Laboratory, Warrington, Cheshire, WA4 4AD, United Kingdom*
[4]*ISIS Science Division, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon, OX11 0QX, United Kingdom*
[5]*Studsvik Neutron Research Laboratory, S-611 82 Nyköping, Sweden*

(Received 25 April 1994)

The relation between fast ion conductivity, glass forming ability, and structure in $(\mathrm{AgI})_x(\mathrm{AgPO}_3)_{1-x}$ glasses has been studied using neutron and x-ray diffraction and extended x-ray-absorption fine structure spectroscopy. Reverse Monte Carlo models based on the data show that AgI doping causes an increase in free volume available for Ag^+ motion, which leads to the considerable increase in conductivity but also limits the glass forming range by decreasing ionic cross-linking of the phosphate network. Analysis of the available free volume shows a percolation transition in the connectivity of Ag^+ pathways for $0.2 < x < 0.3$.

PACS numbers: 61.43.Fs, 61.12.–q

Fast ion conducting glasses are of considerable technological interest because of their possible applications in batteries, sensors, and displays. One of the main scientific challenges is to explain how the disordered structure of the glass is related to the high ionic conductivity that can be achieved at ambient temperatures; without this information it will not be possible to "design" better materials. Because of the complexity of such materials the structural models that have been proposed so far tend to be qualitative and based on "interpretation" of selected features of various types of data, often only indirectly related to the structure itself. In the particular case of AgI doped oxide glasses it has been suggested, for example, that the dopant salt enters into voids in the host glass network and forms connected pathways of disordered AgI clusters resembling the crystalline fast-ion conductor α-AgI, or alternatively that the salt is completely dissolved and the ions are uniformly distributed throughout the structure [1–10]. In this Letter we report on an extensive study of $(\mathrm{AgI})_x(\mathrm{AgPO}_3)_{1-x}$ glasses using the first simultaneous combination of neutron diffraction, x-ray diffraction, and extended x-ray-absorption fine structure spectroscopy (EXAFS) data by reverse Monte Carlo (RMC) modeling [11]. The quantitative structural models produced are used to determine the relationship between the structure, the characteristic features of the data that are produced by that structure, and the ionic conductivity. We show that AgI doping leads to an increase in free volume available for Ag^+ motion, thus leading to high ionic conductivity, but also decreases the number of Ag^+ that cross-link the phosphate network, eventually limiting the glass forming range.

Samples of $(\mathrm{AgI})_x(\mathrm{AgPO}_3)_{1-x}$ with $x = 0$, 0.05, 0.1, 0.2, 0.3, 0.4, and 0.5 were prepared by melt quenching. Neutron diffraction measurements were made at the pulsed neutron source ISIS (United Kingdom) on the LAD diffractometer. X-ray diffraction measurements were made at the synchrotron radiation source SRS (United Kingdom) on the powder diffraction station 9.1, using Warren-Mavel mode [12] at the Zr K edge to suppress Compton scattering. Transmission EXAFS measurements were made at SRS on stations 7.1 at the I L_{III} edge and 9.2 at the Ag K edge. All data have been appropriately corrected and normalized. The EXAFS data provide information primarily on the local structure around Ag and I, the neutron diffraction data on the P and O correlations, and the x-ray diffraction data on the Ag and I correlations.

The RMC method has been described in detail many times (e.g., [13]). It has previously been applied to a study of the structure of vitreous silica, using the combination of neutron and x-ray diffraction data [14]. The application to EXAFS data has been reported in [15] and the method of "coordination constraints" has been developed to include information on chemical bonding [13]. Here, for the first time, all of these applications have been combined. The combination of EXAFS and diffraction data is particularly important since the former provides local, atom specific, information, while the latter provides a wider range of information. This opens up new possibilities for structural studies of complex disordered materials, including those where some atomic species have a low concentration.

From chemical bonding considerations, various spectroscopic studies [9,16], and the structure of crystalline analogs, it is believed that in these glasses tetrahedral PO_4 units form a random network by sharing two corners (bridging oxygens—BO). Two of the corners are not shared (nonbridging oxygens—NBO). Cross-linking of the phosphate chains occurs by ionic bonding of the NBO by Ag^+. This information has been taken into account when constructing the structural models. The number of atoms varied from 3840 for $x = 0.0$ to 5376 for $x = 0.5$; all models were contained in cubic cells with

0031-9007/95/74(5)/726(4)$06.00

periodic boundary conditions. The full RMC algorithm has been described elsewhere [17]. Briefly an initial model of PO_4 chains at an appropriate density is produced by a hard sphere Monte Carlo method with added constraints on the P-O bonding. Ag and I are added at random. RMC is then used to modify the model to fit the experimental data, with the constraint that all original P-O bonds are maintained. The chains can thus change their conformation but not their connectivity. Typical fits to the data are shown in Fig. 1. Exact fits are not obtained because the data contain systematic errors of a form which cannot correspond to a physical structure (this has been discussed in detail elsewhere [18]); these errors are largest for the I L_{III} EXAFS data where the signal is weak and relatively featureless.

The "first sharp diffraction peak" (FSDP) in the neutron diffraction data occurs at an anomalously low momentum transfer, $Q \approx 0.7$ Å^{-1} [19]. The general interpretation has been that the FSDP is due to intermediate range ordering (IRO) of small clusters of Ag and I, probably microcrystals of α-AgI [1,2,4], its narrow width indicating a correlation length of order 20–30 Å. These proposals have been based on neutron diffraction data only, in one case using isotopic substitution [4], and supported by interpretation of Raman scattering data [3]. However, if the FSDP is due to AgI particles, then its intensity in the x-ray diffraction data, which is dominated by Ag and I scattering, should be very high. The data (Fig. 1) show that it is very low, so this explanation cannot be correct.

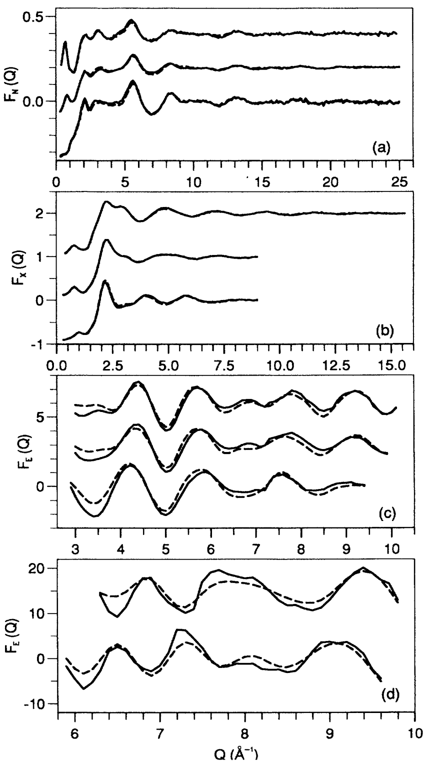

FIG. 1. Experimental structure factors (solid curve) and RMC fits (broken curve) for $(AgI)_x(AgPO_3)_{1-x}$ glasses with $x = 0$ (bottom), $x = 2$ (center), and $x = 0.5$ (top), measured by (a) neutron diffraction, (b) x-ray diffraction, (c) Ag K edge EXAFS, and (d) I L_{III} edge EXAFS. There are no I EXAFS data for $x = 0$

We find that in the initial model of phosphate chains, even before fitting by RMC, a FSDP in the phosphorus-phosphorus partial structure factor $A_{\text{P-P}}(Q)$ occurs at $Q \approx 0.8$ Å^{-1} for the glasses with high x, but not for those with low x. The IRO indicated by the FSDP thus arises naturally from the combination of phosphate density ($\rho_{PO_3} = 0.0308$ Å^{-3} for $x = 0$ and 0.058 Å^{-3} for $x = 0.5$) and contraints on the P-O bonding without the need for any other specific ordering. Fitting to the data by RMC only shifts the FSDP position and changes its intensity slightly. We therefore propose that for the network to maintain its connectivity, i.e., covalent bonding, as more AgI is added the phosphate chains must be pushed further apart by the dopant salt. It is the chain density fluctuation which gives rise to the FSDP, its "anomalously" low position for large x reflecting the low phosphate density. The ratio of the FSDP width to its position (from both experiment and model) is ≈ 0.3. This is a typical ratio for the first structure factor peak in a simple hard sphere liquid at a high packing fraction [see, e.g., [20]), i.e., the FSDP is not unusually narrow and does not require any particularly strong interchain ordering other than that determined by packing.

It has been suggested [1,2,5,6,9,10] that the Ag^+ ions have two different environments, which may be termed "glasslike," i.e., Ag^+ bonded to O^-, and one "saltlike," i.e., Ag^+ bonded to I^-. NMR studies have been inconclusive, one finding two environments at higher temperatures [21] and one only a single environment [22]. However, even a simple structural model can show that such a description cannot possibly be adequate. Unless the AgI "clusters" are large, which they cannot be because of the absence of any significant small angle scattering [2,23], the majority of Ag^+ must lie on the surface of such clusters and have both O^- and I^- neighbors. In our models there is a continuous range of environments, though it may be that Ag^+ not bonded to O^- are significantly more mobile than Ag^+ which are bonded to O^-. The "average" Ag^+ environment, depicted in Fig. 2, may be considered as a chemical complex involving Ag, I, and O. As x increases, and the phosphate chains become further apart, the number of Ag^+ which cross-link two NBO decreases (Fig. 2). These are the bonds which hold the chain structure together. Stoichiometrically at $x = 0.5$ an ordered structure of phosphate chains with no O-Ag-O cross-links could be formed. In a more random structure a transition would be expected in the region of $x = 0.5$, where the number of cross-links is only just sufficient to maintain the overall system connectivity, and a homogeneous glass can no longer be formed. Experimentally the limit is found to be $x \approx 0.58$ [24].

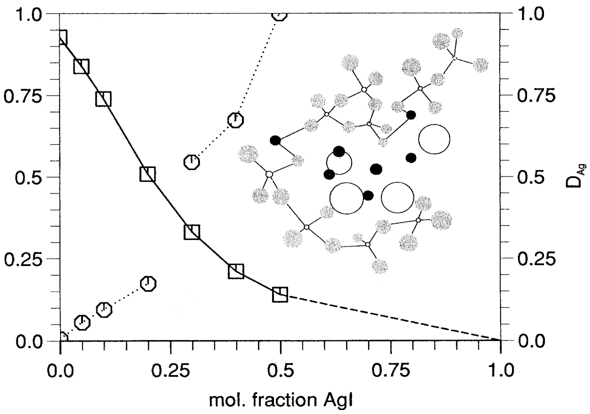

FIG. 2. The squares and solid curve show the probability of Ag^+ cross-linking phosphate chains as a function of AgI content, defined as the number of Ag^+ which have two or more NBO neighbors and no I^- neighbors divided by the number of Ag^+ necessary to cross-link all NBO. The broken curve is an extrapolation to the value of 0 for $x = 1$. The circles and dotted curve show the effective diffusion constants (normalized to 1 for $x = 0.5$) calculated by running a hard sphere Monte Carlo simulation for Ag^+ only, with all other atoms fixed, and taking the slope of the mean square displacement after a fixed time (i.e., number of Monte Carlo moves). Below the percolation transition the diffusion is localized, while above it is nonlocalized; this is indicated by the break in the dotted curve. The inset shows a projection of a "typical" atomic arrangement in the glass. O atoms are shaded, Ag atoms are black, P atoms are small open circles, and I atoms are large open circles. Bonds are drawn between all P and their neighboring O, and also between O and Ag that cross-link chains. All atoms are drawn approximately half size; because of the perspective view like atoms do not all appear exactly the same size.

The best simple description of the structure we can give is that the host glass and the salt form an amorphous complex structure. AgI does not enter the chain structure, but since the phosphate chains are intrinsically one dimensional they are surrounded by AgI. We find no evidence that the salt structure is similar to α-AgI; most Ag are coordinated to both I and O. Any attempt to produce a structure in which even single unit cells of α-AgI existed, i.e., body centered cubes of nine I^- ions with associated Ag^+ ions, would push the chains too far apart to possibly agree with the diffraction data or the density. A better description is the "tissue and bones" used by Ingram *et al.* [25], with the phosphate chains being the bones and the salt the tissue. The "modified random network" [26] and "diffusion pathway" models [6] are also good qualitative descriptions. The Ag^+ environment becomes more dominated by I^- as x increases, so there is a continuous evolution (within the glass forming range) towards a local AgI configuration, as had already been suggested on the basis of x-ray diffraction data [7]. This explains why properties such as conductivity [27] and sound velocity [28] extrapolate to the values for α-AgI.

In order to relate the Ag^+ conductivity to the structural models we have investigated the distribution of the free volume available for Ag^+ motion in the following manner. (1) Select one Ag^+ at random. (2) Move this ion many times in very small steps, moves only being accepted if the closest approach constraints are satisfied. In this way the free volume surrounding the ion is explored. Note the maximum distance moved from the original position. (3) If this maximum distance is greater than the diameter of the ion, i.e., it has "left behind" free volume large enough to be occupied by another Ag^+, then it is classified as a "conducting" ion. (4) If the Ag^+ is conducting, then move it from its original position by a random amount greater than its diameter and less than the maximum distance found earlier, subject to closest approach constraints. (5) Choose one of the neighbors that the Ag^+ had in its original position and repeat from step 2. (6) This produces a chain of conducting ions. When the chain comes to an end, i.e., when a conducting Ag^+ has no neighbors which are conducting, go one step back along the chain and choose a new neighbor at step 5. (7) Continue until no further moves are possible. This produces a "tree" of conducting ion pathways. (8) Repeat from step 1.

Examples of such pathways are shown in Fig. 3. For $x \leq 0.2$ there are many small trees. However, around $x = 0.3$ there is a percolation transition and the majority of conducting Ag^+ are then in a single tree. This observation of a percolation transition agrees with a prediction based on conductivity data [27]. (Note that the conductivity will not strictly show a percolation transition, since Ag^+ not in trees also contribute to conduction, though at a lower level.) If we assign an effective diameter of 2.95 Å to each Ag^+, based on the mean of the Ag-Ag closest approach (2.4 Å) and the first minimum in the partial radial distribution function (3.5 Å), then the volume fraction occupied by Ag^+ between $x = 0.2$ and 0.3 coincides with the value of 0.16 found for bond percolation for random hard spheres [29], i.e., the transition occurs where you would expect it to without the need for any particular ordering within the structure. Ag^+ diffusion is localized below the percolation transition and then increases rapidly above the transition (Fig. 2); clearly this is directly related to the rapid increase in conductivity [27].

It might appear that these arguments would apply to all other similar systems, which should therefore have similar conductivities. However, the dominant factor is the phosphate chain density; this reflects not only the amount of salt added but the bonding between the salt and the chains. For example, LiI doped into $LiPO_3$ has a much lower conductivity and a higher phosphate chain density than the equivalent AgI system; Li has a higher ionicity than Ag, hence the difference in bonding to the phosphate network. Other work we have done on AgBr and AgCl doping indeed shows that the conductivity scales with the phosphate density [30]. Thus we suggest that the main reason for the large increase in conductivity

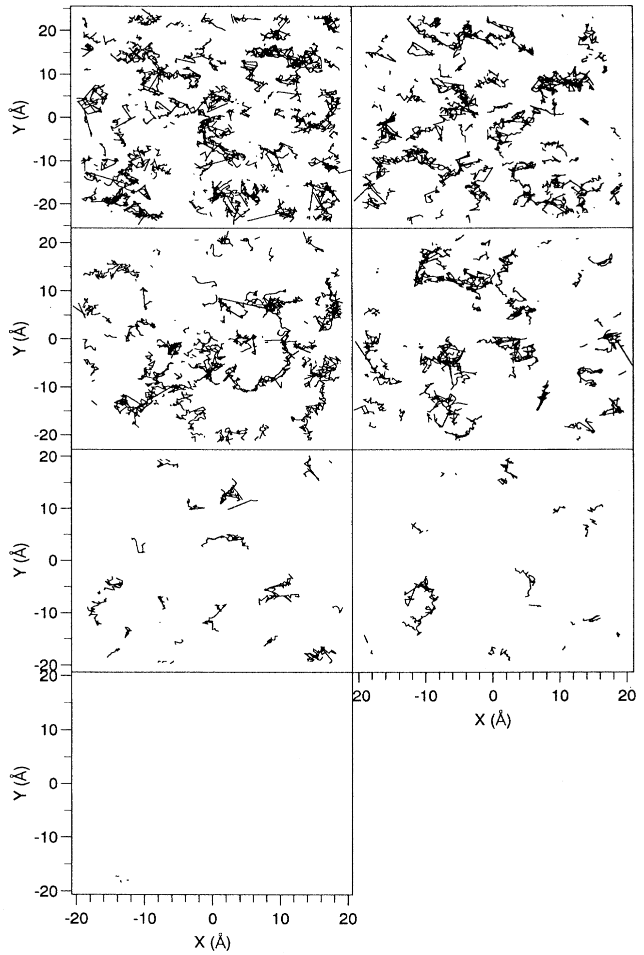

FIG. 3. "Trees" of conducting Ag^+ pathways for, from top left to bottom right, $x = 0, 0.05, 0.1, 0.2, 0.3, 0.4$, and 0.5. The algorithm for producing these pathways is described in detail in the text.

on addition of the dopant salt is the more open structure of the expanded network which provides the necessary free volume for Ag^+ motion.

The region of interest for material applications is clearly that of high ionic conductivity. In this Letter we have shown that a higher I^- content is required to increase the free volume, and hence gives a higher conductivity, but this eventually leads to crystallization. For materials of this type, high ionic conductivity is therefore necessarily related to structural instability. This poses a considerable challenge for design of new materials such as "rubbery electrolytes" [31].

[1] M. Tachez, R. Mercier, J.P. Malugani, and A.J. Dianoux, Solid State Ionics **20**, 93 (1986).

[2] M. Tachez, R. Mercier, J.P. Malugani, and P. Chieux, Solid State Ionics **25**, 263 (1987).

[3] A. Fontana, F. Rocca, and M.P. Fontana, Phys. Rev. Lett. **58**, 503 (1987).

[4] C. Rousselot, M. Tachez, J.P. Malugani, R. Mercier, and P. Chieux, Solid State Ionics **44**, 151 (1991).

[5] P. Benassi, A. Fontana, and P.A.M. Rodriguez, Phys. Rev. B **43**, 1756 (1991).

[6] T. Minami, J. Non-Cryst. Solids **73**, 273 (1985).

[7] G. Licheri, A. Musinu, G. Paschino, G. Piccaluga, G. Pinna, and A. Magistris, J. Chem. Phys. **85**, 500 (1986).

[8] D. Ravaine, J. Non-Cryst. Solids **73**, 287 (1985).

[9] J.P. Malugani and R. Mercier, Solid State Ionics **13**, 293 (1984).

[10] G. Carini, M. Cutroni, A. Fontana, G. Mariotto, and F. Rocca, Phys. Rev. B **29**, 3567 (1984).

[11] R.L. McGreevy and L. Pusztai, Mol. Sim. **1**, 359 (1988).

[12] B.E. Warren and G. Mavel, Rev. Sci. Instrum. **36**, 196 (1965).

[13] R.L. McGreevy and M.A. Howe, Annu. Rev. Mater. Sci. **22**, 217 (1992).

[14] D.A. Keen and R.L. McGreevy, Nature (London) **344**, 423 (1990).

[15] S.J. Gurman and R.L. McGreevy, J. Phys. Condens. Matter **2**, 9463 (1990).

[16] J.W. Zwanziger, K.K. Olsen, and S.L. Tagg, Phys. Rev. B **47**, 14 618 (1993).

[17] J.D. Wicks, R.L. McGreevy, and L. Börjesson, *Methods in the Determination of Partial Structure Factors,* edited by J.B. Suck, D. Raoux, P. Chieux, and C. Riekel (World Scientific, Singapore, 1993), p. 238.

[18] R.L. McGreevy, Nucl. Instrum. Methods (to be published).

[19] L. Börjesson, L.M. Torell, U. Dahlborg, and W.S. Howells, Phys. Rev. B **39**, 3404 (1989).

[20] P.A. Egelstaff, *An Introduction to the Liquid State* (OUP, Oxford, 1992).

[21] S.W. Martin, H.J. Bischof, M. Mali, J. Roos, and D. Brinkmann, Solid State Ionics **18/19**, 421 (1986).

[22] S.H. Chung, K.R. Jeffrey, J.R. Stevens, and L. Börjesson, Phys. Rev. B **41**, 6154 (1990).

[23] L. Börjesson and L.M. Torell, Philos. Mag. **59**, 105 (1989).

[24] J.P. Malugani, A. Wasniewski, M. Doreau, G. Robert, and A. Al Rikabi, Mater. Res. Bull. **13**, 427 (1978).

[25] M.D. Ingram, G.D. Chryssikos, and E.I. Kamitsos, J. Non-Cryst. Solids **131/133**, 1989 (1991).

[26] G.N. Greaves, J. Non-Cryst. Solids **71**, 203 (1985).

[27] M. Mangion and G.P. Johari, Phys. Rev. B **36**, 8845 (1987).

[28] L. Börjesson, S.W. Martin, L.M. Torell, and C.A. Angell, Solid State Ionics **18/19**, 431 (1986).

[29] R. Zallen, *The Physics of Amorphous Solids* (Wiley, New York, 1983).

[30] J.D. Wicks, Ph.D. thesis, University of Oxford, 1993 (unpublished).

[31] C.A. Angell, C. Liu, and E. Sanchez, Nature (London) **362**, 137 (1993).