PHYSICAL REVIEW B VOLUME 39, NUMBER 5 15 FEBRUARY 1989-I

Evidence of anomalous intermediate-range ordering in superionic borate glasses from neutron diffraction

L. Börjesson and L. M. Torell
Department of Physics, Chalmers University of Technology, S-412 96 Gothenburg, Sweden

U. Dahlborg
Department of Reactor Physics, The Royal Institute of Technology, S-100 44 Stockholm, Sweden

W. S. Howells
Rutherford-Appleton Laboratory, Chilton, Didcot, Oxon Oxfordshire, OX11 0QX, United Kingdom

(Received 19 October 1988)

Evidence of intermediate-range ordering in a superionic $(\mathrm{AgI})_x(\mathrm{Ag_2O}+2\mathrm{B_2O_3})_{1-x}$ glass is presented. Comparative neutron-diffraction measurements were performed in a low ($x=0.1$) and a high ($x=0.6$) -AgI-concentration glass. A strong and sharp diffraction peak at an anomalously low Q value of 0.8 Å^{-1} is observed for the $x=0.6$ glass, which is not present in the $x=0.1$ glass. The phenomenon is attributed to an ordering of the intermediate-range structure, due either to formations of AgI clusters or to density deficits in the boron-oxygen network.

Apart from technological aspects, ion-conducting glasses are challenging materials as such due to the high conductivity, which is extraordinary for a glass. In this Brief Report we present a neutron-diffraction study of the structural properties of two glasses belonging to the AgI-doped borate system $(\mathrm{AgI})_x(\mathrm{Ag_2O}+2\mathrm{B_2O_3})_{1-x}$, which contains some of the best glassy ionic conductors and which has served as a model system in investigations of the conduction mechanism in glasses. A high-conducting ($\sigma\approx10^{-3}$ S cm^{-1}) and a low-conducting ($\sigma\approx10^{-7}$ S cm^{-1}) glass of AgI concentrations $x=0.6$ and 0.1, respectively, were chosen for a detailed investigation.

The AgI-doped borate glasses are formed by the oxide glass former $\mathrm{B_2O_3}$ which together with the network modifier $\mathrm{Ag_2O}$ can dissolve the metal halide salt AgI. The structure of the $\mathrm{B_2O_3}$ glass matrix is substantially changed by the network modifier; the addition of $\mathrm{Ag_2O}$ to $\mathrm{B_2O_3}$ causes $\mathrm{BO_4}$ units to form while the number of three-coordinated borons typical of pure $\mathrm{B_2O_3}$ decreases.[1] With the introduction of AgI *the short-range order* of the host glassy matrix seems to be more or less unaffected.[1,2] However, the network becomes systematically weakened and expanded upon increasing the concentration of AgI which is observed in a decrease of the glass-transition temperature T_g,[1] and of the sound velocity.[3] A model has been suggested[4] in which the dopant salt enters into interstices in the boron-oxygen network, which become expanded. As a result, the intermediate-range order of the glass is changed, but without modification of the short-range order of the boron-oxygen matrix. The more open structure is favorable for ion diffusion, which is consistent with the increasing conductivity with increasing AgI content.[1] In another model, the diffusion-path model,[5] the ion diffusion takes place in preferred pathways made up of mostly iodines within the glass structure. It is suggested that the dissolved AgI tends to reproduce, on a local level, microdomains or small clusters with an internal structure similar to that of α-AgI,[2,6,7] which is the model material of a crystalline fast-ion conductor.

The tendency for clustering of AgI has been investigated in another AgI-doped glass, AgI-$\mathrm{AgPO_3}$, by Tachez *et al.*[8] with small-angle neutron scattering (SANS). They reported the presence of inhomogeneities with a mean gyration radius of 20 Å. However, in the case of the AgI-doped borate system, SANS measurements show that there are no clusters present with dimensions >10 Å.[9] Clusters of smaller dimensions are more difficult to study because few experimental techniques are available and there is no investigation of the intermediate-range structure reported for superionic glasses up to date. The aim of the present work is to study the structure of the short- and intermediate-range order in the $(\mathrm{AgI})_x(\mathrm{Ag_2O}+2\mathrm{B_2O_3})_{1-x}$ glasses to investigate if there is any structural ordering on a length scale <10 Å, i.e., outside the normal range of the small-angle neutron-scattering technique. We have therefore taken advantage of a neutron-spallation source, which permits diffraction measurements to be carried out at small scattering angles while maintaining a high resolution.

The experiments were performed at the diffractometer for liquid and amorphous materials (LAD) at the intense neutron-spallation source ISIS, Rutherford-Appleton Laboratory. The measured diffraction patterns were corrected for background, absorption effects, and multiple scattering.[10] In order to decrease the absorption effects, the samples were prepared with isotope-enriched ^{11}B (98% ^{11}B). The preparation is essentially the same as that described in Ref. 5, except that $\mathrm{H_3BO_3}$ is used instead of $\mathrm{B_2O_3}$. A concentration of $x=0.1$ was preferred over, for instance, an $x=0$, due to the more stable glass-forming properties of the former, which is still a poor conductor. The $x=0.6$ glass is on the other structure extreme of the ternary system, i.e., it contains the highest possible concentration of AgI for a stable glass formation.

The structure factors of the two glasses measured at the scattering angles 146° and 10° are shown in Figs. 1 and 2, respectively. The upper curves in the figures are obtained from the AgI-rich $x=0.6$ sample and the lower curves are from the low-concentration $x=0.1$ glass. It should be noted that there exist oscillations with a period of about 5 Å^{-1} in the $S(Q)$ of both glasses up to Q values larger than 30 Å^{-1} (Fig. 1). This indicates the presence of a well-defined interatomic distance of approximately 1.3 Å which we identify with the B—O bond length. The structure factors of the two samples are nearly identical for Q values larger than 2 Å^{-1} (see Figs. 1 and 2), which implies that the short-range order of the boron-oxygen network is unchanged despite the large amount of AgI added to the glass (60 mol %). This part of the structure factors is the subject of a detailed analysis which will be reported separately. In the present study attention is focused on the low-Q range in which dramatic differences in the behavior of the structure factor of the two samples are observed; a strong peak is observed at $Q \approx 0.8$ Å^{-1} in the case of the AgI-rich glass, which is not present in the low-concentration $x=0.1$ glass. The creation of a strong sharp diffraction peak at anomalous low Q values when AgI is added to the glass signals the building up of a considerable intermediate-range structure. In the case of the $x=0.1$ glass there are, however, indications of a peak at a slightly larger Q value, present as a shoulder at $Q \approx 1.3$ Å^{-1}, which is lacking in the structure factor of the $x=0.6$ sample.

Some precautions are needed in relating possible ordering effects to the presence of clusters of AgI or to other structural features since intermediate–long-range fluctuations in the average scattering density may occur in "normal" amorphous solids. A sharp diffraction peak [the first sharp diffraction peak (FSDP)] at a scattering vector between 1 and 1.5 Å^{-1} has been observed for many amorphous solids[11,12] (although not in all glasses) which indicate correlations of periods well beyond the first few nearest-neighbor distances. The interpretation of this peak is extremely controversial; it has been related to the presence of layers, clusters, chemical ordering, or to a random dense packing of basic structural or molecular units.[11,12] Moreover, recent computer-relaxed ball-and-stick models of amorphous topologies, which contain neither layers nor clusters, also reproduce the FSDP in chalcogenide glasses.[13] From these observations it is suggested that the FSDP is caused by the presence of ordered density deficits rather than distinct structural features such as clusters. Thus, a low-Q diffraction peak might be present in the ion-conducting glasses as well, without any reference to their doping characteristics.

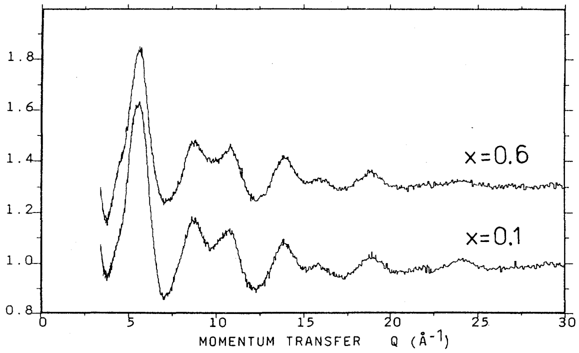

FIG. 1. Experimental average structure factors for two $(\text{AgI})_x(\text{Ag}_2\text{O}+2\text{B}_2\text{O}_3)_{1-x}$ glasses with (a) $x=0.6$ and (b) $x=0.1$ obtained at 146° scattering angle. The upper curve has been shifted vertically by 0.3 units to higher values for clarity.

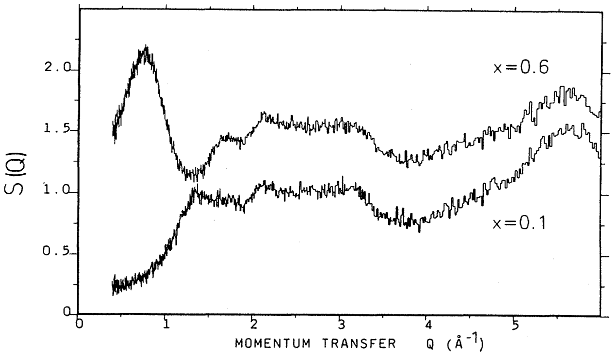

FIG. 2. Same as Fig. 1, but for 10° scattering angle. The upper curve ($x=0.6$) has been shifted vertically by 0.5 units to higher values for clarity.

A universal aspect of the FSDP observed in oxide, halide, and chalcogenide glasses is that when the momentum transfer is scaled to bring the typical distance scales of the different glasses roughly into line by taking $Q'=Qr_{AX}$, where r_{AX} is the nearest-neighbor bond length, the FSDP occurs at $Q' \approx 2.5$.[11,12] The universal behavior has been interpreted as originating from a random packing of basic structural units or molecules.[12] In Fig. 3 the structure factor $S(Q')$ of the $x=0.6$ glass is shown and compared with the $S(Q')$ of some common glasses. A value of $r_{AX}=1.4$ Å has been used for the scaling of the present glass which corresponds to the B—O distance in BO_4^- groups.[14] As seen in Fig. 3, there are small diffraction peaks close to $Q'=2.5$ also for the present superionic glass, which might then be due to a random dense packing of basic structural units, i.e., different borate groups. (This is, of course, also true for the $x=0.1$ glass since the two glasses show similar behavior for $Q > 1.5$ Å^{-1}.) However, there is also a new anomalous feature for the $x=0.6$ glass: an additional sharp and strong diffraction peak appears at considerable lower Q' ($Q' \approx 1.1$). Thus, this peak seems to have a different origin than the FSDP found in normal glasses, and is therefore, in this sense, anomalous.

As discussed above, it is not obvious whether the anomalous low-Q peak observed in the present study reflects a structural ordering of density deficits or real structural features. Both phenomena have in fact been proposed to be present in this system.[2–4,6,7] It has been suggested that units of AgI cause the glassy structure to break up, resulting in an increasing amount of interstices

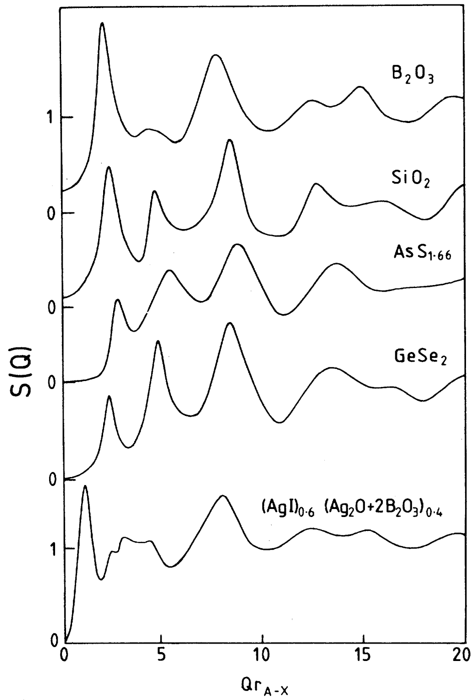

FIG. 3. Reduced structure factors for some common glasses (Ref. 11) and the ($x=0.6$) glass of the present study.

and/or interstices of increasing size and therefore a more open network.[3,4] Reported neutron-diffraction patterns of pure vitreous B_2O_3 reveal a FSDP at 1.59 $Å^{-1}$,[15] which corresponds to a real-space Fourier component of wavelength ~4 Å and has been related to a cage structure of holes in the network formed by boroxol rings. The peak at $Q \approx 1.3$ $Å^{-1}$ observed in the $x=0.1$ glass, which corresponds to a real-space characteristic distance of ~5 Å, might then be related to modified boroxol rings containing one or two BO_4^- units. Accordingly, the more open boron-oxygen structure of the AgI-rich glass ($x=0.6$) can then be described by a characteristic length of ~8 Å corresponding to the peak observed at $Q=0.8$ $Å^{-1}$. The two observed peaks might, on the other hand, be related to the presence of real structure features of AgI. It should be noted that the dimensions of these features are then much smaller than those previously suggested for AgI clusters or microdomains.[6-8]

The correlation length L of the intermediate-range ordering over which the period of the repeat unit survives can be estimated from the expression $L \approx \pi/\Delta Q$, where ΔQ is the half-width at half maximum of the FSDP. For the $x=0.6$ glass $\Delta Q \approx 0.25$, which corresponds to a correlation length of ~13 Å. Correlation lengths, attributed to a reorganization of the borate glass matrix, have been reported from low-frequency Raman experiments of a series of undoped $B_2O_3+nM_2O$ glasses (M=alkali-metal cation).[16] The obtained correlation lengths, which were in the range 5–9 Å, where related to the formation of different borate groups (boroxol rings, diborate triborate, and tetraborate groups). In a similar study[2] of the doped glasses $(AgI)_x(Ag_2O+nB_2O_3)_{1-x}$, it was observed that the correlation length gradually increases with increasing AgI content, from 8 Å for $x=0$ to a maximum value of ~12 Å for the largest AgI content, which indicates increasing order of the glassy matrix with addition of AgI. In the latter study[2] the increasing correlation length is related to the increasing dimensions of AgI clusters within the network, rather than to a changing borate network. Despite the fact that light scattering and neutron diffraction are probing different phenomena (phonon dynamics and mass distribution, respectively), they give indications of intermediate-range order of about the same extent.

In summary, we conclude that anomalous intermediate-range structural ordering has been observed in AgI-doped borate glasses. A strong and anomalously-low-lying diffraction peak at $Q=0.8$ $Å^{-1}$, which is only present in the AgI-rich glass, indicates the presence of repeat units with a typical length of about 8 Å, and which are correlated over distances of ~13 Å. The phenomenon is attributed to either formation of very small AgI clusters or to voids within the boron-oxygen network. The local structure of the borate matrix, however, seems not to be affected by the AgI doping since no significant change in the structure factor could be observed in the Q range $Q > 2$ $Å^{-1}$. At present we are planning to extend the neutron-diffraction investigation of the $(AgI)_x(Ag_2O+2B_2O_3)_{1-x}$ system to ^{107}Ag isotope-enriched glasses and to glasses of a range of AgI concentrations. The aim is to study the dependence of the intensity and position of the low-Q peak on AgI content to clarify the origin of the structural ordering observed in the present study.

The authors are grateful to the Rutherford-Appleton Laboratory for use of the experimental facilities at ISIS and to the Swedish Natural Science Research Council for financial support.

---

[1] C. Chiodelli, A. Magistris, M. Villa, and J. L. Bjorkstam, J. Non-Cryst. Solids **51**, 143 (1982).

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

[3] L. Börjesson, Phys. Rev. B **36**, 4600 (1987).

[4] H. L. Tuller and D. P. Button, in *Transport-Structure Relations in Fast Ion and Mixed Conductors,* edited by F. W. Poulsen, N. Hessel-Andersen, K. Clausen, S. Skaarup, and O. Toft Soerensen (Risø National Laboratory, Denmark, 1985).

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

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

[7] A. Avogadro, S. Aldrovandi, and F. Borsa, Phys. Rev. B **33**, 5637 (1986).

[8] M. Tachez, R. Mercier, and J. P. Malugani, Institut-Laue-Langevin (Grenoble, France), Annual Report–1984 (unpublished).

[9] L. Börjesson, J. Kjems, D. Posselt, and L. M. Torell (unpublished).

[10] W. S. Howells, Rutherford-Report Nos. RAL-80-017 and RAL-86-042, Appleton Laboratory (Didcot, England), 1980 and 1986 (unpublished).

[11] A. C. Wright, R. N. Sinclair, and A. J. Leadbetter, J. Non-Cryst. Solids **71**, 295 (1985).

[12] S. C. Moss and D. L. Price, in *Physics of Disordered Materials,* edited by D. Adler, H. Fritsche, and S. R. Ovshinsky (Plenum, New York, 1985).

[13] T. G. Fowler and S. R. Elliot, J. Non-Cryst. Solids **92**, 31 (1987).

[14] G. Paschina, G. Piccaluga, and M. Magini, J. Chem. Phys. **81**, 6201 (1984).

[15] P.A.V. Johnson, A. C. Wright, and R. N. Sinclair, J. Non-Cryst. Solids **50**, 281 (1982).

[16] J. Lorösch, M. Couzi, J. Pelous, R. Vacher, and A. Levasseur, J. Non-Cryst. Solids **69**, 1 (1984).