

Role of AgI for ionic conduction in AgI-AgPO₃ glasses

B. Roling and M. D. Ingram

Department of Chemistry, University of Aberdeen, Aberdeen AB24 3UE, Scotland, United Kingdom

M. Lange and K. Funke

Institut für Physikalische Chemie, Westfälische Wilhelms-Universität Münster, Schlossplatz 4/7, 48149 Münster, Germany

(Received 31 March 1997)

Using frequency and temperature-dependent conductivity data for x AgI·(1- x) AgPO₃ glasses in the composition range from $x=0.10$ to $x=0.55$, we find that the number density of mobile ions as well as the ionic relaxation mechanism are independent of temperature and composition. We believe that this result is important in order to clarify the controversial role of AgI for the ion transport in these glasses. Moreover, our observation should generally impact on the understanding of fast ion conduction in glass. In the frequency range covered in our study, i.e., at frequencies below a few MHz, a superlinear dependence of the conductivity on frequency as reported recently has not been observed. [S0163-1829(97)01245-9]

I. INTRODUCTION

Fast ion conduction in glass is not only interesting from the viewpoint of the fundamental researcher but is also of great importance for the development of new glassy materials for technological application, e.g., in batteries and in electrochromic displays. Progress in this field has mainly been achieved by empirical findings, e.g., it has been discovered that the conductivity of oxide glasses can be greatly enhanced by the doping with metal halides.¹⁻⁵ Despite considerable effort to obtain a physical understanding of this phenomenon, there is no generally accepted theory that would be helpful with respect to the more specific development of highly conducting glasses.

AgI-AgPO₃ glasses have been widely investigated as model materials since they can be easily prepared, and glass forming is observed over large composition ranges. Several models have been proposed to account for the fast ion conduction found at high AgI concentrations.

Based on the "diffusion path model" of Minami,⁶ many models ascribe a particular role to the creation of pathways where the mobile Ag⁺ ions are mainly coordinated by iodide.

In the so-called "cluster model" of Malugani and co-workers,⁷⁻⁹ the formation of microdomains or clusters of AgI within the host matrix is proposed. The Ag⁺ ions located in these clusters are assumed to be much more mobile than those located in other regions of the glass. As the AgI content of the glasses increases, the ions percolate more easily from cluster to cluster leading to an increase in the ionic conductivity. This model is mainly based on the results of neutron and x-ray-diffraction studies suggesting that AgI does not affect the local structure of the host matrix.^{10,11} This is in agreement with results from Brillouin and Raman studies^{12,13} that indicate a very weak interaction between AgI and AgPO₃.

The "cluster tissue approach" of Rao and Ingram^{14,15} also assumes an inhomogeneous structure consisting of a highly conducting and a less conducting phase, but in this latter model close-packed regions of host network are sur-

rounded by a connective tissue of AgI containing the highly mobile Ag⁺ ions.

Weak electrolyte approaches¹⁶⁻¹⁸ have been proposed where the AgI "solute" may be homogeneously dispersed in the AgPO₃ glass network. This solute is regarded as partially dissociated, and the free Ag⁺ ions so produced contribute to the dc conductivity. The concentration of free ions is, however, small and temperature dependent.

In all the above models, the Ag⁺ ions bonded to iodine play the dominant role in the conduction process. Accordingly, the models require that the number density of Ag⁺ ions determining the ionic conductivity should depend on glass composition.

However, in recent work a different approach was put forward. Reverse Monte Carlo models by Wicks *et al.*¹⁹ based on neutron and x-ray diffraction and on extended x-ray absorption fine-structure spectroscopy suggest that the main role of AgI is to expand the AgPO₃ network and to create free volume. This causes the increase in the ionic conductivity. This result was confirmed by Swenson and Börjesson²⁰ who found a general relationship between network expansion and conductivity enhancement for a large variety of metal-halide-doped oxide glasses.

In order to shed light on the microscopic nature of the conduction process, several authors have performed measurements of the frequency-dependent conductivity. The results of Pathmanathan and co-workers²¹ and of Mangion and Johari²² for AgI-AgPO₃ glasses of various compositions show that in the frequency range from 12 Hz to 100 kHz the ac conductivity depends on frequency in a sublinear fashion. Recently, Le Stanguennec and Elliott²³ have published conductivity data for similar glasses in the frequency range from 1 Hz up to 200 kHz. In contrast to the above studies, they find two contributions to the ac conductivity. One is characterized by a sublinear dependence of the conductivity on frequency, while the second is characterized by a superlinear dependence. These contributions are attributed to long-range diffusion and to localized motions of the Ag⁺ ions, respectively.

In this paper, we present conductivity data for

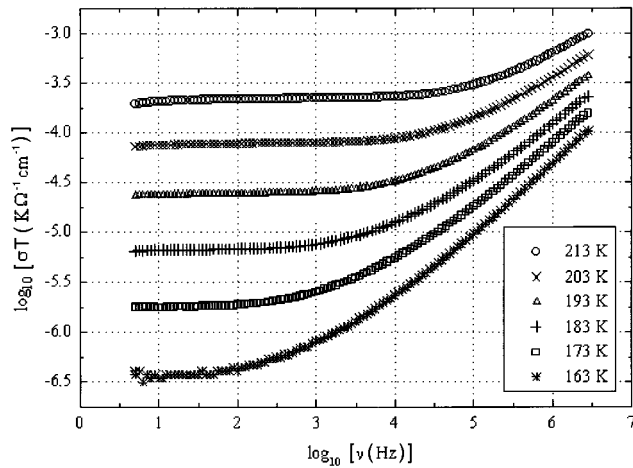


FIG. 1. Frequency-dependent conductivity of the glass 0.3 AgI · 0.7 AgPO₃ at different temperatures.

x AgI · $(1-x)$ AgPO₃ glasses in the frequency range from 5 Hz to 4 MHz and at various temperatures. The data have been taken for a range of compositions from $x=0.10$ to $x=0.55$. In Ref. 24, we have shown for sodium borate glasses of different compositions that an appropriate scaling analysis of frequency and temperature-dependent conductivity spectra can reveal valuable information about the mobility of the charge carriers. Therefore, this kind of analysis will be helpful in deciding whether or not all Ag⁺ ions contribute to the conduction process.

II. EXPERIMENTAL

Dry mixtures of AgI, AgNO₃, and (NH₄)₂HPO₄ were heated in a quartz crucible. After the gas evolution had subsided, the melts were held between 450 and 500 °C, depending on the composition, for one hour. They were then poured into a stainless-steel mold having the same temperature as the melts. The melts were cooled down to room temperature by pressing the mold between two aluminum blocks. This procedure ensured a well-defined cooling rate between 6 K/s and 8 K/s. The samples were then polished, and silver electrodes were evaporated onto the sample surfaces. The samples were mounted in a specially designed sample holder that was placed in a quartz tube flushed with dry nitrogen gas. The frequency-dependent electrical conductivity was measured in the frequency range from 5 Hz to 4 MHz using the If impedance analyzer HP 4192A.

III. RESULTS

In Fig. 1 we present the frequency-dependent conductivity (expressed as product $\sigma' \cdot T$) of the glass 0.3 AgI · 0.7 AgPO₃ at different temperatures. At low frequencies, a constant conductivity is detected. This is the dc conductivity of the glass. In all glasses studied, the dc conductivity obeys an Arrhenius law. The dc activation energy E_A^{dc} , obtained from conventional Arrhenius plots, is shown in Fig. 2 as a function of the AgI content, x . These data are in good agreement with the results from other studies.^{3,22,25}

Let us return to Fig. 1. As described in Ref. 24, we have now analyzed the conductivity data by scaling both axes with

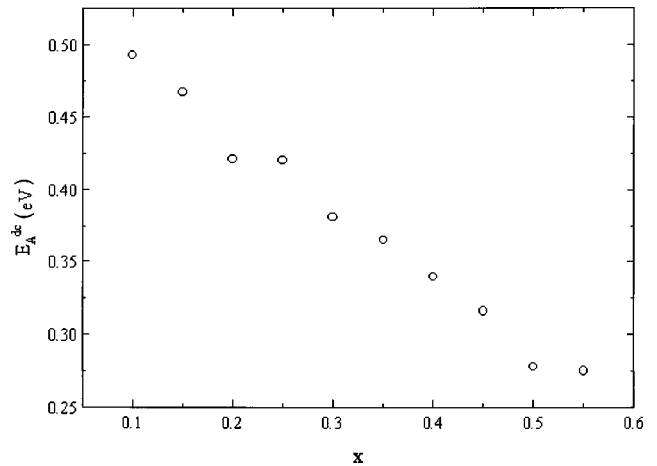


FIG. 2. Activation energy for the dc conductivity E_A^{dc} , as a function of the AgI content of the glasses, x .

the factor $\sigma_{\text{dc}}T$. By doing so, we observe that all conductivity isotherms fall onto one master curve. This not only applies for the 0.3 AgI · 0.7 AgPO₃ glass but for all glass compositions studied. Figure 3 shows the individual master curves for $x=0.10$, 0.30, 0.40, and 0.55. Within the experimental error, all of them coincide.

IV. DISCUSSION

In Ref. 24 we have presented conductivity master curves for sodium borate glasses, y Na₂O · $(1-y)$ B₂O₃, containing different amounts of sodium oxide, y . In these glasses, the individual master curves are shifted to higher values of $\nu/(\sigma_{\text{dc}}T)$ as y decreases. This reflects the decreasing number density of the mobile sodium ions. The individual curves can, however, be superimposed by employing y as an additional scaling factor for the frequency axis, see Ref. 24. As y is roughly proportional to the number density of mobile Na⁺ ions, this procedure implies a scaling of the frequency axis with $\mu_{\text{dc}}T$. Here, μ_{dc} is the dc mobility of the ions.

In the x AgI · $(1-x)$ AgPO₃ system, a corresponding number density effect is absent. The position of the conductivity master curves on the scaled frequency axis does not

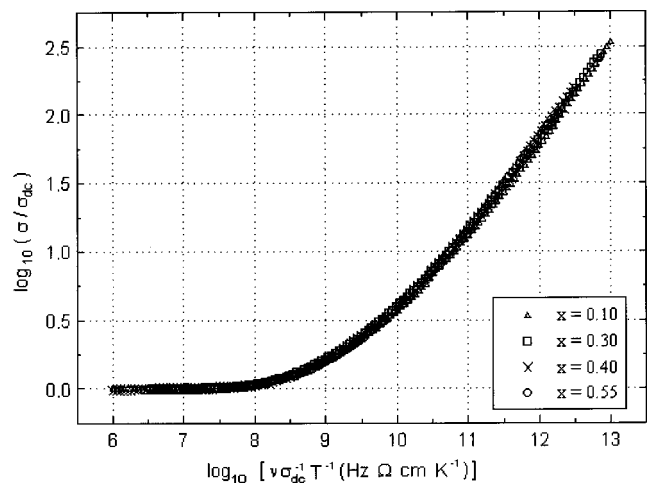


FIG. 3. Conductivity master curves of the x AgI · $(1-x)$ AgPO₃ glasses containing different amounts of AgI.

depend on the compositional parameter x . From this we conclude that AgI does not provide additional charge carriers in a manner analogous to the way Na_2O provides charge carriers in $\text{Na}_2\text{O-B}_2\text{O}_3$ glasses. Instead all the Ag^+ ions must be mobile regardless of whether they come from AgI or AgPO_3 , i.e., it is impossible to distinguish the contribution from different sorts of ions in different environments. Within the experimental error, the shape of the conductivity master curves is identical with the shape observed in the case of other single-ion conducting glasses.²⁶ This suggests a universal transport mechanism in these glass systems, regardless of the presence of AgI.

Taking into account these results, we argue that the main effect of doping AgPO_3 with AgI is to decrease the activation energy required for the ionic transport without affecting the number density of the mobile charge carriers or the relaxation mechanism. Accordingly, neither cluster models nor weak electrolyte approaches seem to be necessary in order to describe the role of AgI for the conduction process. Our results seem to favor an approach that does not focus on particular sites occupied by the Ag^+ ions but instead on some more general influence of AgI on glass structure. This could, e.g., involve the dilatation of the network.^{19,20}

We would like to emphasize that such an approach would not exclude the possibility of different local environments for Ag^+ ions, and accordingly different activation energies for local relaxation processes. In fact, there are experimental results indicating that different types of sites do exist in AgI containing glasses.^{27,28} One would have expected that these structural features affect the short-range dynamics of the mobile ions. Remarkably, the dispersion of the ac conductivity below a few MHz provides, however, no evidence for the existence of these separate microscopic processes since the ac data can be scaled using a single (dc) activation energy. Presently, there is no explanation for this very simple result. On the other hand, in some highly conducting glasses, deviations from the scaling behavior and a superlinear frequency dependence of the conductivity have been observed in the GHz regime.²⁹⁻³³ Possibly, this behavior is more indicative of the effects of short-range order on ion dynamics.

Finally, we would like to point to discrepancies between

our results and those of Le Stanguennec and Elliott.²³ Like Pathmanathan and co-workers²¹ and Mangion and Johari,²² we do not find evidence for a superlinear frequency dependence of the conductivity at frequencies below a few MHz. In a log-log plot, the apparent slope increases with increasing frequency and/or decreasing temperature. At high frequencies and/or low temperatures, the slope approaches but does not exceed unity. A similar kind of frequency response has been found in many other glass systems.³⁴⁻⁴¹

V. CONCLUSIONS

We have measured the frequency and temperature-dependent conductivity of the glass system $x \text{AgI} \cdot (1-x) \text{AgPO}_3$ for a wide range of compositions. Three important results have been obtained from our study.

First, the shape of the conductivity isotherms is independent of temperature and composition. Furthermore, within the experimental error it is identical with the shape found in the case of other single-ion conducting glasses. This suggests a universal transport mechanism in all these systems.

Second, the results of our scaling analysis indicate that the number density of mobile Ag^+ ions does not depend on the AgI content of the glass.

Both of these experimental findings strongly impact on the assessment of models describing the correlation between structure and ionic conductivity. It seems that a very general approach, see, e.g., Ref. 20, which does not focus on structural details, is required to explain these findings.

Third, at frequencies below a few MHz, a superlinear dependence of the conductivity on frequency as published recently²³ has not been observed in any of our glasses. Rather, the frequency response seems to be very similar to what we have found in many other glass systems.

ACKNOWLEDGMENTS

The present work was largely funded by the Deutsche Forschungsgemeinschaft. The authors are grateful to the Fonds der Chemischen Industrie, the DAAD, and the British Council for financial support.

¹D. Kunze, in *Fast Ion Transport in Solids*, edited by W. van Gool (North-Holland, Amsterdam, 1973), p. 405.

²J. P. Malugani and G. Robert, *Mater. Res. Bull.* **14**, 1075 (1979).

³J. P. Malugani, G. Robert, and R. Mercier, *Mater. Res. Bull.* **15**, 715 (1980).

⁴M. Doreau, J. P. Malugani, and G. Robert, *Electrochim. Acta* **26**, 711 (1981).

⁵G. Robert, J. P. Malugani, and A. Saida, *Solid State Ionics* **3/4**, 311 (1981).

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

⁷J. P. Malugani and R. Mercier, *Solid State Ionics* **13**, 293 (1984).

⁸M. Tachez, R. Mercier, and J. P. Malugani, *Solid State Ionics* **20**, 93 (1986).

⁹A. Musinu, G. Paschina, G. Piccaluga, and G. Pinna, *Solid State Ionics* **34**, 187 (1989).

¹⁰M. Tachez, R. Mercier, J. P. Malugani, and P. Chieux, *Solid State Ionics* **25**, 263 (1987).

¹¹A. Musinu, G. Piccaluga, and G. Pinna, *J. Chem. Phys.* **89**, 1074 (1988).

¹²P. Benassi, A. Fontana, and P. A. M. Rodrigues, *Phys. Rev. B* **43**, 1756 (1991).

¹³P. Benassi, A. Fontana, and P. A. M. Rodrigues, *Philos. Mag. B* **65**, 173 (1992).

¹⁴K. J. Rao and C. N. R. Rao, *Mater. Res. Bull.* **17**, 1337 (1982).

¹⁵M. D. Ingram, M. A. Mackenzie, W. Müller, and M. Torge, *Solid State Ionics* **28-30**, 677 (1988).

¹⁶J. C. Reggiani, J. P. Malugani, and J. Bernard, *J. Chim. Phys.* **75**, 245 (1978).

¹⁷D. Ravaine and J. L. Souquet, *Phys. Chem. Glasses* **18**, 27 (1977).

- ¹⁸D. Ravaine and J. L. Souquet, *Phys. Chem. Glasses* **19**, 115 (1978).
- ¹⁹J. D. Wicks, L. Börjesson, G. Bushnell-Wye, W. S. Howells, and R. L. McGreevy, *Phys. Rev. Lett.* **74**, 726 (1995).
- ²⁰J. Swenson and L. Börjesson, *Phys. Rev. Lett.* **77**, 3569 (1996).
- ²¹K. Pathmanathan, S. R. Hope, and G. P. Johari, *J. Non-Cryst. Solids* **94**, 186 (1987).
- ²²M. Mangion and G. P. Johari, *Phys. Chem. Glasses* **29**, 225 (1988).
- ²³M. Le Stanguennec and S. R. Elliott, *Solid State Ionics* **73**, 199 (1994).
- ²⁴B. Roling, A. Happe, K. Funke, and M. D. Ingram, *Phys. Rev. Lett.* **78**, 2160 (1997).
- ²⁵V. Clement, D. Ravaine, and C. Desportes, *Solid State Ionics* **28-30**, 1572 (1988).
- ²⁶B. Roling, *Solid State Ionics* (to be published).
- ²⁷E. I. Kamitsos, J. A. Kapoutsis, G. D. Chryssikos, J. M. Hutchinson, A. J. Pappin, M. D. Ingram, and J. A. Duffy, *Phys. Chem. Glasses* **36**, 141 (1995).
- ²⁸St. Adams, K. Hariharan, and J. Maier, *Solid State Ionics* **86-88**, 503 (1996).
- ²⁹C. Cramer, K. Funke, C. Vortkamp-Rückert, and A. J. Dianoux, *Physica A* **191**, 358 (1992).
- ³⁰B. Durand, G. Taillades, A. Pradel, M. Ribes, J. C. Badot, and N. Belhadj-Tahar, *J. Non-Cryst. Solids* **172-174**, 1306 (1994).
- ³¹C. Cramer, K. Funke, and T. Saatkamp, *Philos. Mag. B* **71**, 701 (1995).
- ³²M. Cutroni, A. Mandanici, A. Piccolo, and C. Tomasi, *Philos. Mag. B* **71**, 843 (1995).
- ³³C. Cramer, K. Funke, B. Roling, T. Saatkamp, D. Wilmer, M. D. Ingram, A. Pradel, M. Ribes, and G. Taillades, *Solid State Ionics* **86**, 481 (1996).
- ³⁴A. Burns, G. D. Chryssikos, E. Tombari, R. H. Cole, and W. M. Risen, Jr., *Phys. Chem. Glasses* **30**, 264 (1989).
- ³⁵W.-K. Lee, J. F. Liu, A. S. Nowick, *Phys. Rev. Lett.* **67**, 1559 (1991).
- ³⁶K. L. Ngai, U. Strom, and O. Kanert, *Phys. Chem. Glasses* **33**, 109 (1992).
- ³⁷A. S. Nowick, B. S. Lim, and A. V. Vaysleyb, *J. Non-Cryst. Solids* **172-174**, 1243 (1994).
- ³⁸H. Jain and C. H. Hsieh, *J. Non-Cryst. Solids* **172-174**, 1408 (1994).
- ³⁹C. H. Hsieh and H. Jain, *J. Non-Cryst. Solids* **203**, 293 (1996).
- ⁴⁰D. L. Sidebottom, P. F. Green, and R. K. Brow, *Phys. Rev. Lett.* **74**, 5068 (1995).
- ⁴¹D. L. Sidebottom, P. F. Green, and R. K. Brow, *J. Non-Cryst. Solids* **203**, 300 (1996).