Effect of Pressure on Conductivity in Liquid and Glassy States of a Superionic Conducting Glass

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Abstract: To observe whether pressure acting on the liquid state of a fast ion conducting vitreous solid electrolyte has a very different effect from pressure acting on the fixed structure vitreous state measurements have been performed on (AgI)40(AgPO4)60 over a range of pressures and temperatures. Below Tg, conductivity decreases according to classic transition state theory expressions with volume of activation close to the mobile ionic volume. Pressure applied above Tg has only slightly different effect than below, in contrast to strong pressure effect on viscosity. An explanation links weak pressure effects to previously known weak quenching (fictive temperature) effects through the decoupling index.

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ABSTRACT

To observe whether pressure acting on the liquid state of a fast ion conducting vitreous solid electrolyte has a very different effect from pressure acting on the fixed-structure vitreous state, measurements have been performed on \((\text{AgI})_{40}(\text{AgPO}_3)_{60}\) over a range of pressures and temperatures. Below \(T_g\), conductivity decreases according to classic transition state theory expressions with volume of activation close to the mobile ion volume. Pressure applied near and above \(T_g\) has only a slightly different effect than the same pressure applied well below \(T_g\) below, in contrast to the strong pressure effect on viscosity above \(T_g\). An explanation links weak pressure effects to previously known weak quenching (fictive temperature) effects, through the high decoupling index.

INTRODUCTION

While there have been a great many studies of electrical conductivity in glassy phases containing silver and other mobile cations,\(^{(1)}\) very few have dealt with the effects of pressure. Those that have\(^{(2-5)}\) have in all cases considered only the effect of pressure on the glassy state of the substance under investigation, leaving uninvestigated, the effects of pressure on a fast ion structure which can rearrange in response to the pressure. In such studies both decreases of conductivity\(^{(2,3,5)}\) and also rather large increases\(^{(4)}\) in conductivity have been observed, depending on the temperature of study and the type of cell construction employed. We felt that if in fact conductivity increases with pressure are obtainable then the possibility of freezing in the structures which are responsible (by vitrifying the liquid while under pressure) should be explored. We have therefore chosen the much studied system \(\text{AgI} + \text{AgPO}_3\)\(^{(1,6,7)}\) for a trial investigation of this phenomenology. The \(\text{AgPO}_3\)-based glass has the advantage that at high \(\text{AgI}\) contents
the glass transition temperature is sufficiently low that oil in contact with the sample can
be used as the pressure-transmitting medium.

EXPERIMENTAL ASPECTS

Samples of AgI–AgPO₃ glass nominally of composition 40 mol % AgI were
prepared by fusion of weighed quantities of analytical grade AgI and AgNO₃ and
(NH₄)₃PO₄. The second sample appears, from the lower conductivity data, to have lost
some iodide by air oxidation during melting (which is not of importance to the main
points of this study). The melt was poured into the twin electrode cell of design shown in
Fig. 1 so as to cover the electrodes to a depth of at least 2 mm. The depth was chosen so
as to avoid interference of the miniscus with the conductance path while maintaining the
sample small enough to minimize the danger of sample cracking. This cell plus sample
was immersed in oil in the interior of a steel pressure bomb described elsewhere,⁸ and
subjected to pressure and temperature variations as described below.

The cell constant was determined with N/10 KCl solution, and was found to be 0.50
cm⁻¹.

The conductivity was measured using a GenRad bridge Digi Model No. 1689 with
frequency varying between 5 and 10⁵ Hz, in two sequences, as follows. In the first series
data were taken during increasing and decreasing pressure at room temperature to a limit
of 1600 bar with the first sample, and up to 1400 bar with the second. In the second
series, and using the second sample, a cyclic path was followed with the object of
separating liquid-like from glass-like effects of pressure on the conductivity. Starting at
room temperature the temperature was raised until the value 57.5°C somewhat below T₉
so that thermal annealing would be avoided was reached, at which point the pressure of
1500 bar was applied. After waiting for a sufficient period for complete structural equili-
rium to be reached, the conductivity was measured during steadily decreasing tempera-
ture back to room temperature. At this point pressure was released resulting in a solid-
like decompression and an increase of conductivity. The conductivity was then measured
while the temperature again raised until T₉ was passed and the frozen in compression
from run 2 was released resulting in a further conductivity increase. The temperature
was then lowered to verify that the starting conductivity at 1 atmosphere pressure and
room temperature could be re-established.

RESULTS

The results of the two series of measurements are shown in Figs. 1 and 2. The solid circles in Fig. 1a is from the earlier ambient pressure study of Malugani, et. al.(6) There is a substantial difference between the conductivities of the two samples which is probably due to air oxidation of iodide in the melt in the second case. However, the interest of the present study lies in variations of the conductivity with pressure at different temperatures, and the absolute accuracy of the measurements is not of great importance. It can be seen that the pressure dependence of the conductivity is very similar in the two cases.

DISCUSSION

The effect of pressure on the glass at temperatures far below the glass transition is as might be expected from previous studies.(2,3) The slope of the plot can be converted to a volume of activation $\Delta V$ using the standard transition state expression

$$\frac{d\log \sigma}{dP} = -\frac{\Delta V}{RT}$$

The values of $\Delta V$ obtained from the slopes of the Fig. 1a plots are 2.6 and 3.8 cm$^3$/mole respectively which compare reasonably well with the volume of a mole of silver ions o. radius 0.95 Å, 2.6 cm$^3$/mole. Hamann(2) found $\Delta V - 3.5 \pm 0.3$ cm$^3$/mol for Na$^+$ conducting in sodium silicate glass ($r_{Na^+} = 0.95$ Å). In each case the activation volume is a little greater than the ionic volume, though this would be reversed if we used the Goldschmidt radius for Ag. If we assign $r_{Ag^+} = 1.26$ Å, for instance, the ionic volume becomes 5.0 cc/mole. The smaller activation volume would in this case need to be explained in terms of the higher polarisability of the Ag$^+$ ion. The larger Van der Waals attraction for I$^-$ anions makes possible a closer approach in the transition state.

The results of principal interest for this study, however, are contained in Fig. 1(b), where we compare the effect of pressure on solid and liquid states of the sample. For instance the compression at 57.5°C, (chosen to permit liquid-like relaxation while avoiding any possibility of crystallization) at the limit of run 1 shows the combined effect of elastic (solid-like) and relaxational (liquid-like) compression on the conductivity.
Decompression at room temperature at the end of run 2, on the other hand, shows only the contribution of elastic compression to the conductivity since no configurational change can occur at 60° below T_g on a short time scale. The effect of temperature on the conductivity of a glass with frozen-in configurational compression is seen in Fig. 2 run 3. Evidently the configurational contribution to the conductivity is relatively small. The depression of conductivity due to the frozen-in compressed state Δσ (conf) is released at the end of path 3 as the temperature approaches the glass transition temperature: the restoration of the original 1 atmosphere pressure conductivity at high temperature is observed satisfactorily. This is confirmed by the conductivity of the same sample on return to ambient temperature, as shown by the filled symbol at the end.

It is striking that the elastic effect is much larger than the relaxation (or configurational) effect. Indeed, in some preliminary experiments conducted at constant temperature above T_g, it appeared that (in disaccord with the Fig. 1(b) result) the effect of pressure on the liquid was actually smaller than that on the glass. In neither case, however, was there any confirmation of initial increases of conductivity with increasing pressure.(4)

The reason for the small contribution to the conductivity of liquid-like compression in a liquid of relatively "fragile" character(9) (as AgI-AgPO_3 appears to be(10)) in which the configurational contribution to the viscosity is dominant,(11) is presumably to be correlated with the unusually small effect of fictive temperature on the conductivity of superionic glasses which has been demonstrated by comparing conductivities of quenched and annealed samples, in previous work.(12–14) The fictive temperature, is a measure of the configurational disorder frozen into the glassy state and it has a large effect on the creep flow properties of glasses below their T_g. The small effect on the conductivity in each case is to be associated with the high degree of decoupling of the conductivity modes from the viscous modes, a process which begins at temperatures far above the glass transition and is responsible for the existence of the superionic conductivity phenomenon. It would be reasonable to anticipate that the \( \frac{Δσ_{\text{conf}}}{Δσ_{\text{total}}} \) will be correlated with B_σ/B_η, where B is the numerator in the Vogel-Tammann-Fulcher equation for liquid state transport properties,
\[
\sigma, \mu^{-1}, D/T = A_i \exp\left(-\frac{B_i}{T-T_0}\right)
\]

where \(A_i\), \(B_i\) and \(T_0\) are constants. For superionic conducting systems, in the liquid state \(B_\sigma\) is much smaller than \(B_\mu\).\(^\text{(14,15)}\) Unfortunately, there is currently a lack of information on the viscosity of the liquid state of fast ion conducting glasses, so this conjecture cannot be confirmed at this time.

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REFERENCES

1. See recent reviews by:

FIGURE CAPTIONS

a. Effect of pressure on two 4AgI-6AgPO₃ glasses, far below Tₙ.

b. Temperature dependence of conductivity of sample 2 of part (a) under ambient pressure (run 1) after compression to 1400 bar at 55°C close to Tₙ (run 2) and after decompression at room temperature. Note restoration of original conductivity on relaxation above 55°C.