

DTIC FILE COPY

④

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1b RESTRICTIVE MARKINGS		
3 DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release and sale; its distribution is unlimited.		
4. PERFORMING ORGANIZATION REPORT NUMBER Technical Report No. 17		
5. MONITORING ORGANIZATION REPORT NUMBER(S)		
6a. NAME OF PERFORMING ORGANIZATION Purdue University Department of Chemistry	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION Division of Sponsored Programs Purdue Research Foundation
6c. ADDRESS (City, State, and ZIP Code) Department of Chemistry Purdue University West Lafayette, IN 47907		7b. ADDRESS (City, State, and ZIP Code) Purdue University West Lafayette, IN 47907
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
8c. ADDRESS (City, State, and ZIP Code) 800 N. Quincy Street Arlington, VA 22217		10. SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO PROJECT NO TASK NO WORK UNIT ACCESSION NO
11. TITLE (Include Security Classification) Effect of Pressure on Conductivity in Liquid and Glassy States of a Superionic Conducting Glass		
12. PERSONAL AUTHOR(S) C.A. Angell and J. Zhou		
13a. TYPE OF REPORT Technical	13b. TIME COVERED FROM TO	14. DATE OF REPORT (Year, Month, Day) 1988, October
15. PAGE COUNT		
16. SUPPLEMENTARY NOTATION		
17. COSATI CODES FIELD GROUP SUB-GROUP		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) Silver Iodide Silver phosphate. (ngm) 2
19. ABSTRACT (Continue on reverse if necessary and identify by block number) 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 $(AgI)_{40}(AgPO_3)_{60}$ 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 ionic volume. Pressure applied above T_g 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. Glass,		
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT ☐ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT ☐ DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION Unclassified
22a. NAME OF RESPONSIBLE INDIVIDUAL		22b. TELEPHONE (Include Area Code) 22c. OFFICE SYMBOL

DTIC
ELECTE
NOV 2 2 1988
S C E

EFFECT OF PRESSURE ON CONDUCTIVITY IN LIQUID AND GLASSY STATES OF A SUPERIONIC CONDUCTING GLASS

C.A. Angell and Jinfeng Zhou
Department of Chemistry
Purdue University
West Lafayette, Indiana 47907



Accession For	
NTIS GRA&I	☒
DTIC TAB	☐
Unannounced	☐
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	

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 AgPO_3 -based glass has the advantage that at high 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 meniscus 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 T_g 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 equilibrium to be reached, the conductivity was measured during steadily decreasing temperature 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 T_g 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 ΔV using the standard transition state expression

$$d \log \sigma / dP = -\Delta V / RT \quad (1)$$

The values of ΔV obtained from the slopes of the Fig. 1a plots are 2.6 and 3.8 cm³/mole respectively which compare reasonably well with the volume of a mole of silver ions of radius 0.95 Å, 2.6 cm³/mole. Hamann⁽²⁾ found $\Delta V = 3.5 \pm 0.3$ cm³/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 $\Delta\sigma$ (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-AgPO₃ 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 $\frac{\Delta\sigma_{\text{conf}}}{\Delta\sigma_{\text{total}}}$ will be correlated with B_σ/B_η , where B is the numerator in the Vogel-Tammann-Fulcher equation for liquid state transport properties,

$$\sigma, \mu^{-1}, D/T = A_i \exp - (B_i/(T-T_0)) \quad (1)$$

where A_i , B_i and T_0 are constants. For superionic conducting systems, in the liquid state B_σ is much smaller than B_μ .^(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.

ACKNOWLEDGEMENT

This work was supported by the Office of Naval Research under Agreement No. N00014-84-K-2089.

REFERENCES

1. See recent reviews by:
 - (a) Minami, J. Non-Cryst. Sol., 56, (1983) 15; 73, (1985) 293.
 - (b) C.A. Angell, Solid State Ionics, 9&10, (1983) 3; 18&19, (1986) 72.
 - (c) M.D. Ingram, Phys. Chem. Glasses, 28, (1987) 215.
2. S.D. Hamann, Aust. J. Chem., 18, (1965) 1.
3. M. Ryan and S. Smedley, J. Non-Cryst. Sol., 65, (1984) 29.
4. H. Senapati, G. Parthasarathy, S.T. Lakshmikumar and K.J. Rao, Phil. Mag., 47, (1983), 29.
5. H. Senapati, G. Parthasarathy, K.J. Rao and E. Gopal, Pramana, 23, (1984) L269.
6. J.P. Malguani, A. Wasniewski, M. Doreau, G. Robert, and A. Al Rikabi, Mat. Res. Bull., 13, (1978) 427.
7. T. Minami, V. Takumo and M. Tanaka, J. Am. Ceram. Soc., 60, (1977) 283.
8. C.A. Angell, J. Phys. Chem. Sol., 49 (8), (1988) 863.
9. C.A. Angell, J. Non-Cryst. Solids, Kreidl Symposium, 73 (1985) 1.
10. C.A. Angell, H.G.K. Sundar, A.R. Kulkarni, H. Senapati and S.W. Martin, in "Molecular Dynamics and Relaxation Phenomena in Glasses," Ed. Th. Dorfmueller and G. Williams, *Lecture Notes in Physics*, Springer-Verlag, 277, (1987) 75.

11. C.T. Moynihan, et. al., Ann. N.Y. Acad. Sci., 1976.
12. L. Boehm and C.A. Angell, J. Non-Cryst. Sol., 40, (1980) 83.
13. M. Yoshigawa and M. Tomazawa, J. de Physique, 43, (1982) C9-41.
14. J. Kawamura and J. Shimoji, J. Non-Cryst. Sol., 88, (1986) 286, 295.
15. M. McLin and C.A. Angell, J. Phys. Chem. (Letters Section), 92, (1988) 2083.

FIGURE CAPTIONS

- a. Effect of pressure on two $4\text{AgI} \cdot 6\text{AgPO}_3$ glasses, far below T_g .
- 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 T_g (run 2) and after decompression at room temperature. Note restoration of original conductivity on relaxation above 55°C .

