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High pressure transport behaviour of $AgI\text{-}Ag_2O\text{-}MoO_3$ glasses and the cluster model†

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Abstract. The effect of pressure on the conductivity of fast ion conducting $AgI\text{-}Ag_2O\text{-}MoO_3$ glasses has been investigated down to 150 K. The observed variation of conductivities appears to support the application of cluster model to the ionic glasses.

Keywords. Conductivity; cluster model; ionic glasses; high pressure transport behaviour.

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In $AgI\text{-}Ag_2O\text{-}MoO_3$ system, melts with the pseudo-binary $AgI\text{-}Ag_2MoO_4$ compositions can be quenched into glasses over a considerable range (Minami *et al* 1977; Hemlata and Rao 1983). Interest in these glasses lies in the fact that they are fast ionic conductors with Ag^+ ions as charge carriers (Minami *et al* 1977; Angell 1983). We have earlier shown that the effect of pressure on electrical conductivity of these glasses at the laboratory temperature can be understood in the light of cluster model of glasses (Hemlata *et al* 1983). Clusters are quasi-ordered regions with a spatial extension of about 50 to 100 Å which pervade the structure of glass and are connected by tissue material of slightly lower density and almost complete positional disorder (Rao and Rao 1982; Parthasarathy *et al* 1984; Rao 1984). In the highly ionic glasses of $AgI\text{-}Ag_2O\text{-}MoO_3$ system studied here, it is conjectured that the clusters most probably correspond to microcrystalline order with a structure akin to that of α-AgI. Ionic transport in clusters is characterized by high mobility and low activation energy, whereas in the tissue, mobility is quite low but activation energy is even lower than in clusters. This results from lower density (larger average void sizes) and higher positional disorder (larger scattering). The stability and self-limiting growth of clusters during glass formation from their respective melts ensue from the possibility of a small degree of compositional disorder which occurs due to the presence of highly mobile cations. These aspects of cluster model are discussed elsewhere (Rao 1984).

From the cluster + tissue description of glasses we expect that log (σ) *vs* $1/T$ plots exhibit an elbow shape in which the low temperature conductivity is dominated by transport in tissue region and the high temperature conductivity by transport in cluster region. An example of log σ *vs* $1/T$ plot (measured at 1 kHz to avoid the polarization problems arising in simple d.c. conductivity measurements) is shown in figure 1. In our earlier study we observed that upon application of pressure the conductivity initially

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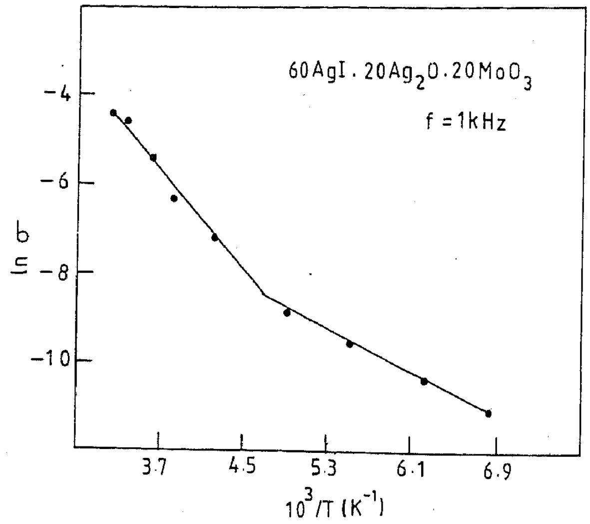

Figure 1. Plot of ln σ *vs* ($10^3/T$) for $60AgI \cdot 20Ag_2O \cdot 20MoO_3$ glass at 1 kHz frequency.

increases and above a certain limiting pressure it begins to decrease (Hemlata *et al* 1983). We attribute the increase in conductivity to a continuous pressure-induced conversion of tissue into clusters. Since the clusters are assumed to be microcrystalline, complete conversion of tissue into the clusters would result in complete crystallization, so that above a certain pressure p_c, the pressure dependence of the ionic conductivity shows the familiar decrease. Since the conductivity exhibits an elbow-type behaviour with temperature, it should be expected that at some low temperature, conversion of tissue into cluster would result in a net decrease of conductivity. Ascertaining this behaviour would provide a strong evidence for the validity of the cluster + tissue model for the ionic glass system of the type discussed. This is the motivation for the present work.

AgI-Ag_2O-MoO_3 glasses are prepared by heating appropriate amounts of AgI, Ag_2O and MoO_3 to 800 K for 5–6 hr and quenching the resulting melts between polished glass plates. The conductivity was measured under pressure using a Bridgman anvil set-up (Parthasarathy and Gopal 1984). The room temperature and low temperature calibration of the pressure system has been discussed by Parthasarathy *et al* (1984). Copper constantan thermocouples were used to measure the temperature.

For very accurate conductivity measurements a.c. conductivities are measured as a function of frequency and d.c. conductivity obtained from extrapolation to zero frequency values. Extensive conductivity measurements at ambient pressure as a function of both frequency and temperature have been performed on these systems and will be published elsewhere (Rao and Hemlata 1984). A point of relevance to this paper is that at all frequencies an elbow type behaviour is exhibited in ln σ *vs* $1/T$ plots. However, such a.c. measurements in a high pressure set-up of the anvil type are extremely difficult. The usual practice has been to measure d.c. conductivities passing extremely low currents for short durations and periodic reversal of current direction (Van Gool 1973; Vashishta *et al* 1979; Hemlata *et al* 1983). We have adopted this procedure to measure the d.c. conductivities. A Keithley constant current source was used and a current of 2–5 nA was passed for less than 5 sec for measurements. The current directions were reversed frequently.

We have measured the conductivity of two extreme glass compositions of the pseudo binary AgI-Ag_2MoO_4 system, both as a function of pressure and temperature. In figures 2(a) and (b) log (normalised conductivity) (values normalised with respect to conductivity at room temperature) *vs* ($10^3/T$) behaviour at four different pressures are shown. In figure 3, the behaviour of isothermal log σ_{dc} (normalised) *vs* pressure plots for two glasses at 150 K, are presented.

It may be noted from figure 2 that conductivity for both compositions of glasses correspond to the low barrier low mobility regions which we have attributed to the dominance of the transport in the tissue region. Therefore the pressure conversion of tissue into cluster should result in a decrease of σ_{dc} as indeed evidenced in figure 3, which after the completion of tissue to cluster conversion begins to exhibit normal pressure dependence expected of ionic materials. The qualitative features of conductivity behaviour as a function of pressure in figure 3 itself provides strong evidence for the validity of cluster + tissue model of ionic glasses (Rao 1984). The activation barriers in the two regions at various pressures and the corresponding elbow temperatures of conductivity plots are given in table 1. In the AgI-rich glasses (60% AgI) the activation barrier characterizing the clusters are far less sensitive to pressure, while the elbow temperature decreases considerably at higher pressures. In the AgI-poor glasses (40% AgI), with increase in pressure the activation barrier of the cluster region seems to decrease, while the elbow temperature remains almost constant within the experimental uncertainties. Also the magnitude of conductivity variation with pressure in AgI-rich glasses is lower as compared to variation in AgI-poor glasses. We tentatively attribute this to the presence of a larger proportion of molybdate anions in AgI-poor glasses. In response to the pressure, molybdate ions may tend to order on lattice sites causing the

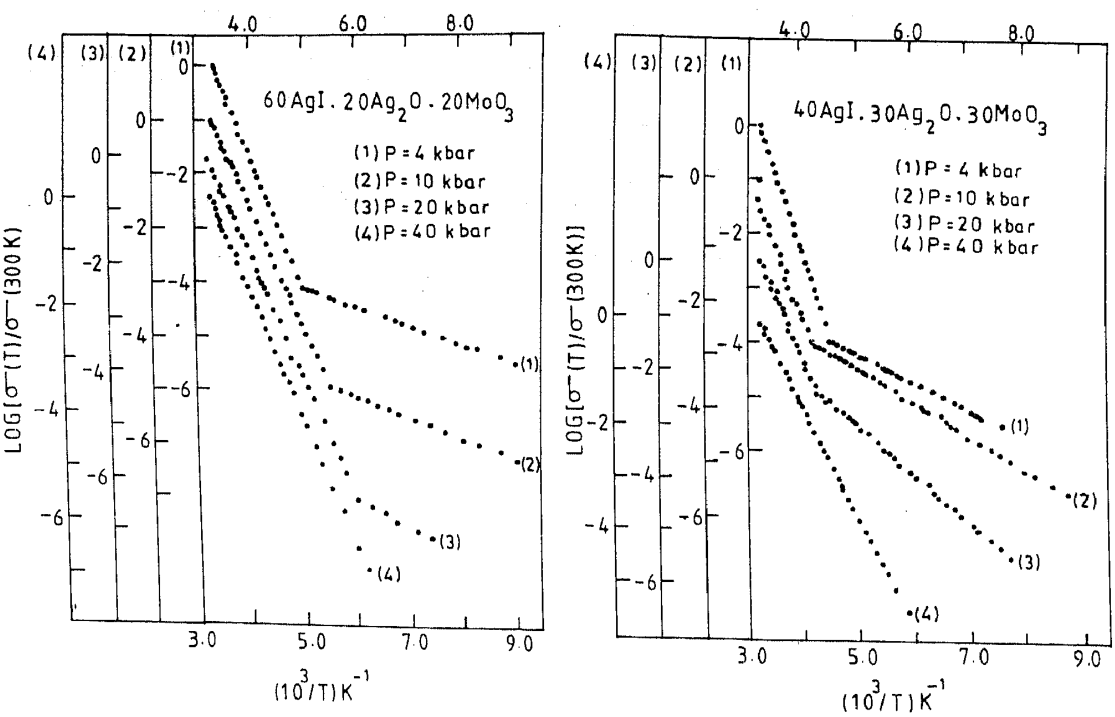

Figure 2. Semilog plot of the normalised conductivity *vs* ($10^3/T$): (**a**) for 60AgI · $20Ag_2O$ · $20MoO_3$ glass and (**b**) for 40AgI · $30Ag_2O$ · $30MoO_3$ glass at different pressures.

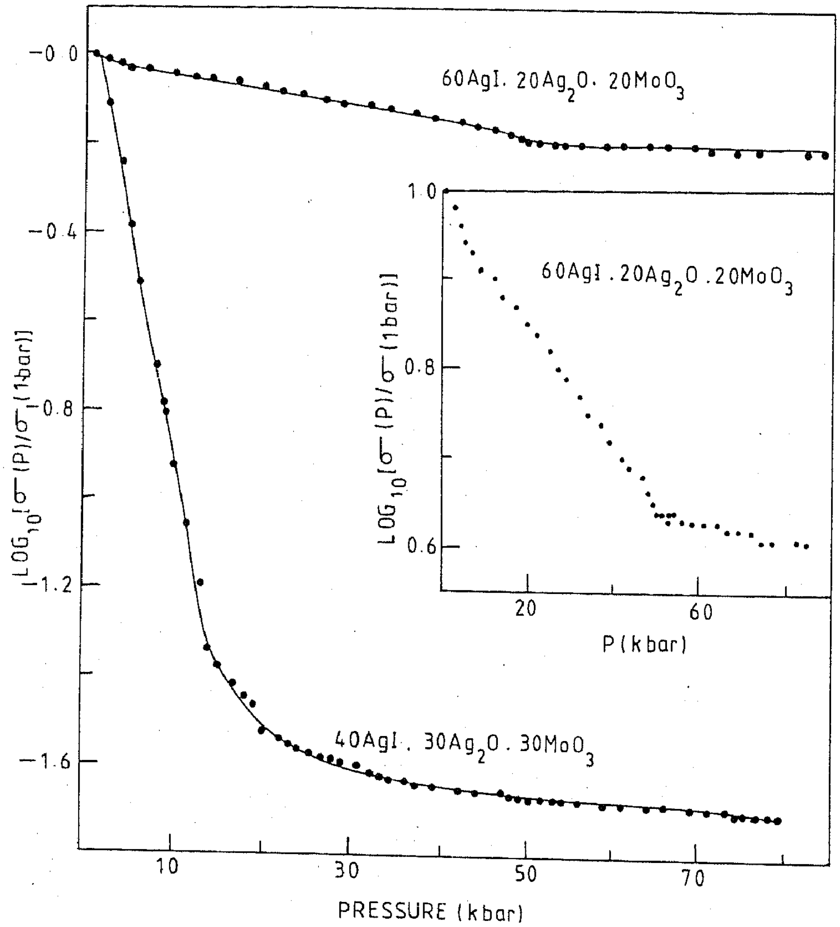

Figure 3. Semilog plot of the normalised conductivity *vs* pressures at $T = 150 \pm 5$ K for the two glasses. Inset: the variation of the normalised conductivity of $60AgI \cdot 20Ag_2O \cdot 20MoO_3$ glass as a function of pressure at $T = 150 \pm 5$ K.

Table 1. Activation energy ΔE (eV) and the elbow temperature T_E (K) values at different pressures for $60AgI \cdot 20Ag_2O \cdot 20MoO_3$ and $40AgI \cdot 30Ag_2O \cdot 30MoO_3$ glasses.

	$60AgI \cdot 20Ag_2O \cdot 20MoO_3$			$40AgI \cdot 30Ag_2O \cdot 30MoO_3$		
Pressure (k bar)	ΔE_1	ΔE_2	T_E	ΔE_1	ΔE_2	T_E
4	0·50	0·07	201	0·61	0·10	223
10	0·44	0·08	181	0·58	0·12	235
20	0·46	0·10	166	0·48	0·18	234
40	0·47	—	—	0·42	—	—

observed decrease in activation barriers particularly for mobility. Such a possibility should be admittedly lower in AgI-rich glasses. But we are not clear why the elbow temperatures would remain constant or decrease in these glasses. The gradual increase in the activation barrier in the tissue region is, however, in accordance with the effect of increasing density as a function of pressure.

In conclusion, we therefore feel that this low temperature investigation of pressure dependence of conductivity of AgI-Ag_2O-MoO_3 glasses provides further support to the cluster model of glasses.

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