PRAMANA
— journal of
physics

© Printed in India

Vol. 43, No. 3,
September 1994
pp. 189–192

High pressure studies on $AgI–Ag_2O–MoO_3$ glasses

B VAIDHYANATHAN, S ASOKAN* and K J RAO**
Solid State and Structural Chemistry Unit,
*Instrumentation and Services Unit, Indian Institute of Science, Bangalore 560012, India
**To whom correspondence should be addressed.

MS received 20 April 1994; revised 7 June 1994

Abstract. The effect of pressure on the conductivity of $AgI–Ag_2O–MoO_3$ glasses has been reexamined. A conductivity maximum is observed around 0·7 GPa. No variation of the sample temperature is noted under pressure. The results are found to agree well with the cluster-tissue model.

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

PACS Nos 61·40; 62·50; 72·20

The effect of pressure on the conductivity of $AgI–Ag_2O–MoO_3$ glasses has been studied a decade ago by Senapati *et al* [1], using a 4 mm Bridgman anvil set up with steatite as the pressure transmitting medium. It was reported that these glasses exhibit a conductivity maxima at high pressures around 1 GPa. The authors have explained the observed results on the basis of the cluster-tissue model [2, 3], according to which the glass is composed of quasi-ordered clusters which are connected by the disordered tissue. The initial increase in conductivity with pressure, is attributed to the transformation of the low density tissue regions to the high density clusters. The existing clusters in the material serve as a ready template for this transformation. The high pressure-low temperature conductivity measurements, undertaken by these authors, also provided a supporting evidence for the cluster-tissue description of these glasses [4].

Recently, Hutchinson *et al* [5] have studied the effect of pressure (up to 1 GPa) on the conductivity of $AgI–Ag_2O–MoO_3$ glasses using a piston-cylinder apparatus with castor oil as the pressurizing medium. These studies indicate a monotonic decrease in the normalized conductivity as a function of pressure. Experiments of Oyama and Kawamura [6], conducted on a piston-cylinder type high pressure vessel with silicone oil as the hydrostatic pressure fluid, also show a linear decrease in the conductivity of $AgI–Ag_2O–MoO_3$ glasses under pressure.

In this background, high pressure conductivity studies have been performed again on a few $AgI–Ag_2O–MoO_3$ glass compositions, to examine the reproducibility of the results of Senapati *et al* [1]. The present experiments have been carried out in a 12 mm tungsten carbide opposed anvil system. Pyrophyllite is used as the gasket material and steatite as the pressure transmitting medium. In situ calibration with Bi has been adopted, for accurate measurement of pressures. A chromel-alumel thermocouple is mounted inside the cell along with the sample, to monitor any change in sample temperatures under pressure. Pressurization of the samples has been carried

out very slowly, to enable the samples to reach equilibrium conditions. Experiments have also been repeated several times to ensure repeatability.

Figure 1 shows the variation of conductivity with pressure of $60\,AgI–20\,Ag_2O–20\,MoO_3$ and $50\,AgI–25\,Ag_2O–25\,MoO_3$ glasses. The inset in figure 1 gives the pressure dependence of resistivity of the in situ calibrant (Bi). It is seen from the figure that in both the glasses studied, a maximum in normalized conductivity is observed. It is found that the conductivity maximum with pressure is repeatable, with a small variation in the peak conductivity value. Also there is no appreciable change in the sample temperature with pressure (figure 2).

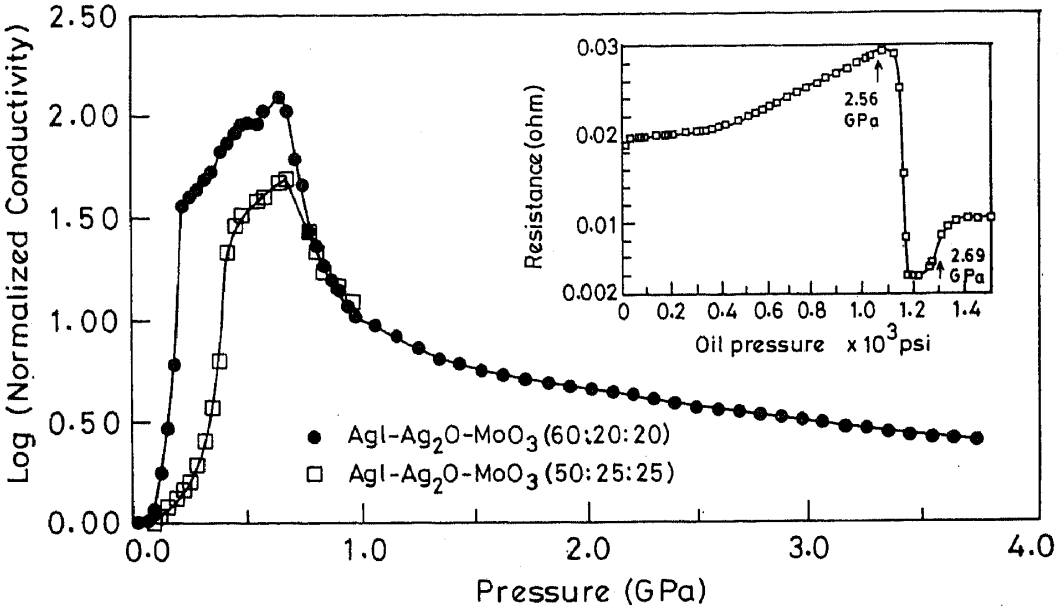

Figure 1. Variation of log of normalized conductivity with pressure for the $AgI–Ag_2O–MoO_3$ glasses. **Inset**: Plot of resistance versus pressure for the in situ Bi calibrant.

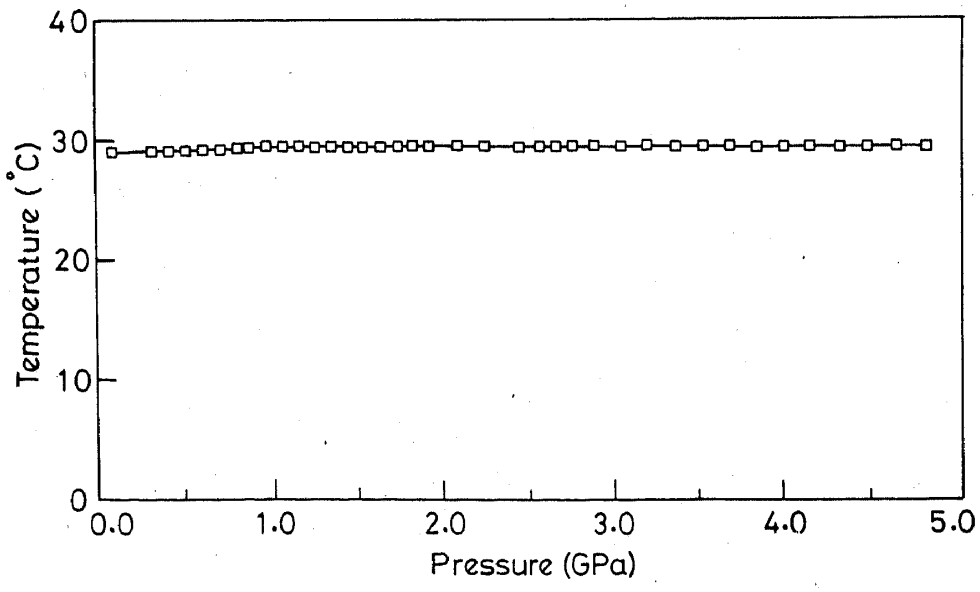

Figure 2. Temperature changes in the pressure chamber measured in situ using a chromel-alumel thermocouple.

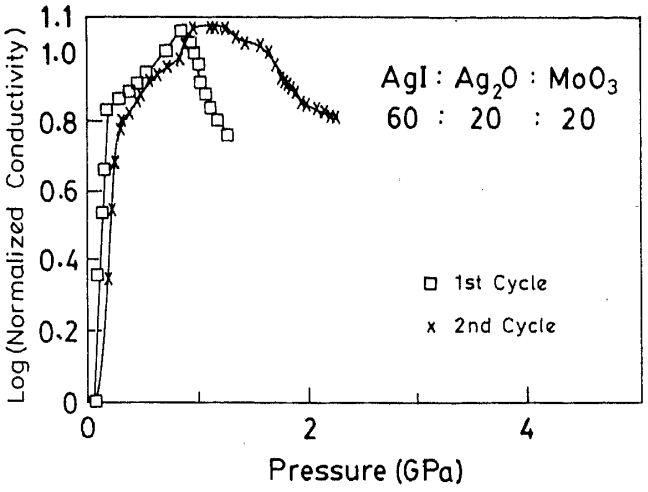

Figure 3. Pressure dependence of normalized conductivity of 60 AgI–20 Ag_2O–20 MoO_3 glass during the first and the second cycle.

The pressure dependence of conductivity observed in the present studies matches well with the results of Senapati *et al* [1]. The transformation pressure of 60 AgI–20 Ag_2O–20 MoO_3 sample is around 0·7 GPa in the present studies, whereas it was reported to be around 1 GPa earlier. The marginal difference in the transformation pressure, may be due to the fact that smaller anvils were used and in situ calibration was not employed in the earlier investigations (Senapati *et al* [1]).

It is possible to suspect that spurious conductivity maxima could have been observed by us in single-pass pressure experiments, particularly since the conductivity maxima occur around a relatively low pressure of 0·7 GPa. Hence, the conductivity measurements were repeated with pressure cycling up to 2·0 GPa. The results are shown in figure 3. Except for a slight increase in the pressure corresponding to the conductivity maximum and a slight broadening of the peak, the essential features are completely reproduced in the second cycle also.

As the earlier results of Senapati *et al* [1] have now been reconfirmed, the different results observed by Hutchinson *et al* [5] and Oyama and Kawamura [6] can only be due to the inherent differences in the Bridgman anvil and the piston-cylinder techniques. The large compressibility of the fluid transmitting media in a piston-cylinder set up, results in a Joule–Thomson heating (of up to 10 K) which in turn may affect the sample behaviour. The combined effect of applied pressure and local increase in temperature may bring about an accelerated tissue-cluster conversion which suppresses the conductivity maximum. However, we do not intend to explain completely the observations made in the piston-cylinder experiments. It is also possible that the shear component of the quasi-hydrostatic pressure generated in the Bridgman anvil technique, is partially responsible for causing the observed difference in the pressure behaviour.

At present, the cluster-tissue model seems to provide the only available appropriate explanation for the conductivity behaviour of $AgI–Ag_2O–MoO_3$ glasses, observed in Bridgman anvil high pressure experiments. It would be interesting to examine the role of shear component of pressure in the tissue-cluster transformation suggested in the model.

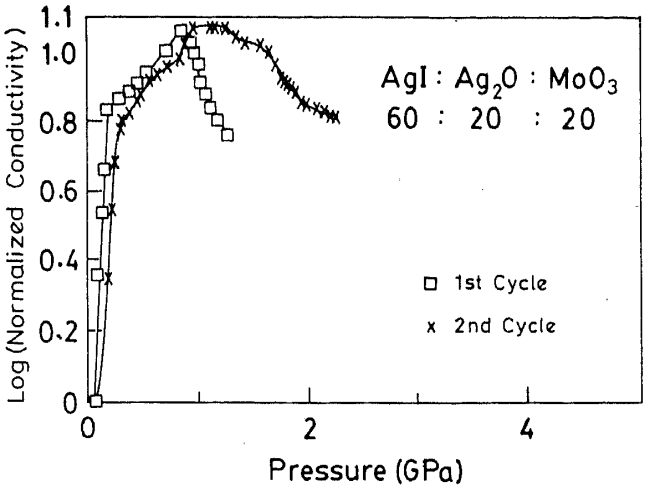

Figure 3. Pressure dependence of normalized conductivity of 60 AgI–20 Ag_2O–20 MoO_3 glass during the first and the second cycle.

The pressure dependence of conductivity observed in the present studies matches well with the results of Senapati *et al* [1]. The transformation pressure of 60 AgI–20 Ag_2O–20 MoO_3 sample is around 0·7 GPa in the present studies, whereas it was reported to be around 1 GPa earlier. The marginal difference in the transformation pressure, may be due to the fact that smaller anvils were used and in situ calibration was not employed in the earlier investigations (Senapati *et al* [1]).

It is possible to suspect that spurious conductivity maxima could have been observed by us in single-pass pressure experiments, particularly since the conductivity maxima occur around a relatively low pressure of 0·7 GPa. Hence, the conductivity measurements were repeated with pressure cycling up to 2·0 GPa. The results are shown in figure 3. Except for a slight increase in the pressure corresponding to the conductivity maximum and a slight broadening of the peak, the essential features are completely reproduced in the second cycle also.

As the earlier results of Senapati *et al* [1] have now been reconfirmed, the different results observed by Hutchinson *et al* [5] and Oyama and Kawamura [6] can only be due to the inherent differences in the Bridgman anvil and the piston-cylinder techniques. The large compressibility of the fluid transmitting media in a piston-cylinder set up, results in a Joule–Thomson heating (of up to 10 K) which in turn may affect the sample behaviour. The combined effect of applied pressure and local increase in temperature may bring about an accelerated tissue-cluster conversion which suppresses the conductivity maximum. However, we do not intend to explain completely the observations made in the piston-cylinder experiments. It is also possible that the shear component of the quasi-hydrostatic pressure generated in the Bridgman anvil technique, is partially responsible for causing the observed difference in the pressure behaviour.

At present, the cluster-tissue model seems to provide the only available appropriate explanation for the conductivity behaviour of $AgI–Ag_2O–MoO_3$ glasses, observed in Bridgman anvil high pressure experiments. It would be interesting to examine the role of shear component of pressure in the tissue-cluster transformation suggested in the model.

References

[1] H Senapati, G Parthasarathy, S T Lakshmikumar and K J Rao, *Philos. Mag.* **B47** 291 (1983)
[2] K J Rao and C N R Rao, *Mater. Res. Bull.*, **17**, 1337 (1982)
[3] K J Rao, *Proc. Indian Acad. Sci. (Chem. Sci.)*, **93**, 389 (1984)
[4] S Hemlata, G Parthasarathy, K J Rao and E S R Gopal, *Pramana – J. Phys.* **23**, 269 (1984)
[5] J M Hutchinson, M D Ingram and A H J Robertson, *Philos. Mag.* **B66**, 449 (1992)
[6] Y Oyama and J Kawamura, *Solid State Ionics*, **53–56**, 1221 (1992)