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Preparation and electrical conductivity of some chalcogenide glasses at high temperatures

E. H. BAKER, L. M. WEBB
Nuffield Research Group in Extraction Metallurgy, Imperial College, London, UK

Chalcogenide glasses have been synthesized rapidly by heating the constituents at temperatures in the range 1000 to 1500° C under high pressure argon in internally heated pressure vessels. Some glasses of molecular constitution $As_2Se_3Mn_x$, and glasses of the Ovshinsky type, e.g. $As_{30}Te_{48}Ge_{10}Si_{12}$, have been made by this method. The conductivities of the glasses prepared have been measured at temperatures up to about 1200° C, an atmosphere of high pressure argon being employed to suppress volatilization. The liquid glasses were found to change from semiconductors to metallic-type conductors as the temperature was raised.

The technique of conductivity measurement has been applied to liquid tellurium to obtain data up to temperatures beyond the normal boiling point. The conductivity was found to increase with temperature to a maximum at around 900° C, and thereafter to diminish. At the highest temperatures, where the liquid can be regarded as virtually metallic, the resistivity was found to show approximately a positive linear dependence of temperature.

1. Introduction

Chalcogenide glasses containing arsenic, e.g. $As_{30}Te_{48}Ge_{10}Si_{12}$, have potential uses in the semiconductor field owing to their ability to behave as simple switches [1]. The glasses are prepared conventionally by heating the elements together in sealed vials at temperatures around 700° C for 20 h or more. However, a more rapid synthesis has been developed in which higher temperatures (1000 to 1500° C) are employed so that all the components are liquified and the preparation time is only about 3 h [2]. In this method, the elements are heated under an argon pressure of 40 to 70 atm in a silica bulb of capacity 15 ml, inside an internally heated pressure vessel. The bulb is fitted with a long tubular outlet and the high pressure gas inside the latter acts as a diffusion barrier and virtually eliminates vaporization from the melt. The triple point for arsenic lies at about 817° C and 35.5 atm, so that at first sight, a marked vaporization of liquid arsenic might be expected at the high temperatures used. However, this does not occur because the liquid arsenic undoubtedly reacts rapidly with the tellurium (or selenium) present to form a melt, which considerably reduces its vapour pressure.

The above technique is particularly useful for incorporating high melting metals in these glasses, and exploratory studies of the preparation of some glasses of constitution $As_2Se_3Mn_x$ have formed part of this work. A modification of the above technique has been developed, which employs radio frequency heating. This method allows considerable flexibility of temperature control and has been used for synthesizing the switching and memory glasses, $As_{30}Te_{48}Ge_{10}Si_{12}$ and $As_{50}Te_{40}Ge_{10}$, respectively. This method should have a general application for making Ovshinsky-type glasses.

In the liquid state, the chalcogenide glasses behave as semiconductors at low temperatures, but tend to become metallic conductors at high temperatures. To enable these changes to be studied, the conductivity cells must be kept under high-pressure argon to prevent volatilization of the materials. Conductivity measurements made in this manner on the above glasses have also formed part of the present work. Liquid tellurium has also been studied, as this high pressure technique is similarly required for measurements of its conductivity above the normal boiling point (993° C).

2. Experimental

2.1. Preparative procedure

The starting materials used throughout were the appropriate elements of purity better than 99.999%; high purity argon was the pressure medium.

For the preparation of the manganese-containing glasses, the silica reaction bulbs and the internally heated pressure vessel used, were identical to those employed for the study of arsenic triselenide [2]. The operational procedure was also similar, the pressure of argon over the reactants being 70 atm. In this case, however, the reactants were maintained at the higher temperature of 1400° C for 1 h to establish homogeneity, before cooling under pressure. Three glasses in batches of $\sim$ 25 g were thus prepared, the molecular constitutions being $As_2Se_3Mn_{0.25}$, $As_2Se_3Mn_{0.375}$ and $As_2Se_3Mn_{0.75}$. The first was homogeneous, but the last two appeared to have some phase separation in the solid state; however, this is not important with liquid phase studies.

The radio frequency furnace used for the preparation of the glasses, $As_{30}Te_{48}Ge_{10}Si_{12}$ and $As_{50}Te_{40}Ge_{10}$, incorporated a steel vessel with a brass lid, and is shown sectionally in Fig. 1. Since the body was ferromagnetic, a copper liner was fitted. The water-cooled induction coil was made from copper tubing of outer diameter 4.6 mm and 3 mm bore, and was sealed into the alumina insulator with Araldite. The fields of the emergent feeders largely cancelled, so that little power was dissipated in the lid. The frequency was 450 kHz. The silica vessel shown was for making $\sim$ 25 g of material; the annular clearance between the thermocouple sheath and the outlet tube was typically $\sim$ 0.1 mm.

To prepare the switching glass $As_{30}Te_{48}Ge_{10}Si_{12}$, the temperature of the reactants was raised over a period of 20 min to 1470° C under an argon pressure of 45 atm, and held at this temperature for 15 min to ensure melting and mixing in of the silicon. The temperature was then lowered to a convenient value of about 1250° C and maintained constant for 1 h to establish homogeneity of the melt. The latter was then cooled to 600° C, the argon pressure reduced to 1 atm over a period of 1 h and the melt cooled to room temperature. For the glass $As_{50}Te_{40}Ge_{10}$, the procedure was very similar except that the melt was kept at 1050° C for 1 h to establish homogeneity, prior to cooling. The cooling rate in the temperature region 280 to 180° C within which the liquid-glass transitions occur [3] was about 7° C min^{-1}, which was sufficiently fast to produce glasses of good homogeneity in both cases.

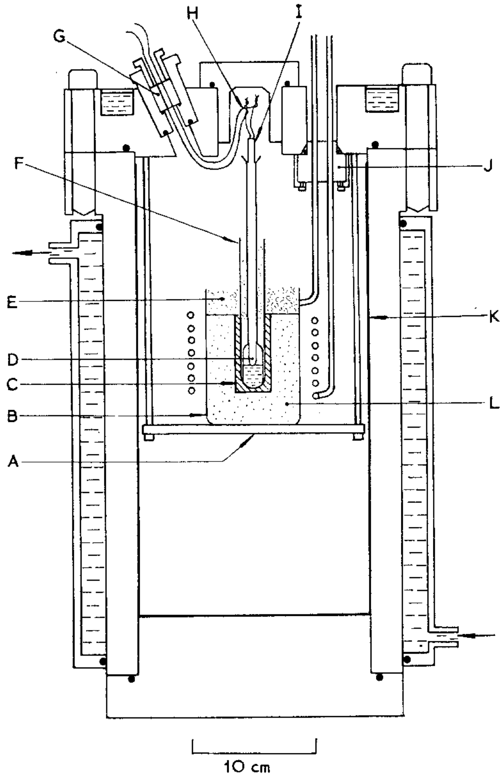

Figure 1 Radio frequency melting furnace for use at high pressures. A, alumina platform; B, silica beaker; C, graphite susceptor; D, thermojunction; E, refractory fibre; F, silica tube; G, araldite block; H, thermocouple wires (Pt—Pt + 13% Rh); I, silica thermocouple sheath; J, alumina block; K, copper liner; L, alumina powder.

2.2. Conductivity measurements

For the manganese glasses and $As_{50}Te_{40}Ge_{10}$, two-electrode capillary cells were employed, which were of the U-tube design used in the study of selenium and arsenic triselenide [2, 4]. The cells were of silica and the electrodes were Specpure graphite rods. The cell constants varied from 2069 to 14 200 according to the conductance range required. For the other materials, four electrode cells were used which incorporated two additional electrode chambers, sealed in near the tops of the capillaries; the cell constants lay in the range 1864 to 2380.

The evacuation and filling procedures for the cells in the internally heated pressure vessel were similar to those used with arsenic triselenide [2]. With the liquid manganese glasses, the argon pressure employed during the measurements was 70 atm, with the other liquid glasses and liquid tellurium, the pressures were 45 and 25 atm, respectively.

For these electronically conducting liquids at high temperatures, conductivities determined by d.c. and low frequency a.c. methods, do not differ significantly. With the two-electrode cells, a Wayne-Kerr bridge (1592 Hz) was used; in the case of the four-electrode cells, d.c. measurements were used with a current reversal procedure to minimise errors resulting from small thermo e.m.fs. D.c. potentials of 30 to 50 mV were measured across the capillaries.

3. Results and discussion

3.1. Conductivities of the manganese-containing glasses

The conductivity temperature relations for the manganese glasses, with a comparison plot for arsenic triselenide, are shown in Fig. 2. At the lower temperatures, the plots are linear, indicative of semiconductive behaviour, and can be expressed by relationships of the form

$$\sigma = \sigma_0 \exp(-E/kT) \qquad (1)$$

where E is the activation energy. Activation energies usually diminish approximately linearly with temperature according to a relation of the type

$$E = E_0 - \gamma T. \qquad (2)$$

Extrapolation [5] of the thermoelectric measurements of Edmond [6] on liquid arsenic triselenide yields a value for γ of about 10^{-3} eV K^{-1}; a similar value would reasonably be expected for the manganese glasses. For a moderate temperature range up to say 750 K, σ_0 for the liquid can be assumed sensibly constant with temperature, so that Equations 1 and 2 lead to the relation

$$\sigma = \sigma_0' \exp(\gamma/k) \exp(-E_0/kT). \qquad (3)$$

The slope of the log σ versus $1/T$ plot thus yields E_0 directly [6].

For the linear portions of the plots for the manganese glasses, E_0 is 1.03 eV and does not show any significant increase with manganese content; the value is only slightly lower than that for arsenic triselenide (1.07 eV). For the latter, σ_0 is 6.86×10^4 Ω^{-1} cm^{-1} whilst for the glasses $As_2Se_3Mn_{0.25}$, $As_2Se_3Mn_{0.375}$, and $As_2Se_3Mn_{0.75}$, the σ_0 values are 7.57×10^4, 1.11×10^5, and 2.38×10^5 Ω^{-1} cm^{-1} respectively.

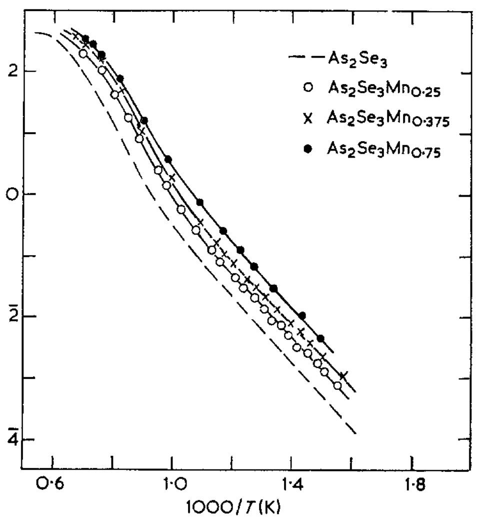

Figure 2 Conductivity-temperature relations for liquid arsenic triselenide with increasing manganese content.

A peculiarity of the chalcogenide glasses, is that the sign of the Hall coefficient is negative, whilst that of the thermopower is positive. Emin *et al.* [7, 8] explain this *n-p* anomaly in the solid, by considering that the carriers are hole-like small polarons, the Hall sign being determined by their probability of direction in a triangular array of nearest neighbour sites; this type of site arrangement is approximated by the structures of several of these glasses. In the liquid glasses of the As–Se–Te system, this *n-p* anomaly is also found [6, 9]. However, owing to thermal motion, only short range order will exist in the liquids, so that the application of the above model is less certain. For these liquids, the Hall mobilities are found to be around 0.1 cm^2 V^{-1} sec^{-1}, which implies a mean free path of the carriers of around atomic dimensions, and casts doubt on the interpretation of the conductivity in terms of an intrinsic semiconductor of the conventional band type.

Mott [10] suggests that in these liquids, the density of states curves exhibit tails at the edges of the valence and conduction bands, in which localized electron states exist. If the conduction is accepted as p-type, then holes will be activated near E_V, producing in effect, a mobility shoulder with a mobility gap corresponding to $E_F - E_V$; the latter will diminish with temperature according to Equation 2 yielding the value of E_0 as above. To date this appears to give the best picture of the energy gap in the liquid glasses.

Manganese is not a typically glass forming element and tentatively its effect on the conductivity of arsenic triselenide could be ascribed to the formation of metallically conducting regions between the As_2Se_3 chains or layers. The semiconducting properties of the latter would be largely preserved, and the activation energy would not alter much, but the increasing manganese content would raise the conductivity by assisting transport of the carriers between the layers. The last process should have little temperature dependence and would, therefore, be expected mainly to increase σ_0, as is observed.

Near 1000 K, all the plots in Fig. 2 turn upward, even though the energy gap whichever way it is interpreted must be disappearing. This rise in conductivity can be ascribed to the release of free carriers resulting from the increasing thermal break-up of the covalent bonds in the polymeric structure; the liquid thus becomes increasingly metallic in this region.

At still higher temperatures, the flattening-off of the plots for the manganese glasses, indicates that a metallic conduction, with σ virtually independent of temperature will be reached near 1700 K as in the case of arsenic triselenide.

3.2. Conductivities of the germanium-containing glasses

The conductivity-temperature relation for $As_{30}Te_{48}Ge_{10}Si_{12}$ obtained from two sets of measurements with that for $As_{50}Te_{40}Ge_{10}$ from three sets of measurements, is shown in Fig. 3. Even at 750 K, the high values of σ indicate that the liquids must already be in a semi-metallic state. The marked flattening-off of the plots in the region of 1200 K shows that the polymeric structure has largely been destroyed and that a metallic conduction more in keeping with that of conventional alloys takes place. It is not therefore surprising to find the limiting values of σ in both cases to be $\sim 3 \times 10^3\ \Omega^{-1}\ \text{cm}^{-1}$.

3.3. Conductivity of liquid tellurium

The conductivity-temperature relation for liquid tellurium from two sets of measurements is shown in Fig. 4; the straightforward plot of σ against T has been adopted as it brings out best the conductivity behaviour.

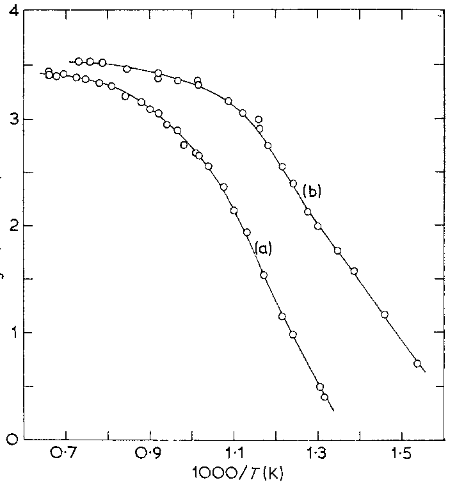

Figure 3 Conductivity-temperature relations for the liquid glasses (a), $As_{30}Te_{48}Ge_{10}Si_{12}$, and (b), $As_{50}Te_{40}Ge_{10}$.

Liquid tellurium supercools markedly, and in one run, values of σ were determined below the melting point (724 K), the supercooling portion in Fig. 4 being similar to that obtained by Epstein *et al* [11]. Of the previously reported values of σ at the lower temperatures [11-13], those of Perron appear to agree best with these here, to within about $\pm$ 4%.

Viscosity measurements on tellurium [14] show that η is approximately 25 cP close to the melting point, but by 800 K, the viscosity has already dropped to about 1 cP and thereafter remains virtually constant with temperature. Any conventional chain structure thus appears to be significant only in the region of the melting point. A viscosity of about 1 cP is roughly the value expected for a liquid metal, but tellurium cannot be a typical liquid metal because the conductivity (Fig. 4) still continues to rise markedly above 800 K; it must therefore be regarded as a "semimetal". For the latter state, Mott [10, 15] interprets the conductivity behaviour in terms of a "pseudogap" in the density of states resulting from an overlap of the conduction and valence bands. The overlapping is considered to increase with temperature, so that eventually the gap vanishes and a virtual metallic condition is reached.

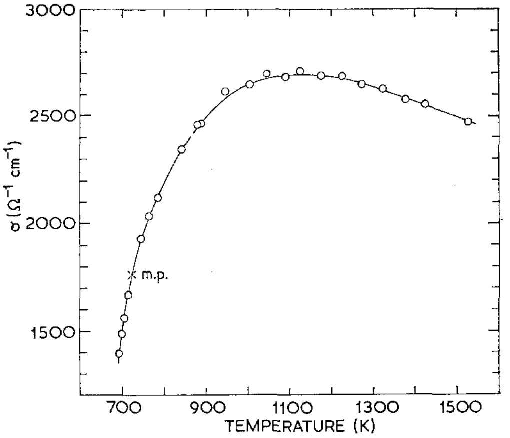

Figure 4 Conductivity-temperature relation for liquid tellurium.

From the results of neutron diffraction, and electrical studies, Cabane and Friedel [16] postulate that in liquid tellurium, local order consists of sites of two or three first neighbours joined by covalent-type bonds, the order persisting up to the second neighbours. The bonds, however, have a short lifetime of $\sim 10^{-12}$ sec, which can account for the low viscosity. The number of nearest neighbours near the melting point is about two but this increases with temperature and reaches a maximum of three at around 1200 K where the conductivity maximum occurs. At this point the "pseudogap" can be considered to have disappeared and the liquid to be as metallic as it can become. Unfortunately there are no structural data for higher temperatures, but the decrease in σ above 1200 K (Fig. 4) shows that in this region, the conductivity variation must be determined principally by increased thermal scattering of the carriers, and thermal expansion of the liquid.

Above 1300 K, the results in Fig. 4 can be expressed approximately by a resistivity relation of the form $\rho = \beta + \alpha T$ where $\beta = 236 \times 10^{-6}$ Ω cm and $\alpha = 0.11 \times 10^{-6}$ Ω cm. Cabane and Friedel consider that there is still some covalent bonding present even at 1200 K which would seem to be in keeping with the rather high β-value found here for the metallically conducting region. For antimony and bismuth which are among the liquid metallic elements of highest resistivity, the values of β are 87.9×10^{-6} and 99.2×10^{-6} Ω cm respectively [17] which are much less than the value for tellurium.

It is likely that negative temperature coefficients of conductivity would be exhibited by the chalcogenide glasses in Fig. 3, if measurements could be made at even higher temperatures.

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