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Electrical conductivity studies of some chalcogenide glasses over a large temperature range

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The electrical conductivities of chalcogenide glasses, two of which contained selenium: $Se_{15}Ge_{23}As_{31}Te_{31}$ and $Se_{15}Ge_{33}As_{27}Te_{25}$, and two of which contained sulphur: $S_{15}Ge_{23}As_{31}Te_{31}$ and $S_{15}Ge_{33}As_{27}Te_{25}$, have been determined over the temperature range 20 to 1150° C. To prevent volatilization loss from the liquid glasses, the conductance cells were enclosed in an internally heated pressure vessel containing high-pressure argon. At the lowest temperatures the plots of log σ against $1/T$(K) for the solid glasses were found to be linear, indicative of semiconductive behaviour. At temperatures just above the glass transition regions, these plots deviated from linearity and showed a marked upward curvature; this suggested that a conduction process, involving both metallic and semiconductive modes in the melt, was already operating. Comparison with the results for arsenic triselenide lent support to this idea. A similar study was carried out on the well-known switching glass, $As_{30}Te_{48}Ge_{10}Si_{12}$. In all cases, the liquid glasses showed metallic levels of conductivity at the highest temperatures.

1. Introduction

One drawback with many chalcogenide glasses which appear to be attractive for electronic switching applications is their tendency to devitrify with use. In the case of switching glasses of the As–Ge–Te type, the possibility arose that the incorporation of sulphur or selenium would stabilize these glasses and a study of the structural changes on switching of $S_{15}Ge_{33}As_{27}Te_{25}$ was made by Allinson *et al.* [1]. Of particular interest was the conclusion by these authors that, on switching, filamentary conducting regions which formed in the glasses reached temperatures greater than 500° C.

In view of the above work, it was considered worthwhile to carry out conductivity determinations on the above glass and other glasses containing sulphur and selenium. To obtain as complete a picture as possible, the conductivity measurements reported here were made on the solid and liquid glasses over a continuous range of temperature through the glass transition regions. To prevent evaporation loss from the liquid glasses at high temperatures, the silica conductance cells were enclosed in a pressure vessel containing argon as the confining gas at pressures up to 50 atm.

2. Experimental details

2.1. Preparative method

The glasses were synthesized by the method developed previously, in which the elements of purity better than 99.999% were heated together to a temperature above the melting point of the highest melting component. To prevent vaporization loss, the specially designed silica vessels were used, in conjunction with a radio frequency melting furnace, operating in high-pressure argon [2].

To prepare a glass, the components were heated to 1000° C under argon at 45 atm pressure, and kept at this temperature for 45 min, to achieve homogeneity of the melt. The temperature was then lowered to 600° C and the system depressurized to 1 atm over a period of 25 min. The final cooling rate in the region of the glass-transition temperature (~ 270° C) was at least 10° C min^{-1}, which was sufficient to produce glasses of good homogeneity. Samples of 25 g in weight were produced.

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2.2. Conductance measurements

For conductance measurements on the liquid chalcogenide glasses, the internally heated pressure vessel employed was that used for similar studies on liquid arsenic triselenide, and has been described in detail [3]. The silica conductance cells were of U-shaped capillary design as used in previous studies [2, 4]. They incorporated Specpure graphite rods as electrodes as these were not attacked by the molten glasses.

For studies in the range 250 to 550° C, two-electrode cells were used. To fill a cell, one electrode chamber was packed with the powdered glass and the cell positioned in the pressure vessel. After evacuating and flushing several times with argon, the apparatus was pressurized to 10 atm and the temperature raised to 500° C. After 30 min, the pressure was increased to 30 atm, and the temperature to 650° C. After 45 min the temperature was lowered to ~ 250° C for commencement of the measurements.

For studies above 550° C, four-electrode cells were used and a similar filling procedure was employed; the working pressure for the measurements was 50 atm.

The cell constants lay in the ranges 200 to 400 and 1000 to 2000 for the two- and four-electrode cells, respectively.

For measurements on the solid glasses below 250° C, machined blocks 5 mm square and 3 mm thick, with evaporated gold faces, were used. Green *et al.* [5] found that oxidation of the surface of similar solid glasses enhanced the conductance. For this reason, the uncoated surfaces of the blocks were cleaned with emery paper prior to the measurements which were carried out in high-purity argon.

A Wayne Kerr bridge (1592 Hz) was used for most of the measurements, but with the four-electrode cells above 550° C, d.c. conductance measurements were largely employed. No significant differences were observed between the a.c. and d.c. results.

3. Results and discussion

The conductivity–temperature relations for the selenium- and sulphur-containing glasses are plotted in Figs 1 to 4. The glass transition temperatures were not specifically sought but estimated to lie at around 270° C where softening of the solid specimens occurred.

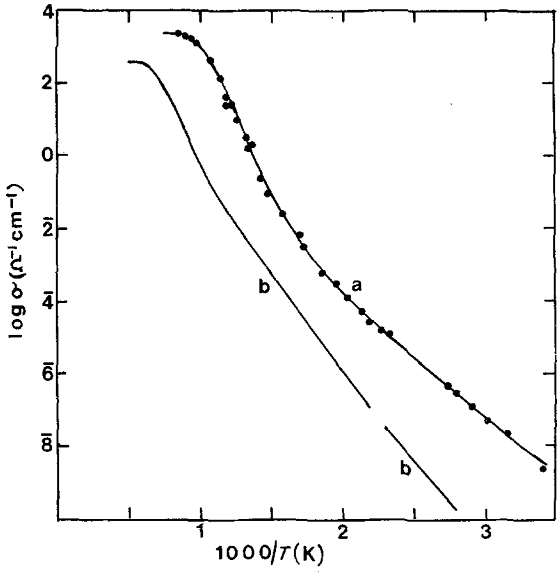

Figure 1 Conductivity–temperature relations (a) for $Se_{15}Ge_{23}As_{31}Te_{31}$ and (b) for As_2Se_3.

For the solid glasses below the glass transition regions, the plots show a good degree of linearity indicative of semi-conducting behaviour and can be expressed by the relation

$$\sigma = \sigma_0 \exp\left[-E/kT\right], \qquad (1)$$

where E is the activation energy.

For a small temperature range, the true energy gap will diminish linearly with increasing temperature according to the relation $E_G = E_0 - \gamma T$ where γ is the temperature coefficient. By means

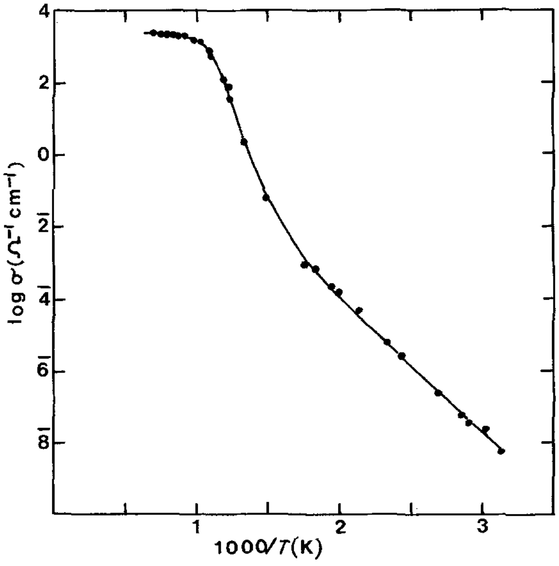

Figure 2 Conductivity–temperature relation for $Se_{15}Ge_{33}As_{27}Te_{25}$.

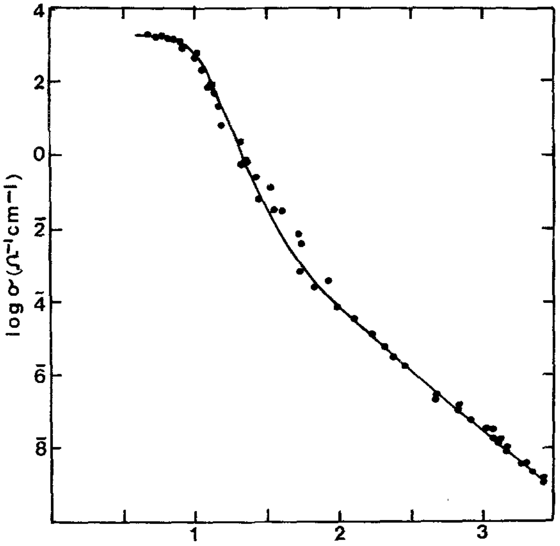

Figure 3 Conductivity–temperature relation for $S_{15}Ge_{23}As_{31}Te_{31}$.

of this relation and Equation 1, the relation

$$\sigma = \sigma_0 \exp[\gamma/K] \exp[-E_0/kT] \qquad (2)$$

is obtained; thus the slope of the plot of log σ against $1/T$ actually yields the value for E_0 [6, 7].

Chalcogenide glasses exhibit the n-p anomaly whereby Hall effect measurements show them to be n-type while thermopower measurements show them to be p-type; the latter mode of conduction is considered to be the correct one and it is reasonable to assume that the glasses discussed here will be p-type. The band-gap model for chalcogenide glasses is still conjectural; the general picture, however, is that, for the conduction and valency bands, respectively, there are tails which extend beyond E_C and E_V into the optical gap, and in which localized energy states can exist [8]. An elaboration of this idea proposes additional localized states in trapping sites existing between the band tails and the Fermi energy E_F [9, 10]. The last would be expected to be located near the middle of the optical gap, but closer to the valency band edge, for p-type conduction. For the temperature range of about 20 to 260° C studied here for the solid glasses, conduction can be attributed mainly to positive holes activated near E_V which is associated with a "mobility shoulder" so that E_G will be given by $E_F - E_V$ corresponding to a mobility gap [8].

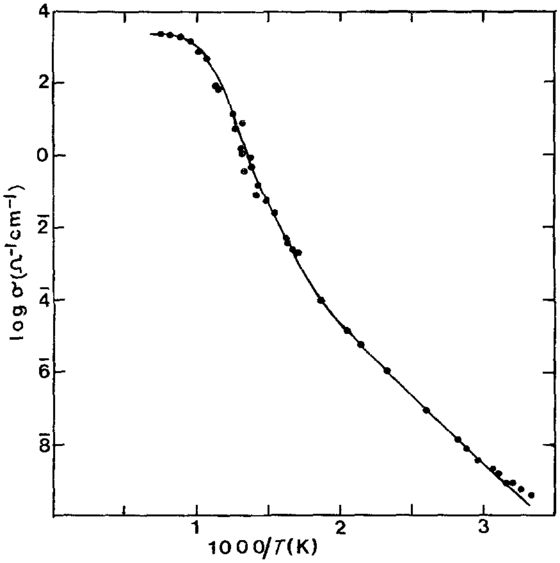

Figure 4 Conductivity–temperature relation for $S_{15}Ge_{33}As_{27}Te_{25}$.

The value of the temperature coefficient, γ, is not known for these glasses but could be estimated to be around 5×10^{-4} eV K^{-1} [7] so that whichever way the gap is interpreted, E_G would be expected to have diminished by about 0.12 eV as the glass transition region is neared, in comparison with its value at room temperature.

The conductivity levels of these quaternary glasses do not show any distinct trend with composition, except that the values are a little lower for the glasses of higher germanium content. Within the experimental errors, the values of E_0 for the glasses $Se_{15}Ge_{33}As_{27}Te_{25}$ and $S_{15}Ge_{33}As_{27}Te_{25}$ are both 0.75 ± 0.02 eV, while those for $S_{15}Ge_{23}As_{31}Te_{31}$ and $Se_{15}Ge_{23}As_{31}Te_{31}$ are 0.67 ± 0.02 eV. Germanium is the element of which the concentration difference is greatest in the two sets of glasses. The reason for the marked difference in the E_0 values is not obvious; possibly it is connected with a difference in the degree of covalent bonding of the germanium with the chalcogenide elements present.

It is of interest to compare the conductivity temperature relations obtained here with that for arsenic triselenide, which is also incorporated in Fig. 1. For the solid glass, the plot has been interpreted from the measurements made by Edmond [11] which yield a value for the energy gap (on the above interpretation) of 0.90 eV. For the liquid region above the glass transition temperature (187° C) the curve is that obtained by Webb and Baker [3] from measurements under high-pressure argon up to 1425° C. The portion of the curve for lower temperatures

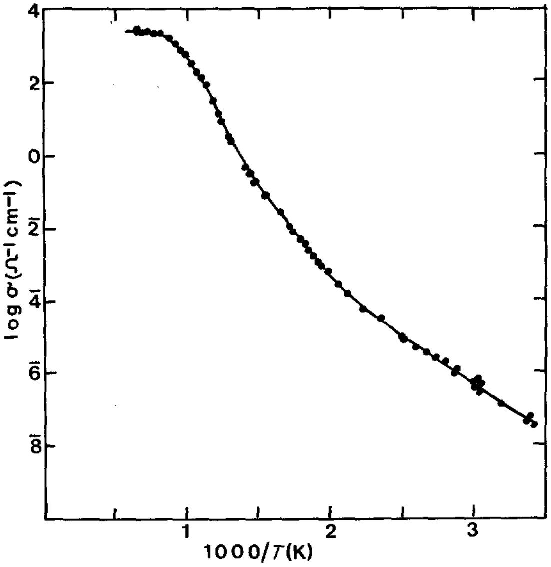

Figure 5 Conductivity–temperature relation for $As_{30}Te_{48}Ge_{10}Si_{12}$.

above the glass transition region shows a marked linearity so that it is reasonable to interpret this in terms of an energy gap. The value for the latter is found to be 1.07 eV. In contrast, this linearity is not observed for the glasses containing selenium and sulphur in the liquid state just above the glass transition regions; in these cases the plots all show a distinct upward curvature. Although the tangent at any point on the curve in this liquid region will yield an activation energy, its interpretation in terms of an energy gap is conjectural It appears that, even at these relatively low temperatures these quarternary glasses are already exhibiting enhanced conduction from a metallic contribution.

In Fig. 5 is shown the conductivity temperature relation for the switching glass $As_{30}Te_{48}Ge_{10}Si_{12}$ prepared under argon at elevated pressure [2]; this glass was originally developed by Ovshinsky [12]. The activation energy for the solid glass is 0.52 eV and the glass transition temperature is ~ 230° C. The plot is markedly similar to those for the glasses containing selenium and sulphur, so that similarity of the conduction process can be inferred.

At higher temperatures, the plots for all the glasses steepen further, indicative of a marked break-up of the polymeric structure as the melts become even more metallic in character. At the highest temperatures where the melts will contain only small molecules and atoms, the conductivity becomes virtually constant with temperature showing that the conduction is effectively metallic.

The conductivity of liquid tellurium was found by Baker and Webb [2] to reach a maximum value near 990° C, approximately the same as the maximum values found here for the quarternary glasses. With further increase in temperature, the conductivity diminished; this behaviour of tellurium was later confirmed by Endo *et al.* [13] At temperatures above those used here, it is to be expected that values of σ for the glasses would diminish with temperature in a similar manner to those of tellurium, in character with metallic-type conduction.

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