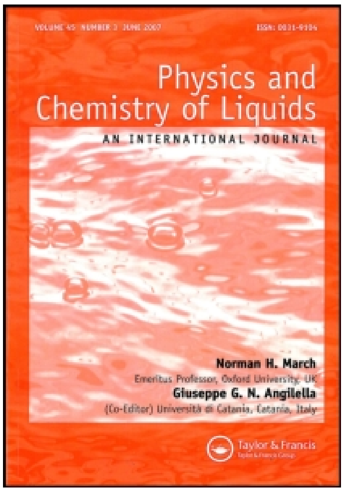

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Viscosity and Structural Transition in $As_{1-x}S_x$ Glass Forming Liquids

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The kinematic viscosity of $As_{1-x}S_x$ liquids exhibits a strong continuous change when x reaches a critical value $x_s^c = 0.525$. In the Arrhenius' representation the apparent activation energy changes abruptly at $x = x_s^c$ this transition is attributed to a structural change from a dissociated to a polymeric associated liquid. The high viscosity range corresponds exactly to the easy glass forming compositions.

La viscosité cinématique des liquides $As_{1-x}S_x$ présente une transition importante à $x = x_s^c = 0.525$. En représentation d'Arrhenius, l'énergie d'activation change brusquement pour $x = x_s^c$ Cette transition indique une profonde modification de structure correspondant au passage d'une zone polymérique à forte association vers une zone fortement dissociée. Les compositions correspondant à la zone fortement associée à haute viscosité sont aussi celles qui permettent d'obtenir des verres homogènes par refroidissement lent du liquide.

I INTRODUCTION

Viscosity measurements are used for precising the liquid structure and the composition range of easy glass formation is $As_{1-x}S_x$ system. So, these semiconducting glasses are turned toward infrared optical materials applications. Some relevant parameters for glass forming ability are the liquid viscosity, the liquidus temperature and the cooling rate.[1]

Moreover the viscous flow is sensitive to the size of structural units, the cohesive forces, the structural transition and the polymerization degree.

The temperature dependence of the viscosity is studied in the sulfur rich part of the As-S phase diagram.[2,3,4,5]

II EXPERIMENTAL AND RESULTS

II.1 Glass Preparation

Glasses are prepared from Hoboken 5 N arsenic and Koch light 6 N sulfur. In order to remove moisture, sulfur is distillated in hydrogen immediately before used. Appropriate amounts of high purity elements are then sealed in evacuated silica tubes. Before the tubes are baked out overnight at 800°C under vacuum. To ensure adequate mixing, batches of 50 g are melted for 10 hours at 600–900°C in a rocking furnace. After melting the glasses are cooled down to room temperature, removed from silica reaction tubes and then sealed under argon pressure into special viscosity measurement tubes.

II.2 Viscosity Measurements

The kinematic viscosities of liquids are measured with a Meyer–Schvidkovski torsional oscillating cup viscometer. The absolute value of ν is determined with an estimated error of 10% but, for the temperature dependence of the viscosity the relative precision is 2%.[6,7]

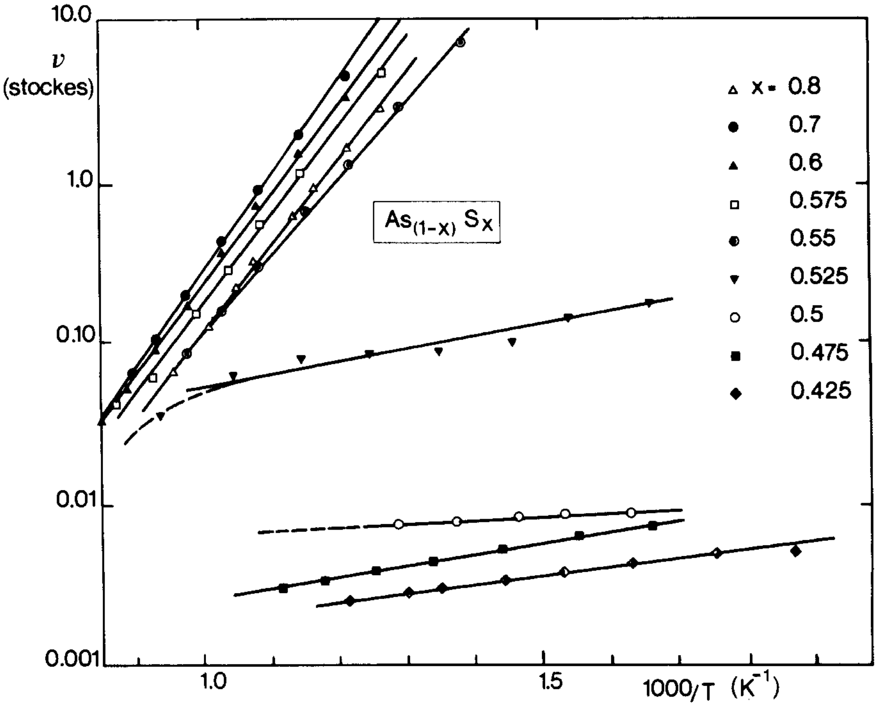

FIGURE 1 Arrhenius plots of kinematic viscosities for different compositions.

II.3 Results

The logarithm of kinematic viscosity ν is plotted versus $1/T$ in Figure 1 for different molar fraction (Xs) of sulfur. In the studied temperature range all the viscosities follow the Arrhenius type behaviour, except for a critical concentration $X_s^c = 0.525$ where the data show a small discrepancy from the straight line.

An activation energy W is calculated from each plot and then reported in Figure 2. The values of W are strongly different on each side of the critical concentration. One is close to $W_L = 0.1$ eV and the other one is about ten times greater ($W_H = 1.2$ eV). In fact the transition starts at $X_s^c = 0.525$ and becomes complete at $X_s^f = 0.575$.

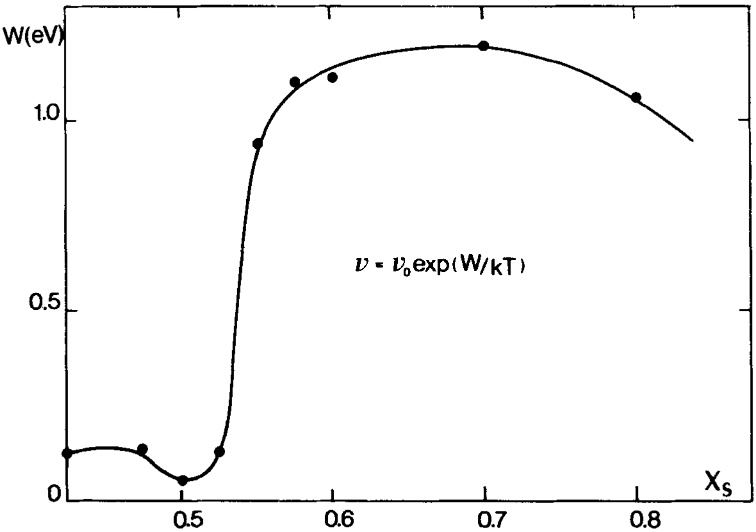

FIGURE 2 Activation energy of kinematic viscosity versus sulfur atomic fraction.

The existence of a critical transition composition is also pointed out by the isotherms of viscosity curves (log ν versus X_s, Figure 3). The two displayed temperatures 820°K and 900°K correspond to limits of the available experimental temperature data for the whole set of compositions.

At the critical concentration the viscosity increase is about one thousand times the 820°K measurement ones. Moreover a smooth maximum appears at the vicinity of $X_s = 0.65$. For high sulfur concentration $X_s \geqslant 0.8$ both viscosity and the activation energy decrease.

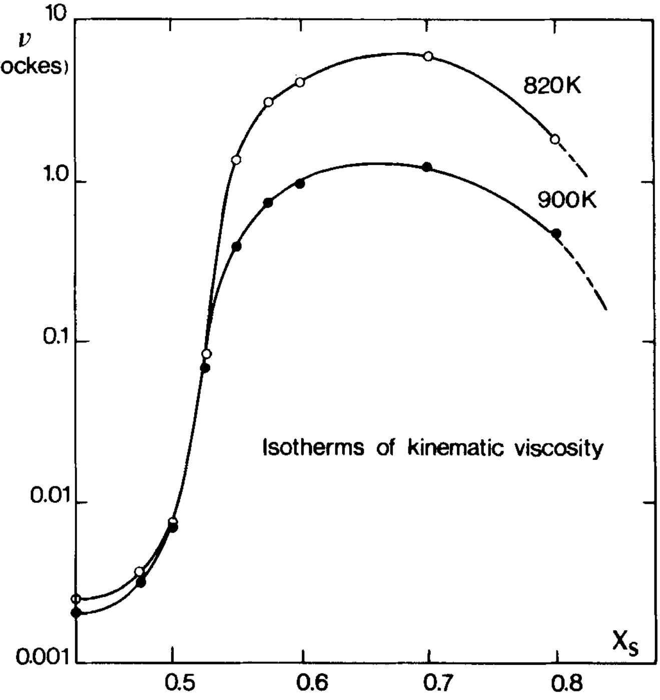

FIGURE 3 Isotherms of viscosity.

III DISCUSSION AND CONCLUSION

From these results it appears that a transition occurs between As_4S_4 and As_2S_3 compositions. The phase diagrams (Figure 4) are in controversy for number and position of eutectic compositions due to experimental determinations. As shown by the structural analysis of the glasses in the same composition range, only As_2S_3 is a well-defined composition.[2–5]

The glass transition temperature (Tg) is also reported in Figure 4 and supports the existence of structural changes. These thermal analysis measurements agree well with those of Myers and Felty,[4] Y. Kawamoto and S. Tsuchihashi.[8]

From the phase diagram interpretations the melts are strongly dissociated for $X_s = 0.5$ and associated for $X_s = 0.6$. This behaviour can be correlated to our viscosity transition.

The low viscosity melts with low activation energy insure the molecular dissociated character, the high viscosity melts with high activation energy are consistent with the associated character. A chain-like structure hypothesis may be reasonable for this sulfur rich part of $As_{1-x}S_x$.

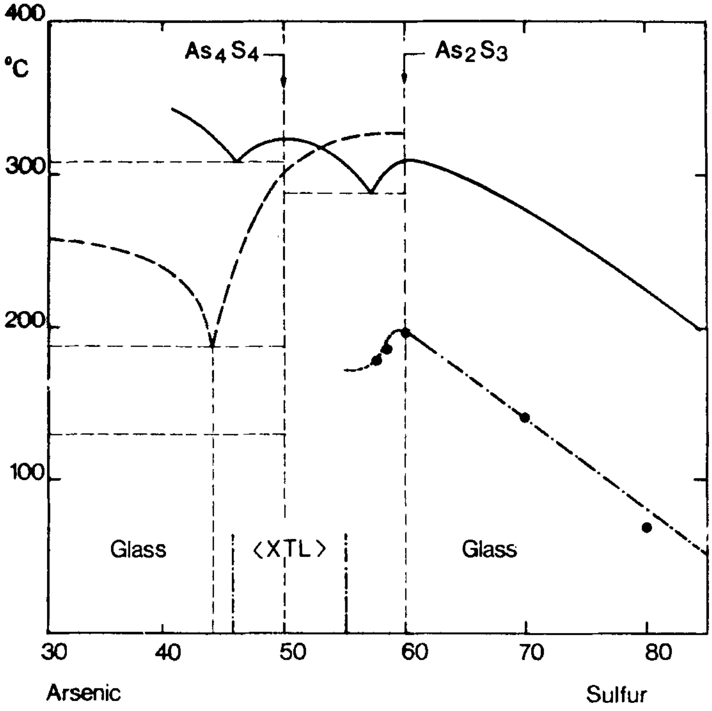

FIGURE 4 Phase equilibrium diagram of the As-S system from Ref. 4 (——) and from Ref. 5 (– – –). Glass transition temperature from Ref. 9 (–·–·–) and present work (●).

The viscosity transition composition can be also correlated with the limit of glass formation compositions found by A. Hruby[5] and S. Maruno.[9]

From polymeric structure hypothesis the smooth viscosity maximum can be explained. When arsenic atoms are added to pure liquid sulfur (polymeric Sn) a branching effect occurs.

Near $X_s = 0.65$ the liquid is dipolymeric and can be represented by a linked mixture of polymeric sulfur and polymeric arsenic trisulfide. When approaching composition the sulfur chains are shortened and finally at $X_s = 0.6$ only $(As_2S_3)_n$ polymers are present. For higher arsenic content near the transition the weaker

$$>\mathrm{As}-\mathrm{As}<$$

bonds concentration increases and drastically reduces the structural units.

In conclusion the viscosity measurements of $As_{1-x}S_x$ melts show a strong transition between $X_s = 0.525$ and $X_s = 0.575$. This transition indicates a structural change from dissociated to associated melts. The associated liquids which polymeric structural units lead to melts with high viscosity, these ones being good glass formers.

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