Densities, microhardnesses and electron microscopic studies of As-Se glasses*

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Abstract. Densities and microhardnesses of As-Se glasses have been measured over a wide range of composition. Anomalous variations of densities and microhardnesses have been noted. It has been found possible to explain the variation on the basis of chemical ordering in these glasses. Scanning electron microscopy has been used to investigate the nature of etching in various compositions. The chemical stabilities of these glasses towards etchants also seem to support chemical ordering in them.

Keywords. As-Se glasses ; density ; microhardness ; scanning electron microscopy.

1. Introduction

As-Se glasses have been widely investigated in the literature (Kolomiets 1964; Myuller 1971; Hulls and McMillan 1974; Hurst and Davis 1974; Webber and Savage 1976). The composition dependence of properties like glass transition, electrical conductivity, etc. (Mohan *et al* 1980; Rao and Mohan 1980) exhibit anomalous variations as a function of composition. Such variations can, however, be fairly well understood from a chemically ordered network model (Betts *et al* 1970; Lucovsky *et al* 1974; Lucovsky *et al* 1977). In order to further explore the implications of a chemically ordered network model for As-Se glasses we have studied variations of densities and microhardnesses of these glasses over a wide range of compositions. Further, in chemically ordered As-Se glasses we expect the presence of Se-Se and As-As bonds exclusively on one side of As_2Se_3 composition. It would therefore be interesting to investigate the stability of these glasses towards chemical attack. We report in this paper a scanning electron microscopic examination on the nature of chemical attack by two powerful etchants namely, aqua-regia and hydrofluoric acid on these glasses. These studies also seem to imply the validity of chemical ordering model.

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2. Experimental

As–Se glasses were prepared from 5 nine-purity elemental arsenic and selenium obtained from Koch-Light Co., UK. The method of preparation has been described elsewhere (Mohan *et al* 1980). Density measurements were made on these glasses by Archimedes method using double distilled water at room temperature. The measurements were repeated several times for consistent accuracy in the measurements. The density is accurate to ± 0.001 g cm^{-3}.

Microhardnesses were determined by Vicker's diamond indentation method. Glass specimens with plane parallel faces were obtained for these measurements by lapping and polishing with rouge powder. A load of 50 g was used on each glass for indentation. The reported microhardnesses are accurate to $\pm 5\%$.

Scanning electron microscopic studies were performed using a Cambridge Stereo-scan-150 electron microscope. The specimens for examination were first polished using rouge powder. Glasses were then subjected to chemical attack by aqua-regia or hydrofluoric acid for a fixed period of time. After etching the glasses were thoroughly washed in distilled water and dried. Since these glasses are non-conducting, they were coated with 150–200 Å thick gold-palladium alloy film using a polaron sputter coater before scanning their surfaces in the electron microscope.

3. Results and discussion

It was found to be extremely difficult to obtain glasses beyond 60% As ($As_{60}Se_{40}$). The glassy nature of various compositions were confirmed both from x-ray diffraction patterns and from differential scanning calorimetric runs (occurrence of glass transition temperature followed by crystallization peaks). The densities of glasses are shown as a function of composition in figure 1. The density of pure arsenic glass reported in the literature (Greaves *et al* 1979) is also shown in figure 1. Other reported density values have been included in the figure for comparison (Myuller 1971). $As_{40}Se_{60}$ composition corresponds to a maximum in the densities. But this maximum is anomalous in the sense that the densities of these glasses do not extrapolate to the correct value of the density of glassy arsenic (figure 1). The increase in density with incorporation of more and more arsenic in the selenium rich glasses is possibly due to (a) enhanced cross-linking and (b) degradation of selenium chain fragments. This results in more efficient packing of the constituent atoms. Beyond $As_{40}Se_{60}$ composition, occurrence of As–As linkages will only produce steric hindrance for efficient packing unless we assume that there is a very large concentration of broken bonds. In covalently bonded and chemically ordered As–Se glasses, we expect the concentration of broken bonds to be very much smaller than is required to give rise to such high densities. Therefore the density of glass decreases with further increase in arsenic concentration beyond the stoichiometric composition $As_{40}Se_{60}$. It is perhaps because of this reason that beyond $As_{60}Se_{40}$ the system prefers to phase separate and glasses are extremely difficult to prepare.

The microhardnesses of As–Se glasses as a function of composition are shown in figure 2. Here again the trend appears to be very similar to that of densities in figure 1. Reported microhardness values (Myuller 1971 ; Webber and

Figure 1.   Variation of densities as a function of composition.

Figure 2.   Variation of microhardnesses as a function of composition.

Savage 1976) for some of the compositions are also indicated in figure 2.   Micro-hardness is a property which is difficult to define clearly but is widely used in characterising many types of glasses.   The indentation processes in microhardness measurements is generally believed to involve one or all of the following processes : (i) a permanent densification, (ii) plastic flow and (iii) breaking of bonds.   Permanent densification has usually a negligible effect in microhardness measurements.

Also these glasses have been found to be vary brittle. Hence, we ignore the first two effects and assume that breaking of bonds is the only important factor which determines the microhardnesses of these glasses. We therefore expect that microhardness to be a monotonic function of bond energy. In figure 3a a plot of microhardness vs average bond energy (average bond energy has been evaluated as the total cohesive energy divided by the total number of bonds assuming a chemically ordered network of fully valence saturated atoms) is given. With the exception of $As_{60}Se_{40}$ glass, microhardness of other glasses seem to be quite linear with the average bond energy.

Microhardness is dimensionally equivalent to elastic moduli and it would be reasonable to expect a relation between microhardness and elastic moduli of the material and indeed such relations for glasses have been discussed in the literature (Sakka and Mackenzie 1971; Yamane and Mackenzie 1974). In the case of ionic materials where interaction potential is of Born–Lande or Born–Mayer type, it is possible to show that bulk modulus K is approximately equal to specific cohesive energy (Born and Huang 1966). For example if

$$U = -(A/r) + (B/r^n),$$

$$1/\beta = K = -v\,(dp/dv) = A/9v_0r_0\,(-1 + n),$$
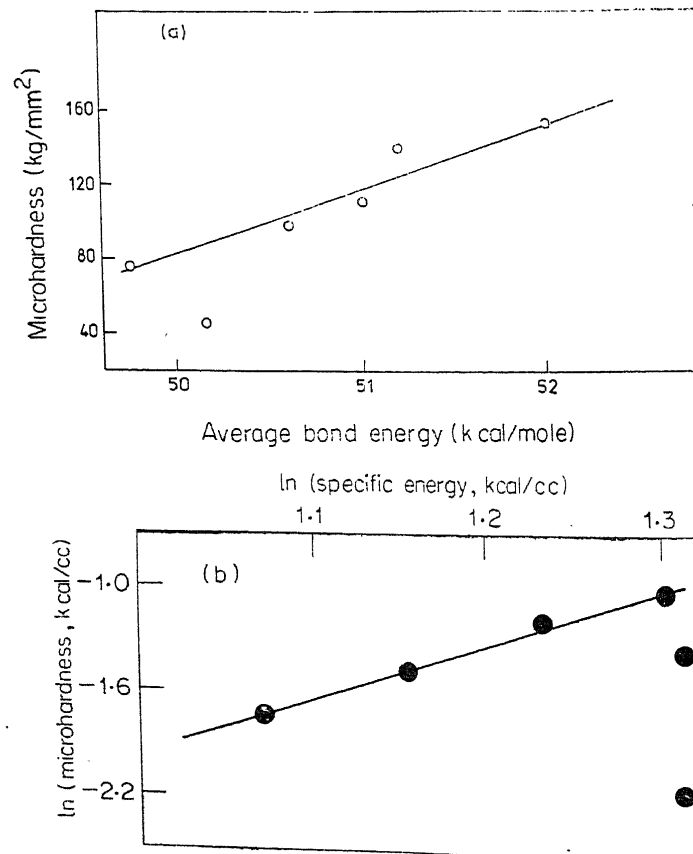

Figure 3. a. Variation of microhardnesses as a function of average bond energy and b. Log-log plot of microhardness vs specific energy.
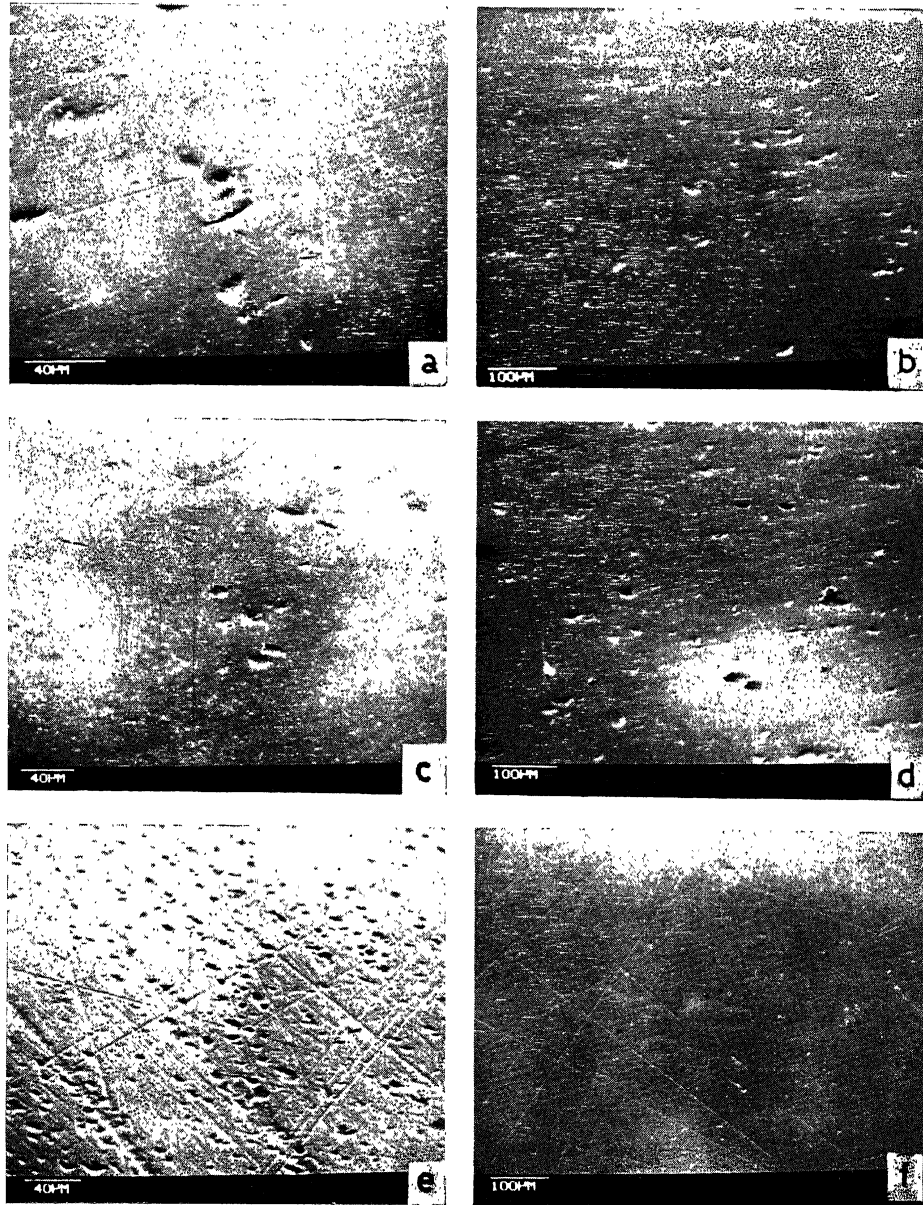
Figure 4. SEM micrographs of etched As-Se glasses. a, b. $As_{30}Se_{70}$; c, d. $As_{40}Se_{60}$; e, f. $As_{60}Se_{40}$; a, c and e were etched in aqua-regia for 10 minutes; b, d and f were etched in hydrofluoric acid for 15 minutes.
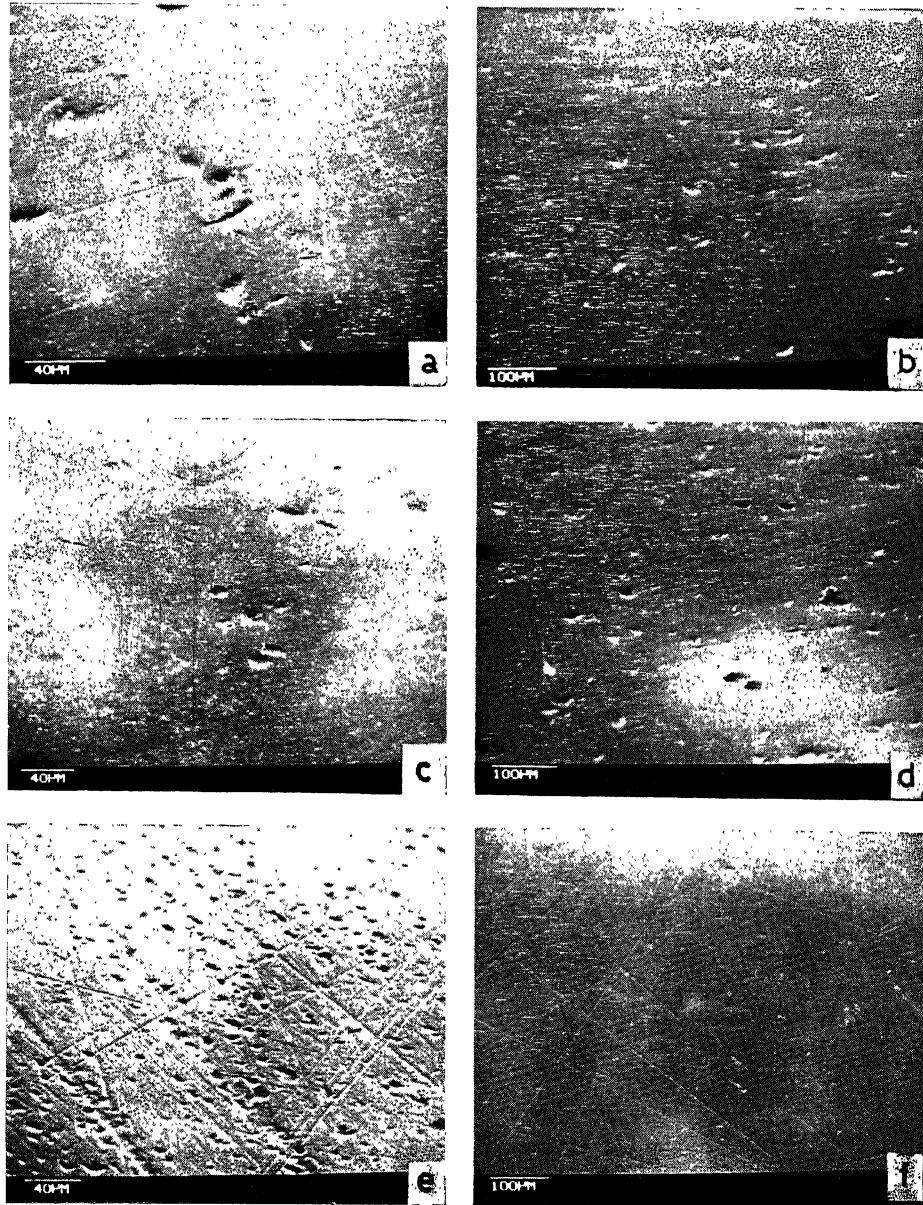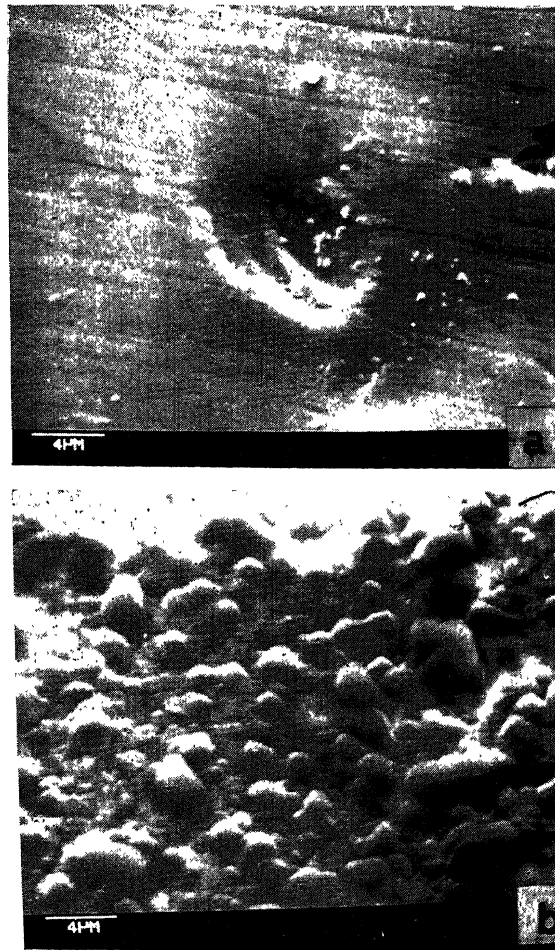
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Figure 5. SEM micrographs of etched a. $As_{30}Se_{70}$ glass in hydrofluoric acid (35 min) and b. $As_{60}Se_{40}$ glass in aqua-regia (21 min) at higher magnifications.

which indicates that for $n \sim 9$

$$K \simeq U/v_0$$

(using the equilibrium relation $A/r_0 = nB/r_0^n$).

In the above expression, v_0 is the volume of a pair of ions. Hence bulk modulus can be considered to be approximately equal to the specific cohesive energy of the material. If we assume that this relation is approximately true for covalently bonded materials also, we should expect microhardness and specific cohesive energy to be functionally related. In figure 3b log-log plot of microhardness expressed in

$$\text{kcal/cm}^3 \left(\frac{H_g \times 10^3}{10^{-2}\,\text{cm}^2} \times \frac{980\,\text{cm}}{\text{sec}^2} \times \frac{\text{cm}}{\text{cm}} \times \frac{1\,\text{kcals}}{4.186 \times 10^{10}\,\text{ergs}} \right)$$

(where H is the microhardness in kg/mm^2)
vs specific cohesive energy is given. Arsenic-rich glasses do not seem to fall in line with selenium-rich glasses. In glass compositions up to $As_{40}Se_{60}$ the slope indicates that microhardness is a high power function of the specific energy and hence of the elastic moduli. However, the relation between microhardness and cohesive energy shown in figure 3a reflects the general validity of a chemically ordered network model.

In figure 4 are shown the scanning electron micrographs of $As_{30}Se_{70}$, $As_{40}Se_{60}$ and $As_{60}Se_{40}$ samples which were etched in aqua-regia and hydrofluoric acid. These samples were taken from a single batch of glasses and etched for equal lengths of time and the micrographs correspond to identical magnification. The following observations can be made. Arsenic-rich glasses are readily etched by aqua-regia, which is known to be a powerful oxidising agent. The rate of etching of arsenic rich glass in hydrofluoric acid is negligible in comparison. The selenium-rich glasses are more prone to attack by hydrofluoric acid than by aqua-regia. $As_{40}Se_{60}$ composition is somewhat midway between in its behaviour. In figure 5, the nature of pits formed are shown at higher magnifications for two samples, $As_{60}Se_{40}$ etched in aqua-regia and $As_{30}Se_{70}$ etched in hydrofluoric acid. The photographs reveal that the attack of aqua-regia on arsenic-rich glass is quite severe while that of hydrofluoric acid on selenium-rich glass is slow and retarded.

If these glasses corresponded to a random network, we would have expected no such drastic changes in chemical stability towards the etchant. Though more detailed structural work is necessary to establish the nature of etching action, we would like to point out that such profound changes in etching behaviour is likely to be a consequence of chemical ordering. It is only in arsenic-rich compositions that As-As bonds are formed and it is well-known that arsenic is readily oxidised to As_2O_3 (Fritzsche 1973). The etching process is likely to involve oxidation of As followed by dissolution of As_2O_3.

Thus the apparently anomalous variation of physical properties of As-Se glasses is directly related to the nature of chemical ordering in these glasses.

M.S.—5

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