CRYSTALLISATION STUDIES ON As-Sb-Se GLASSES

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ABSTRACT

Results of non-isothermal crystallisation studies performed at various heating rates on nine glass compositions of the As-Sb-Se system with compositions represented by $(\text{As}, \text{Sb})_{40}\text{Se}_{60}$ and $\text{As}_x\text{Sb}_{15}\text{Se}_{85-x}$ are presented. Composition dependence of T_p , $T_c - T_g$, ΔH and E_g are discussed.

The crystallisation data are examined using an analysis developed for non-isothermal crystallisation. Bulk nucleation with two and three dimensional growth are indicated respectively for the $\text{As}_x\text{Sb}_{15}\text{Se}_{85-x}$ and $(\text{As}, \text{Sb})_{40}\text{Se}_{60}$ glasses. The activation energy for crystal growth obtained by these experiments and analysis agree with the electron microscopy data.

INTRODUCTION

Results of crystallisation studies using Differential Scanning Calorimetric (DSC) technique on $(\text{As}, \text{Sb})_{40}\text{Se}_{60}$ (with Sb at 0, 5, 10, 15 and 18 at.%) and $\text{As}_x\text{Sb}_{15}\text{Se}_{85-x}$ (with x at 10, 20, 30 and 35 at.%) are reported. The composition dependence of the crystallisation temperature (T_c), the peak temperature of crystallisation (T_p), $T_c - T_g$, the enthalpy of crystallisation (ΔH_c) and the activation energy of crystal growth (E_g) are discussed. The crystallisation data has been analysed using a procedure (1) developed specifically for non-isothermal studies.

EXPERIMENTAL

Bulk glasses were prepared by quenching of the melts and crystallisation studied at six heating rates from 1.25 K/min. to 40 K/min. using Perkin Elmer DSC-2 equipment. Further experimental details and the methods of evaluation of T_c , T_p , ΔH_c and E_g are all described in detail elsewhere (2).

RESULTS AND DISCUSSION

Figures 1 and 2 show the T_p -composition data for these glasses. For the $\text{As}_x\text{Sb}_{15}\text{Se}_{85-x}$ glasses (figure 1), T_p decreases slightly as the Se content increases from 50 at.% to 55 at.% after which there is a rapid fall for higher Se contents. The thermal stability of these glasses as inferred from ($T_c - T_g$) is seen (inset, figure 1) to be the lowest for the stoichiometric $\text{As}_{25}\text{Sb}_{15}\text{Se}_{60}$ composition. For the $(\text{As}, \text{Sb})_{40}\text{Se}_{60}$ glasses, T_p decreases slightly as the Sb content is increased from 5 to 10 at.%. In the region of 12 to 14 at.% of Sb, there is a steep fall of T_p before the T_p -composition dependence

figure 1: T_p vs. composition^p for $As_xSb_{15}Se_{85-x}$ glasses at three heating rates. The inset shows $(T_c - T_g)$ vs. composition^p at 10K/min

figure 2: T_p vs. composition^p for $(As,Sb)_{40}Se_{60}$ glasses at six heating rates. The inset shows $(T_c - T_g)$ vs composition at 10K/min

figure 3: ΔH_c vs. composition for $(As,Sb)_{40}Se_{60}$ and $As_xSb_{15}Se_{85-x}$ glasses

tapers off for Sb contents higher than 15 at.% (figure 2). The composition dependence of $(T_c - T_g)$ of these glasses (inset, figure 2) is similar to that of their T_p .

For the $(As,Sb)_{40}Se_{60}$ glasses, ΔH_c is seen (figure 3) to decrease initially as Sb content is increased from 0 to 10 at.%. A steep fall of ΔH_c is seen for compositions around 12 to 14 at.% of Sb before flattening off for Sb contents higher than 15 at.%. For the $As_xSb_{15}Se_{85-x}$ glasses, a peak in ΔH_c -composition data is seen for the stoichiometric $As_{25}Sb_{15}Se_{60}$ composition. Higher ΔH_c is associated with the least stable i.e. glasses with smaller $(T_c - T_g)$ values (3,4). This is found to be valid for the $As_xSb_{15}Se_{85-x}$ glasses which show a maximum in ΔH_c and a minimum in $(T_c - T_g)$ far the $As_{25}Sb_{15}Se_{60}$ glass. However,

for the $(As,Sb)_{40}Se_{60}$ glasses. As_2Se_3 and glasses with low at.% of Sb have high values of ΔH_c and their corresponding $(T_c - T_g)$ values are also large. a result similar to that of As-Te glasses (5,6). As already discussed. (2), while ΔH_c and $(T_c - T_g)$ Correlation is valid in general. structural information of the glassy and the corresponding crystalline states are necessary to understand their ΔH_c behaviour.

The crystallisation data was further analysed based on a method developed for non-isothermal crystallisation (1).

For non-isothermal crystallisation the volume fraction of crystals precipitated in a glass heated at a uniform rate α is shown (1) to be related to the activation energy E through the equation

$$\ln[-\ln(1-x)] = -n \ln \alpha - 1.052 m E_c / RT + \text{Constant}$$

Here m and n are numerical constants having values between 1 and 4 depending on the morphology (whether it is surface or bulk nucleation and whether the crystal growth is predominantly one, two or three dimensional). Values of m and n under various conditions are already listed (1,7). When nuclei formed during the heating at a constant rate α are dominant, $n=m+1$ and when nuclei formed during any previous heat treatment are dominant, $n=m$.

Figure 4 shows $\ln[-\ln(1-x)]$ versus $1/T$ for one of the compositions (at different heating rates) and the plot is seen to be linear over most of the range; mE_c is obtained as the average value of the slope of these lines. The value of n is given by the slope of the linear $\ln[-\ln(1-x)]$ versus $\ln \alpha$ plots at fixed temperatures.

An examination of the values of n obtained for these glasses indicated that n had a value of around 4 for $(\text{As,Sb})_{40}\text{Se}_{60}$ and around 3 for $\text{As}_x\text{Sb}_{15}\text{Se}_{85-x}$ glasses. As no prior thermal treatment was given to deliberately nucleate these glasses, m turns out to be 3 and 2 respectively for these glasses.

Figure 5 shows the values of E_c obtained for these glasses using the values of mE_c , n and m as outlined above.

The activation energies to be considered in a crystallisation process are the activation energy for nucleation (E_n), activation energy for crystal growth (E_g) and that for the whole process of crystallisation, called the activation energy for crystallisation E_c . The thermal analysis methods enable

figure 4: plot of $\ln[-\ln(1-x)]$ vs. $1/T$ for one of the glasses at six heating rates.

figure 5. E_c vs. composition for $(\text{As,Sb})_{40}\text{Se}_{60}$ and $\text{As}_x\text{Sb}_{15}\text{Se}_{85-x}$ glasses. Δ indicate the E_g of these glasses obtained by electron microscopy.

the determination of E_c (8,9). It has been pointed out (10) that in non-isothermal measurements, generally, due to a rapid temperature rise and big differences in the latent heats of nucleation and growth, the crystallisation exotherm characterises the growth of the crystalline phase from the amorphous matrix; nucleation is more or less calorimetrically unobservable at temperatures below the crystallisation exotherm, or it takes place very rapidly after overheating of the material. Based on this, the values of E_c (figure 4) can be taken to represent the activation energy for growth, E_g of these glasses. Data on direct measurement of E_g of As_2Se_3 and $(As,Sb)_{40}Se_{60}$ glasses by electron microscopy techniques (11,12) are also included in figure 4. Good agreement is seen between these E_g values and the E_c values obtained presently indicating that analysis of non-isothermal data give activation energy for crystal growth. X-ray diffraction studies on $(As,Sb)_{40}Se_{60}$ glasses (12) have indicated that glasses with low at.% of Sb crystallised in the monoclinic systems of Sb_2Se_3 , while glasses with high Sb crystallised in the orthorhombic system of Sb_2Se_3 , with both being equally present around 12 at.% of Sb.

CONCLUSIONS

For $(As,Sb)_{40}Se_{60}$ and $As_{15}Sb_{85-x}$ glasses, the composition dependence of T_g , T_c , T_g , ΔH_c and E_g are presented and discussed. For $(As,Sb)_{40}Se_{60}$ glasses, a steep variation in these properties is seen between 12 to 14 at.% of Sb, which coincides with the change over from crystallisation essentially in the monoclinic type structure to orthorhombic type of structure. The activation energy obtained by non-isothermal measurements correspond to the activation energy for crystal growth. Analysis of results indicate bulk nucleation, with two and three dimensional growth respectively for the $(As,Sb)_{40}Se_{60}$ and $As_{15}Sb_{85-x}$ glasses.

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