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Crystallization kinetics of bulk amorphous $(Se_{65}Te_{35})_{100-x}Sb_x$

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Kinetic studies of crystallization in $(Se_{65}Te_{35})_{100-x}Sb_x$ with $0 \leqslant x \leqslant 10$ glasses, using the differential scanning calorimetry technique, were performed. Crystallization enthalpy data, ΔH_c, were collected as a function of composition. The crystallization data were examined in terms of recent analyses developed for non-isothermal crystallization studies, to arrive at E_c. The results indicate bulk nucleation and crystallization with two- and three-dimensional growth, respectively, for the $(Se_{65}Te_{35})_{98}Sb_2$ and $(Se_{65}Te_{35})_{92}Sb_8$ glass composition.

1. Introduction

Because it is widely accepted that the addition of a third element to binary chalcogenide glasses produces a higher stability of these glasses, the effects of an element as an additive to binary glasses have been extensively studied. The present paper report kinetic studies of crystallization in $(Se_{65}Te_{35})_{100-x}Sb_x$ glasses using the differential scanning calorimetry (DSC) technique with a view to understand the mechanism of crystallization in these glasses. The activation energy, E_c, has been evaluated from the heating-rate dependence of T_c. Crystallization studies have been made under non-isothermal conditions with samples heated at several uniform rates. Using a recent analysis developed for non-isothermal crystallization studies, information on some aspects of the crystallization process has been obtained.

2. Composition dependence of the crystallization enthalpy, ΔH_c

From the area of the exothermic peaks at different heating rates, ΔH_c was evaluated for all the compositions. For a given composition, ΔH_c was found to be approximately the same for all the heating rates. Fig. 1 shows the variation of ΔH_c with composition. The vertical bars denote the spread in ΔH_c obtained for all the heating rates used in the experiment. ΔH_c could not be evaluated at a heating rate above $10\,\mathrm{K\,min^{-1}}$, because the Sb_2Se_3 crystallization exothermic peak occurs before completion of the main crystallization (see [1]) for the compositions $x > 4$.

It is interesting to compare the composition dependence, ΔH_c, with the corresponding $(T_c - T_g)$ of these glasses. Because the release of energy, ΔH_c, is associated with the metastability of the glasses, large values of ΔH_c are associated with the least stable glasses, namely, glasses with smaller $(T_c - T_g)$ values. This is roughly found to be true (Fig. 1). Glasses corresponding to $x = 1$ and 2, glasses with low at % Sb, have a high value of ΔH_c and their corresponding $(T_c - T_g)$ values are rather low. This indicates, once more, the particular situation of these compositions in comparison with ones with higher antimony content and it is probably related to a structural characteristic of the glass.

3. Activation energy for crystallization

When a glass is heated at a constant rate, crystal nuclei are formed at a temperature higher than the glass transition temperature and the crystal particles grow in size. The variation of crystal volume fraction is expressed by

$$\mathrm{d}X/\mathrm{d}t = K(1 - X)\alpha - (n - 1) \times \exp[-1.052\, mE/kT)] \qquad (1)$$

where X is the crystal volume fraction, K is a constant and α the heating rate. $n = m + 1$ for a quenched glass containing no nuclei and $n = m$ for a glass containing a sufficiently large nuclei. Also, $m = 3$ for three-dimensional growth of crystal particles, $m = 2$ for two-dimensional growth and $m = 1$ for one-dimensional growth. The n-values can be obtained from the plot of $\ln[-\ln(1 - x)]$ against $\ln \alpha$ at a specific temperature. Theoretically, the maximum value of n is 4 and minimum value is 1, and in these cases the corresponding m values must be 3 and 1, respectively. In order to obtain the activation energy Matusita *et al.* [2, 3] have written the expression

$$\ln\alpha = -1.052 m/n\, E/(RT) - 1/n \ln[-\ln(1 - X)] + \text{constant} \qquad (2)$$

Thus the plot of $\ln\alpha$ against $1/T$, where T is the temperature at which the crystal volume fraction

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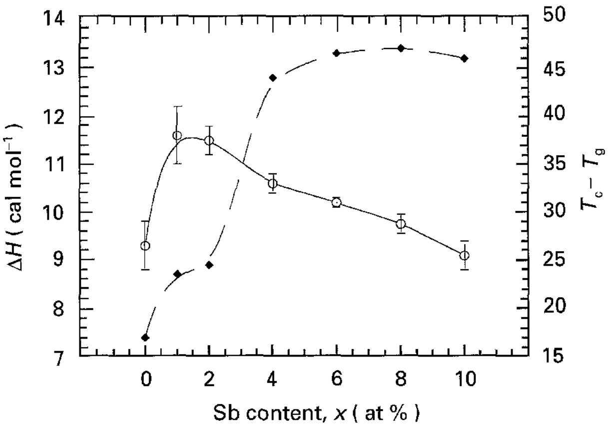

Figure 1 The composition dependence of (◆) $(T_c–T_g)$ of $(Se_{65}Te_{35})_{100-x}Sb_x$ $0 \leqslant x \leqslant 10$, at the heating rate $< 10\ K\,min^{-1}$; and (○) data of ΔH_c as a function of these glasses.

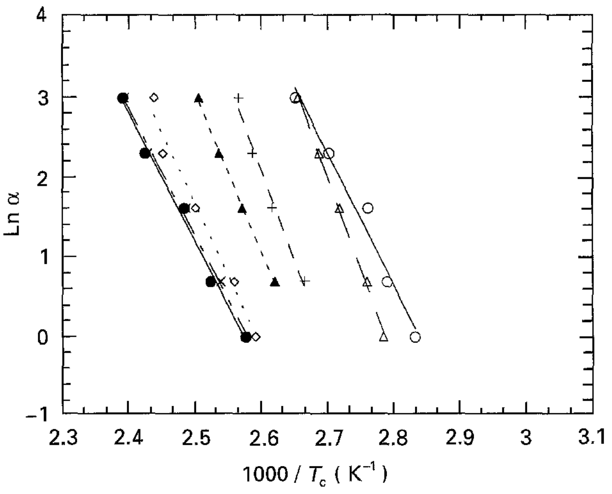

Figure 2 $\ln\alpha$ as a function of $1000/T_c$ for $(Se_{65}Te_{35})_{100-x}Sb_x$ glasses. x: (○) 0, (△) 1, (+) 2, (▲) 4, (◇) 6, (×) 8, (●) 10.

reaches a specific value, gives a straight line and the slope gives the value of $1.052(m/n)E$. This plot is very similar to the Ozawa plot [4]. The activation energy can be obtained when the ratio m/n is known.

The rate of increase of X reaches its maximum at a temperature T_0. Solving Equation 1 for $d(dX/dt)/dt = 0$, the following equation is obtained

$$\ln[\alpha^n/(T_0)] = -1.052mE/(RT_0) + \text{constant} \quad (3)$$

which is very similar to the Kissinger [5] equation when $n = m = 1$. Rewriting Equation 2, it follows

$$\ln[-\ln(1 - X)] = n\ln\alpha - 1.052mE/(RT) + \text{constant} \quad (4)$$

The plot of $\ln[-\ln(1 - X)]$ against $1/T$ gives another value of mE.

4. DSC experimental results

The crystallization data have been collected from DSC thermograms, obtained with different heating rates ($\alpha = 1, 2, 5, 10$ and $20\ K\,min^{-1}$) and different compositions $(Se_{65}Te_{35})_{100-x}Sb_x$ $(0 \leqslant x \leqslant 10)$. Values of the slope of the curve $\ln\alpha$ against $1/T$, T being the onset temperature of the crystallization peak, that is $E_c = 1.052(m/n)/E$, have been calculated from a modified Ozawa-type plot (Fig. 2). The departure of experimental points from the calculated average value is expressed by a vertical bar. The values have been summarized as a function of composition in Fig. 3.

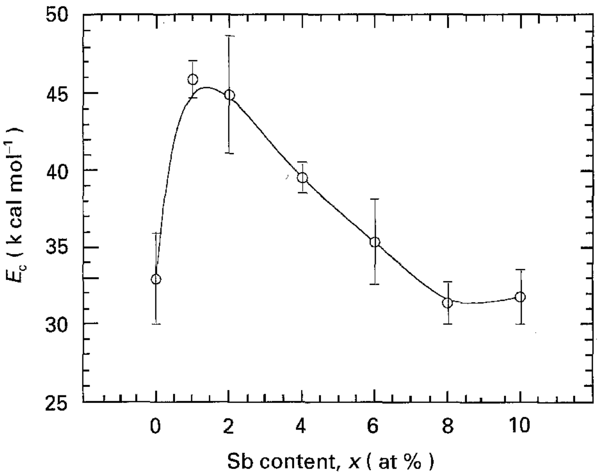

Figure 3 Composition dependence of ΔE_c in glassy $(Se_{65}Te_{35})_{100-x}Sb_x$ alloys.

A knowledge of m and n, that is, some details of the crystallization process, are needed to evaluate E_c. Therefore, to evaluate E_c, m, n (and to determine the crystallization mechanism), the results were analysed using the method suggested specifically for non-isothermal crystallization by Matusita *et al.* [2, 3]. This was undertaken for the compositions $x = 2$ and 8 due to their particular position on Fig. 3.

5. Results for $(Se_{65}Te_{35})_{98}Sb_2$ and $(Se_{65}Te_{35})_{92}Sb_8$ compositions

The same heating rates were used as previously chosen to study $(Se_{65}Te_{35})_{98}Sb_2$. Much lower heating rates ($\alpha = 0.65$, 1.25, 1.8 and $2.5\ K\,min^{-1}$) have been used

TABLE I Data for m, n and E_c for the glasses

Compositions	From $\ln[-\ln(1-X)]$ versus $1/T$ and versus $\ln\alpha$				From $\ln\alpha$ versus $1/T$ data. Ozawa modified		From $\ln(\alpha n/T_{20})$ versus $1/T_0$ data. Kissinger modified	
	mE_c (kcal mol^{-1})	n	m	E_c (kcal mol^{-1})	m/nE_c (kcal mol^{-1})	E_c (kcal mol^{-1})	mE_c (kcal mol^{-1})	E_c (kcal mol^{-1})
$(Se_{65}Te_{35})_{98}Sb_2$	132.4	3.15	2	66.2	44.91	70.7	150	75
$(Se_{65}Te_{35})_{92}Sb_8$	153	4.5	3	51	31.4	47.1	144.4	48

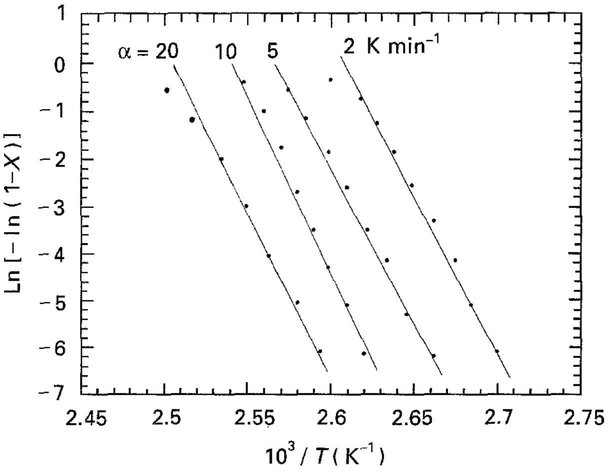

Figure 4 Ln[$-\ln(1-X)$] versus $1000/T$ for $(Se_{65}Te_{35})_{98}Sb_2$ glass at different heating rates (K min^{-1}) indicated.

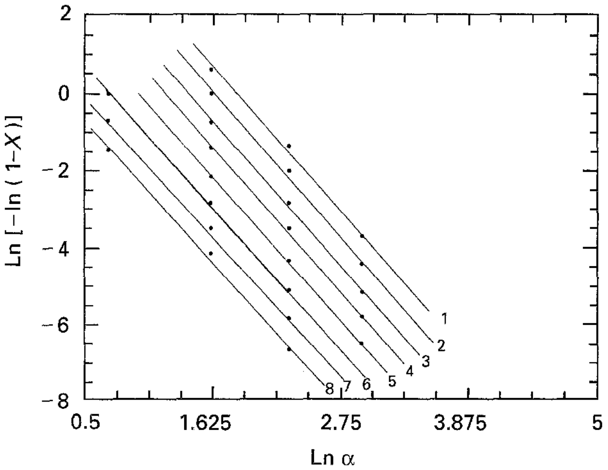

Figure 5 Ln[$-\ln(1-X)$] versus $\ln\alpha$ for $(Se_{65}Te_{35})_{98}Sb_2$ glass at various temperatures: (1) 390.6 K, (2) 389.1 K, (3) 387.6 K, (4) 386.1 K, (5) 384.6 K, (6) 383.1 K, (7) 381.7 K, (8) 380.7 K.

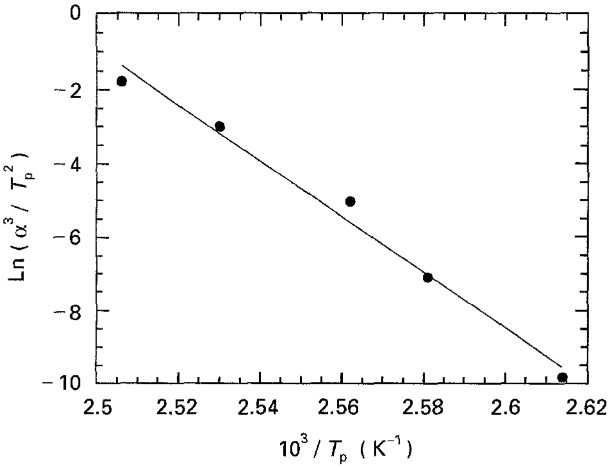

Figure 6 Modified Kissinger plot of $\ln(\alpha^3/T_p^2)$ versus $1000/T_p$ of $(Se_{65}Te_{35})_{98}Sb_2$ glass.

for $x = 8$ due to Sb_2Se_3 crystallization (see [1]). Table I summarizes the results and makes it possible to compare different values of E_c calculated either from ln[$-\ln(1-X)$] versus $1/T$ (Figs 4 and 7) or from the Ozawa-type model or the Kissinger-type model. n values are obtained as the slope of the lines Figs 5 and 8. The value of n is found to be about 3 for low values of x (and then m is taken equal to 2) and about 4 for higher values of x (and $m = 3$). Figs 6 and 9 refer to the Kissinger-type model taking into account the value of n already determined.

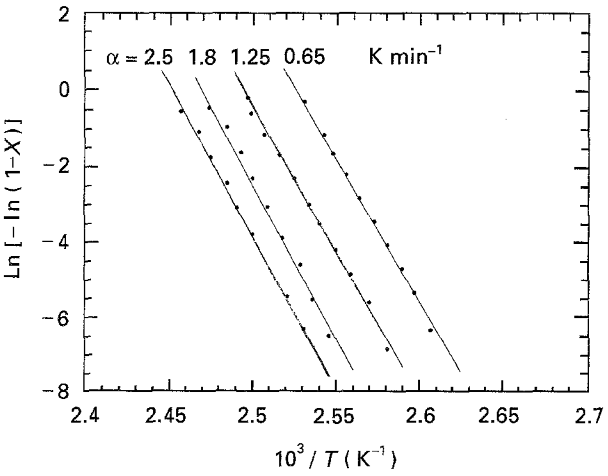

Figure 7 Ln[$-\ln(1-X)$] versus $1000/T$ for $(Se_{65}Te_{35})_{92}Sb_8$ glass at different heating rates (K min^{-1}) indicated.

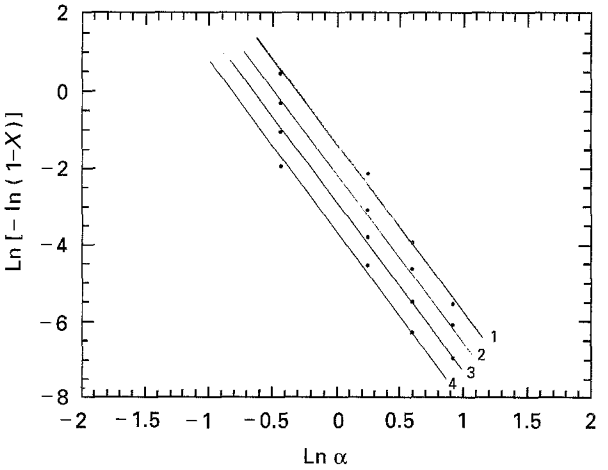

Figure 8 Ln[$-\ln(1-X)$] versus $\ln\alpha$ for $(Se_{65}Te_{35})_{92}Sb_8$ glass at various temperatures: (1) 396.82 K, (2) 395.26 K, (3) 393.70 K, (4) 392.15 K.

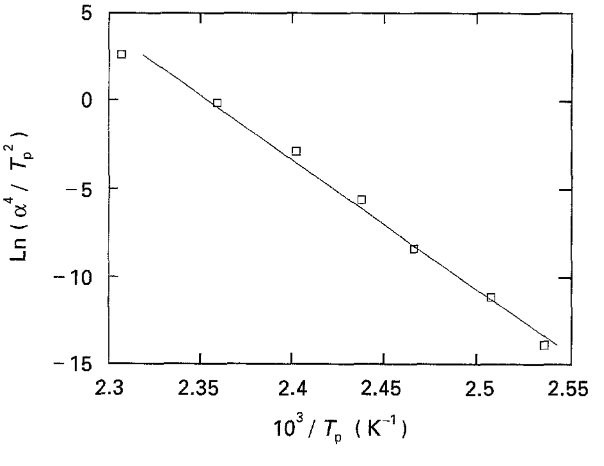

Figure 9 Modified Kissinger plot of $(\ln(\alpha^4/T_p^2)$ versus $1000/T_p$ of $(Se_{65}Te_{35})_{92}Sb_8$ glass.

6. Conclusion

Results on thermal analysis measurements performed at various heating rates on glasses of the Se–Te–Sb system with compositions $(Se_{65}Te_{35})_{100-x}Sb_x$ with $0 \leqslant x \leqslant 10$ are reported and discussed. The crystallization behaviour of these glasses has been studied under non-isothermal conditions. The crystallization temperature varies from 360–450 K depending on the composition and heating rate. The composition dependence of several properties associated with the crystallization process, $(T_c - T_g)$, ΔH_c and E_c have been reported. A steep variation in these properties is seen for the $(Se_{65}Te_{35})_{98}Sb_2$ glass. ΔH_c as well as E_c are maximum when a small amount of antimony is added to the SeTe system. It is supposed that such addition leads to cross-linking of the chains to a small extent, creating a two-dimensional network. Further addition of antimony leads to a breaking of the chains and the formation of a large number of smaller chains. The natural tendency of antimony atoms is to create either a trigonal, bipyramidal or octagonal environment with more or less covalent bonds. Thus it is not surprising that antimony leads to a decrease in the glass-forming ability of Se–Te; it contributes to changing the weak bonding between the Se–Te polymeric chain to relatively strong covalent bonds. Our results suggest that Sb_2Se_3 structures apparently begin to form as the antimony concentration exceeds 1–2 at % or so. Then, crystalline growth tends to take a three-dimensional character (with $n = 4$). The values of E_c obtained by Ozawa, Kissinger or Matusita's approach are not very different from each other and lie in the same order as those reported in the literature.

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