

Crystallization behavior of bulk amorphous Se-Sb-In system

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In the present work crystallization behavior of the amorphous $\text{Se}_{90-x}\text{Sb}_{10}\text{In}_x$ ($0 \leq x \leq 15$) system has been investigated using Differential Scanning Calorimetry (DSC). The DSC data was taken at different heating rates varying from $1^\circ\text{C}/\text{min}$ to $90^\circ\text{C}/\text{min}$. From the heating rate dependence of the crystallization temperature, the activation energy for crystallization has been determined using the Kissinger equation and Matusitas equation for non-isothermal crystallization of materials. The effect of addition of In to the Se-Sb system on the dimensionality of crystal growth has been investigated. © 2001 Kluwer Academic Publishers

1. Introduction

Chalcogen based semiconductors have attracted much attention recently due to their applications in reversible phase change optical recording, optical fibres, photoresists, photoconductors etc. [1–5]. Erasable optical recording is usually considered to be a potential replacement for conventional recording due to its high storage density and archival stability. The addition of In to the Se-Sb system is expected to modify the material properties to make it more suitable for reversible optical recording with an eraser time less than 1 micro second. In order to view the suitability of a material for the above applications, it is necessary to investigate the crystallization behavior of the material concerned. In the present work a systematic investigation of the crystallization kinetics of amorphous $\text{Se}_{90-x}\text{Sb}_{10}\text{In}_x$ ($0 \leq x \leq 15$) system has been made. The thermal stability and crystallization kinetics have been reported for the Se-Te-In system for different Se : In ratios. Calorimetric studies were made under non-isothermal conditions at different heating rates. From the heating rate dependence of T_p the activation energy for crystallization has been evaluated.

2. Experimental procedure

Bulk samples of the $\text{Se}_{90-x}\text{Sb}_{10}\text{In}_x$ ($0 \leq x \leq 15$) were prepared by the melt quenching technique. Appropriate amounts of 5 N purity elements were sealed off in quartz ampoules (4 mm diameter) and placed in the furnace at a temperature of 650°C for 48 hours. The furnace was constantly rocked to ensure a homogeneous mixing of the constituents. The melt was then rapidly quenched in ice water. Quenched samples were removed from the ampoules by dissolving the ampoule in a mixture of $\text{HF} + \text{H}_2\text{O}_2$ for about 48 hours. Amorphous nature of the samples was ensured by the absence of any peaks in the X-ray diffractograms.

Differential Scanning Calorimetry (DSC) measurements were made using a DSC3100, MacScience instrument. DSC thermograms for various compositions of the samples were obtained at different heating rates (1 – $90^\circ\text{C}/\text{min}$.) in the temperature range 20 – 300°C in order to scan the samples through their T_g (glass transition), T_p (peak crystallization) and T_m (melting point). The samples (9–10 mg) in powder form were placed in standard platinum pans and scanned over a temperature range of 270°C . T_g was taken as the temperature corresponding to the intersection of the two linear portions adjoining the transition elbow in the DSC traces. T_c is the temperature corresponding to the onset of crystallization. The fraction X crystallized at a temperature T is given by $X = A_T/A$ where A is the total area of the exotherm between T_c where the crystallization just begins and the temperature T_1 where the crystallization is completed. A_T is the area between T_c and T .

3. Results and discussion

DSC curves for $\text{Se}_{85}\text{Sb}_{10}\text{In}_5$ are shown in Fig. 1. It can be seen that the T_g and T_p of the samples shift to higher temperature with the increase in heating rate. Similar trend is also observed for all the other samples. All the samples show a single glass transition temperature and a single crystallization peak. The glass transition temperature does not show any discernible change with change in composition and lies in the range from 322 K – 328 K at the heating rate of $5^\circ\text{C}/\text{min}$ for different samples. The variation in the peak crystallization temperature with heating rate is shown in Fig. 2. It can be seen that the rate of increase of T_p is much higher upto a heating rate of $10^\circ\text{C}/\text{min}$ and increases linearly at a much slower rate thereafter. Variation of T_p with composition for the $\text{Se}_{90-x}\text{Sb}_{10}\text{In}_x$ ($0 \leq x \leq 15$) system is shown in Fig. 3. The peak crystallization temperature shows an initial decrease

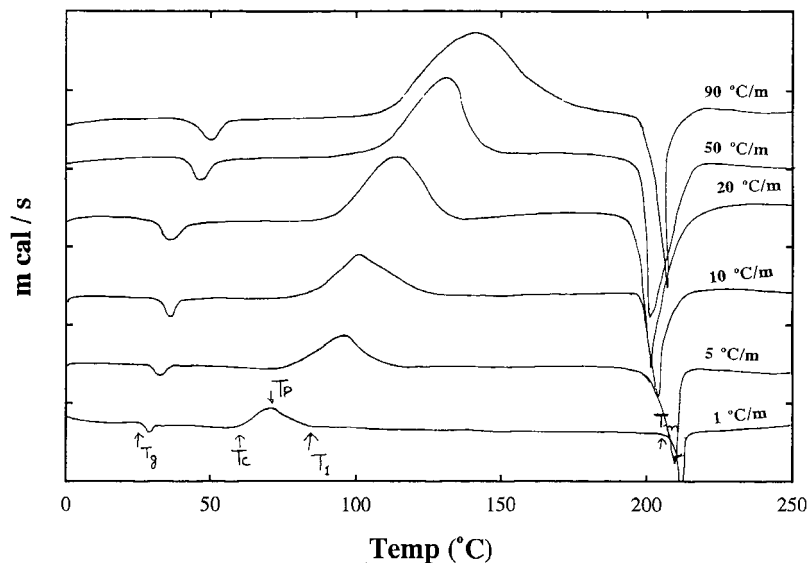


Figure 1 DSC thermograms for $\text{Se}_{85}\text{Sb}_{10}\text{In}_5$ at different heating rates showing the glass transition temperature, the peak crystallization temperature and the melting point.

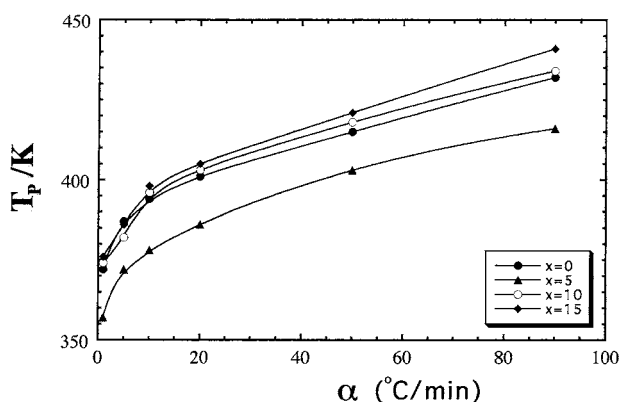


Figure 2 Variation of T_p with heating rate (α) for $\text{Se}_{90-x}\text{Sb}_{10}\text{In}_x$ ($0 \leq x < 15$) samples.

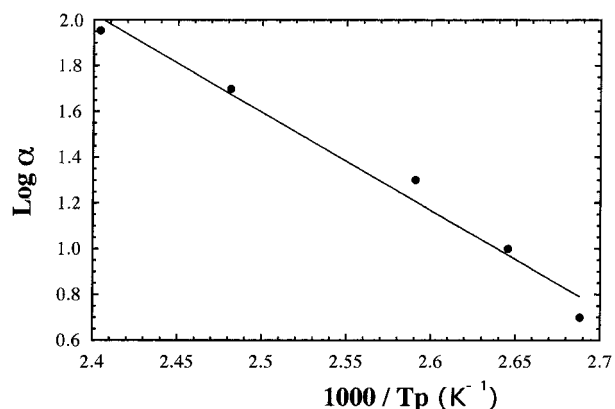


Figure 4 $\text{Log } \alpha$ versus $1000/T_p$ for $\text{Se}_{85}\text{Sb}_{10}\text{In}_5$.

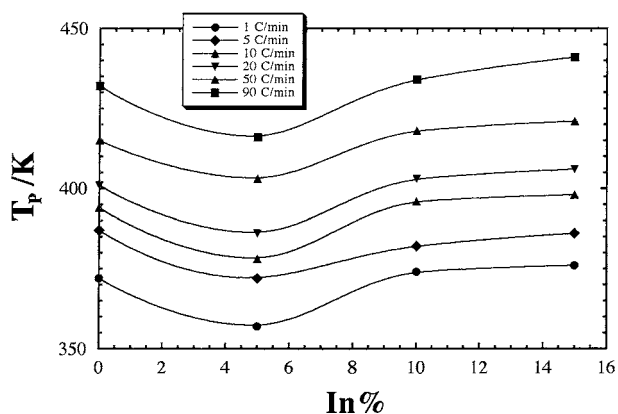


Figure 3 Variation of T_p with In content.

for In = 5 at% and then increases for In > 5 at% as shown in Fig. 3. The melting point shows little variation with change in composition.

The activation energy for crystallization E_c has been obtained using the modified Kissinger equation [6, 7]

$$\ln(\alpha^n / T_p^2) = -mE_c / RT_p + \ln k \quad (1)$$

where k is a constant containing factors depending on

the thermal history of the samples, n and m are constants having values between 1 and 4 depending on the morphology of growth. The value of mE_c/n was determined from the slope of $\ln \alpha$ versus $1000/T_p$ curves as shown in Fig. 4. The values of mE_c/n are listed in Table I.

According to Matusita *et al.* [8] for non-isothermal crystallization

$$\ln[-\ln(1-X)] = -n \ln \alpha - 1.052mE_c / RT + \text{constant} \quad (2)$$

where X is the volume fraction of crystals precipitated in the glass heated at uniform rate, E_c is the activation energy for crystallization and R is the gas constant. The

TABLE I Parameters determined from the heating rate data on $\text{Se}_{90-x}\text{Sb}_{10}\text{In}_x$ samples

Sample	mE_c/n kcal/ mol	n	m	E_c kcal/ mol	mE_c kcal/ mol	E_c kcal/ mol	K_{gl}
$\text{Se}_{90}\text{Sb}_{10}$	22.23	2.90	2	32.23	26.84	13.92	0.37
$\text{Se}_{85}\text{Sb}_{10}\text{In}_5$	19.49	2.48	2	24.16	23.28	11.64	0.30
$\text{Se}_{80}\text{Sb}_{10}\text{In}_{10}$	18.05	2.61	2	23.56	17.81	9.78	0.33
$\text{Se}_{75}\text{Sb}_{10}\text{In}_{15}$	18.25	1.37	1	25.00	19.24	19.24	0.37

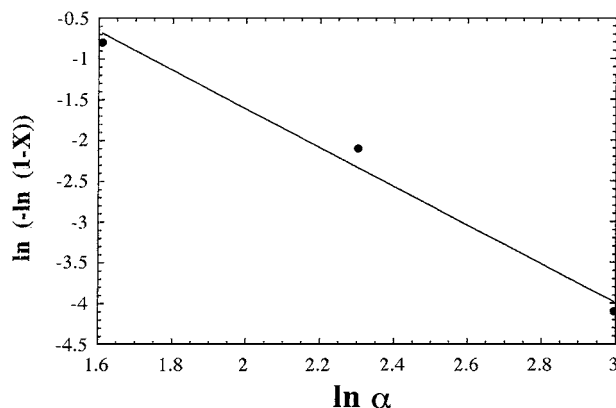


Figure 5 $\ln(-\ln(1-X))$ versus heating rate (α) for $\text{Se}_{85}\text{Sb}_{10}\text{In}_5$.

value of n is obtained from the slope of $\ln(-\ln(1-X))$ versus $\ln\alpha$ curve as shown in Fig. 5. The value of m is taken to be $n-1$ since no prior heat treatment was given to the samples [9] before the thermal analysis runs.

It can be seen from the values of n and m in Table I that the mechanism of crystal growth changes with the addition of In to the Se-Sb system. For the $\text{Se}_{90-x}\text{Sb}_{10}\text{In}_x$ ($0 \leq x < 15$) samples $n=3$ which gives $m=2$ suggesting bulk nucleation with two dimensional growth. However for the sample containing In = 15% the value of n becomes 2 and consequently $m=1$ which suggests bulk nucleation with one dimensional growth to be the dominant crystallization mechanism. The values of E_c evaluated using these values of m and n are given in Table I column 5. The value of mE_c (Table I) is obtained from the slope of the $\ln(-\ln(1-X))$ versus $1000/T$ curve (Fig. 6). The curve is a straight line for most of the temperature range but shows a break at higher temperatures which is attributed to the saturation of nucleation sites in the final stages of crystallization [10] or to the restriction of crystal growth by the small size of the particles [11]. The analysis is restricted to the initial linear region extending over a larger range. E_c is again obtained using the value of m and mE_c . These values are listed in Table I column 7. Although the values of E_c determined in columns 5 and 7 show similar behavior there is a discrepancy in the values obtained by the two methods. The reason for this discrepancy is not clear although such results have been obtained in the case of $\text{Li}_2\text{O}-2\text{SiO}_2$ glass [12] and amorphous Se-Te-Sn system [13]. The value of E_c is found to decrease with the addition of a small amount of In ($x=5, 10$ at%) to the Se-Sb system indicating an increase in the speed of crystallization which is also consistent with an initial decrease in the T_p of the sample (Fig. 3). However with the increase in In content ($x > 10$ at%) the speed of crystallization decreases resulting in an increase in the activation energy for crystallization.

The thermal stability is determined from Hrubys parameter K_{gl} given by [14]

$$K_{gl} = (T_c - T_g)/(T_m - T_c) \quad (3)$$

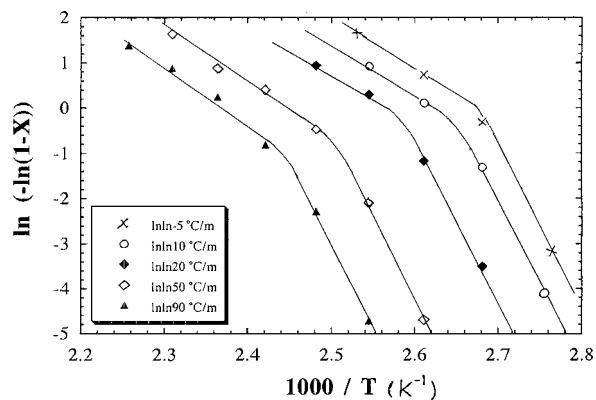


Figure 6 $\ln(-\ln(1-X))$ versus $10^3/T$ for $\text{Se}_{85}\text{Sb}_{10}\text{In}_5$ at different heating rates.

The values for different compositions vary from 0.30 to 0.37 and are listed in Table I. These values indicate good glass forming tendency for all the samples.

4. Conclusion

The effect of addition of In to the Se-Sb system on the crystallization kinetics and thermal stability of the material has been investigated. It is found that the glass transition temperature shows little variation with the addition of In. The crystallization mechanism is found to change from bulk nucleation in two dimensions for the sample containing In < 15 at% to bulk nucleation in one dimension for the samples containing In = 15%. All the samples show a good glass forming tendency.

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