EFFECT OF In IMPURITY ON CRYSTALLIZATION KINETICS OF $(Se_{.7}Te_{.3})_{100-x}In_x$ SYSTEM

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Abstract

The effect of In impurity on the crystallization kinetics and the changes taking place in the structure of (Se_7Te_3) have been studied by DTA measurements at different heating rates ($\alpha = 5$ deg·min^{-1}, 10 deg·min^{-1}, 15 deg·min^{-1} and 20 deg·min^{-1}). From the heating rate dependence of the values of T_g, T_c and T_p, the glass transition activation energy (E_t) and the crystallization activation energy (E_c) have been obtained for different compositions of $(Se_7Te_3)_{100-x}In_x$ ($0 \leq x \leq 20$). The variation of viscosity as a function of temperature has been evaluated using Vogel-Tamman-Fulcher equation.

The crystallization data are analysed using Kissinger's and Matusita's approach for non-isothermic crystallization. It has been found that for samples containing In=0, 10, 15, 20 at%, three dimensional nucleation is predominant whereas for samples containing In=5 at%, two dimensional nucleation is the dominant mechanism. The compositional dependence of T_g and crystallization kinetics are discussed in terms of the modification of the structure of the Se–Te system.

Keywords: crystallization kinetics, Se–Te–In system

Introduction

The effect of an impurity on the conduction mechanism and the structure of a binary chalcogenide may be widely different for different impurities [1]. The addition of an impurity e.g. Sb [2–4], Ge [5, 6], halogens [7], Ga [8], Sn [9], In [10] and Cu [11] in Se–Te binary alloy has been useful in understanding the structure and transport properties. It has been shown that incorporation of In modifies the transport properties like dark and photoconductivity [12, 13]. The Se–Te–In system is also a potential candidate for reversible phase change optical recording because the incorporation of In in binary chalcogenide glasses will affect the minimum eraser time [14]. No detailed study of electronic properties and crystallization kinetics of Se–Te–In are reported in the literature.

In the present work the effect of In impurity on the crystallization kinetics and the structure of ($Se_{.7}Te_{.3}$) has been studied. Crystallization kinetics, activation energies and structure of Se–Te has been studied by DTA measurements using the non isothermal method.

Experimental

Bulk samples of the $(Se_{.7}Te_{.3})_{100-x}In_x$ ($x = 0, 5, 10, 15, 20$) system were prepared by melt quenching technique. 5N purity elements taken in appropriate atomic percents were sealed in quartz ampules at a pressure $\sim 10^{-6}$ Torr and heated in a microprocessor controlled rocking furnace (Harrop U.S.A 73211) at 800°C for 30 h. The ampule was rocked continuously to ensure a homogeneous mixing of the constituents. The melt was then quenched in ice cold water to obtain glasses. The amorphocity of the samples was confirmed by the absence of any sharp peak in the X-ray diffraction pattern. The compositional analysis was performed by ESCA (Shimadzu) and the composition was found to be in the vicinity of ±1% of the actual percentage taken initially.

The thermal behaviour of the samples was investigated using a RIGAKU 8150 Differential Thermal Analyser, which was initially calibrated with
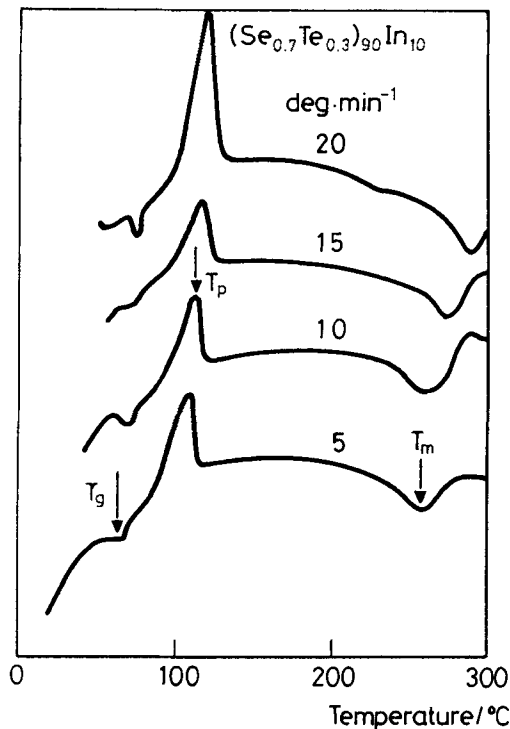

Fig. 1 DSC curves at different heating rates for $(Se_{.7}Te_{.3})_{90}In_{10}$

well known melting temperatures of high purity In. For DSC measurements, 30 mg of the samples in powdered form were taken in platinum pans of the thermal analyser. DSC curves were taken at various heating rates (5 deg·min^{-1}, 10 deg·min^{-1}, 15 deg·min^{-1} and 20 deg·min^{-1}) in the temperature range 30–400°C in order to scan the samples through their glass transition temperature, crystallization temperature, and the melting point. The fraction X crystallized at any temperature T, is given as $X = A_T/A$ where A_T is the area between temperature T_c (onset of crystallization) and T, A is the total area of exotherm between temperature T_c and T_2 where crystallization is completed [4].

Results and discussions

DSC curves for $(Se_7Te_3)_{90}In_{10}$ are shown in Fig. 1. It is observed from the figure that the glass transition temperature (T_g) and the peak crystallization temperature (T_c) shift to a higher temperature with increasing heating rate (α).
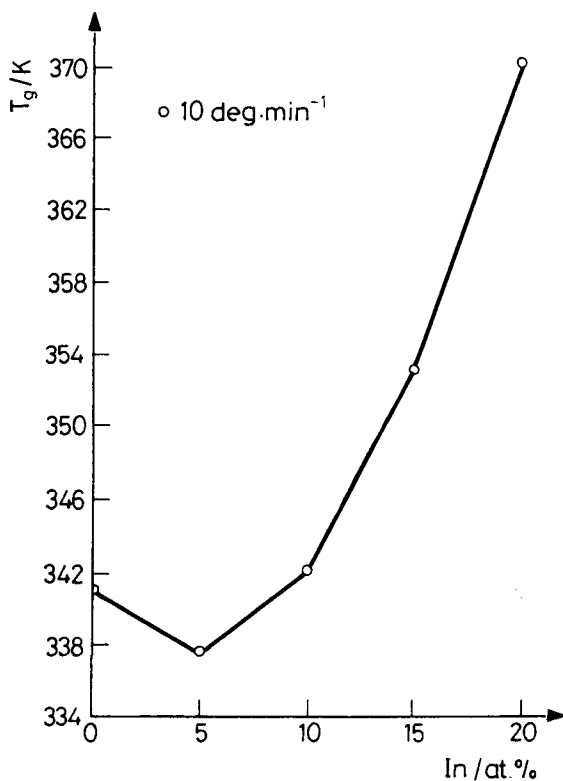

Fig. 2 Variation of T_g with composition for bulk amorphous $(Se_{.7}Te_{.3})_{100-x}In_x$ $(0 \leq x \leq 20)$ at heating rate $\alpha = 10$ deg·min^{-1}

The variation of glass transition temperature T_g with composition for $(Se_{.7}Te_{.3})_{100-x}In_x$ $(0 \leq x \leq 20)$ is shown in Fig. 2. When In is added to the Se–Te system, a decrease in T_g of the system is observed for In content ≤ 5 at%. However, for In >5 at% the T_g is found to increase. The results are shown in Table 1.

Table 1 Variation of T_g and T_p with heating rate

Composition	T_g/K			T_p/K		
	Heating rate/deg·min^{-1}			Heating rate/deg·min^{-1}		
	5	10	20	5	10	20
$Se_{.7}Te_{.3}$	338	341	345	418	423	429
$(Se_{.7}Te_{.3})_{95}In_5$	335	337.5	341	390	394	404
$(Se_{.7}Te_{.3})_{90}In_{10}$	340	342	346	379	385	391
$(Se_{.7}Te_{.3})_{85}In_{15}$	350	353	359	380	384	394
$(Se_{.7}Te_{.3})_{80}In_{20}$	366	370	376	397	401	410

The activation energy (E_t) for glass transition, has been calculated using the Kissinger's formula [15]

$$\ln(T_g^2/\alpha) + \text{const.} = E_t/RT_g \qquad (ii)$$

Plots of $\ln(T_g^2/\alpha)$ vs. $1000/T_g$ for these glasses are shown in Fig. 3. A linear behaviour for all the heating rates for all composition of the samples have been observed. E_t is found to vary from 35–52 kcal/mol and the values are listed in Table 2. The value of the peak crystallization temperature T_p for different samples at different heating rates are listed in Table 1. The modified Kissinger Equation (16–21) relating T_p and is

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

where k is a constant containing factors depending on the thermal history of the samples, m and n are constants having values between 1 and 4 depending on the morphology of growth and R is the gas constant. Values of mE_c/n obtained from the slope of $\ln \alpha$ vs. $1000/T_p$ (Fig. 4) are listed in Table 2. To evaluate the value of E_c, a knowledge of m and n, that is, some details of the crystallisation process are necessary.

According to Matusita, [21] for non-isothermal crystallization the volume fraction X of crystals precipitated in a glass heated at a uniform rate is shown to be related to E_c through the expression

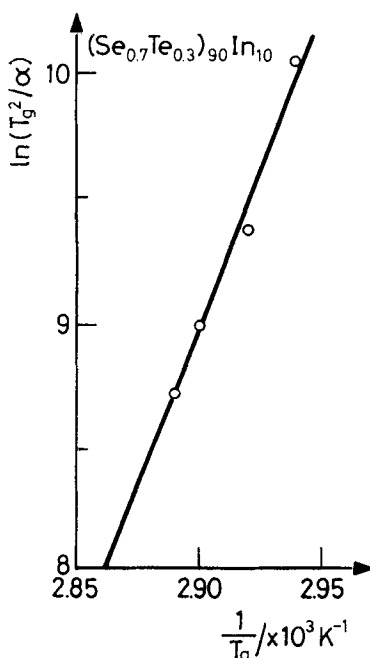$$\ln[-\ln(1-x)] = -n \ln \alpha - 1.052\, mE_c/Rt + \text{const.} \qquad (iv)$$

Fig. 3 Variation of $\ln(T_g^2/\alpha)$ vs. $1000/T_g$ for $(Se_{.7}Te_{.3})_{90}In_{10}$ for different heating rates (x)

As no heat treatment was given to the samples before the thermal analysis runs in the present case, nuclei formed during the heating at constant heating rate α are dominant so n is taken to be equal to $m+1$.

The value of mE_c was found from the slope of the graph $\ln(-\ln(1-x))$ vs. $1000/T$ (Fig. 5). The non-linearity of the plots at higher temperatures is attributed to the saturation of nucleation sites in the final stages of crystallization [22, 23] or to the restriction of crystal growth by the small size of particles [24]. The value of mE_c was found to be independent of the heating rate and are listed in Table 2. From the data of Fig. 5, n is obtained from the slope of $\ln(-\ln(1-x))$ vs. $\ln \alpha$ using Eq. (iv). The data for n evaluated for all sample is tabulated in Table 2. The value of n is found to be about 4 for the samples containing In= 0 at%, 10 at%, 15 at%, and 20 at% which gave the value of $m=3$, as m was taken as equal to $n-1$. This indicated bulk nucleation process with three dimensional growth is dominant in these samples. On the other hand for samples containing In=5 at% the value of m is found to equal to 2 indicating dominant nucleation process as two dimensional. Using these values m and n in m/nE_c, the value of E_c for all the samples is calculated and is listed in Table 2 column 8. E_c was also obtained using the value of m and mE_c. These values are given in Table 2 column 5. The two values of E_c thus obtained are not same. The reason for this discrepancy is yet not clear, however, such results are also obtained in the case of Se–Te–Sb [4].

Table 2 Parameters determined from the heating rate data of $(Se_{.7}Te_{.3})_{100-x}In_x$ samples

Sample composition	Mean molecular weight	E_t/ kcal·mol⁻¹	mE_c/ kcal·mol⁻¹	mE_c/n/ kcal·mol⁻¹	E_c/ kcal·mol⁻¹	m	n	E_c/ kcal·mol⁻¹	E_{np}/ kcal·mol⁻¹
$Se_{.7}Te_{.3}$	93.5520	35.75	80.00	44.13	26.66	3	4.03	59.28	34.66
$(Se_{.7}Te_{.3})_{95}In_5$	94.6154	51.63	74.04	39.72	37.02	2	2.80	55.61	35.75
$(Se_{.7}Te_{.3})_{90}In_{10}$	95.6788	49.00	64.20	34.42	21.40	3	3.84	44.05	32.96
$(Se_{.7}Te_{.3})_{85}In_{15}$	96.7422	43.00	60.40	32.62	20.13	3	3.81	41.42	30.38
$(Se_{.7}Te_{.3})_{80}In_{20}$	97.8056	40.51	56.30	30.41	18.76	3	3.80	38.52	24.15

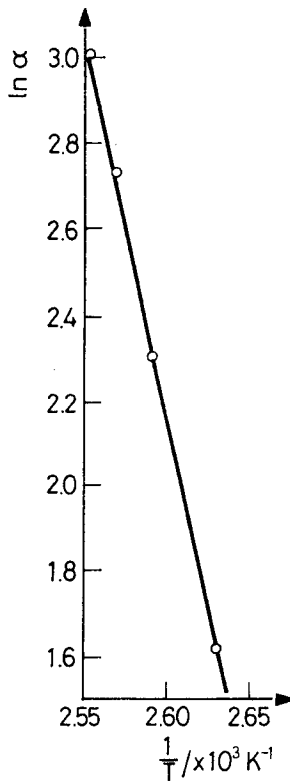**Fig. 4** Variation of ln x vs. $1000/T_p$ for $(Se_{.7}Te_{.3})_{90}In_{10}$

The thermal stability and ease of glass formation has also been evaluated using the expression [25]

$$K_{gl} = (T_c - T_g)/(T_m - T_c) \qquad \qquad (v)$$

The value of $T_c - T_g$ is found to decrease with increasing In concentration, which indicates a decrease in the thermal stability of the glasses [26] with increasing In content. K_{gl} also varies from 0.51 to 0.12 indicating that glasses with higher In content are difficult to form as compared to Se–Te glasses.

Viscosity

Using the data on the heating rate (α) dependence of T_g and T_p, the theoretical curves for the temperature dependence of viscosity (η) have been generated with the help of Vogel-Tamman-Fulcher Eq. (27)

$$\eta = \eta_o \exp(B/R(T-T_o)) \qquad \qquad (v)$$

The activation energies for glass transition E_t and for crystallization E_{np} (from plots of T_p^2/α vs. 1000/T), which have been evaluated using Kissinger equation are listed in Table 2 using the Eq. (28).
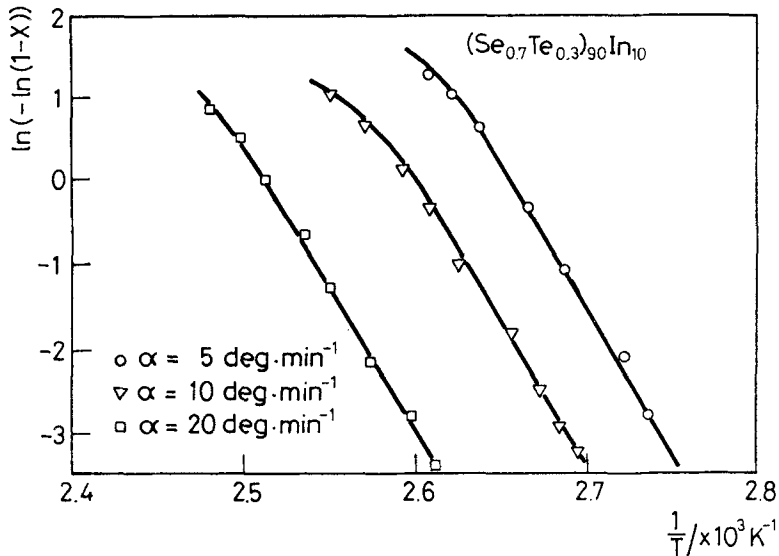

Fig. 5 Variation of $\ln(-\ln(1-x))$ vs. 1000/T for $(Se_{.7}Te_{.3})_{90}In_{10}$

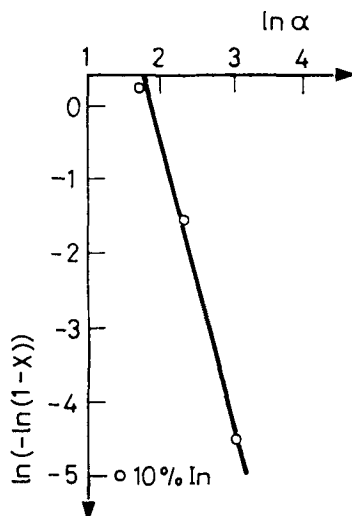**Fig. 6** $\ln(-\ln(1-x))$ vs. $\ln\alpha$ for $(Se_{.7}Te_{.3})_{90}In_{10}$
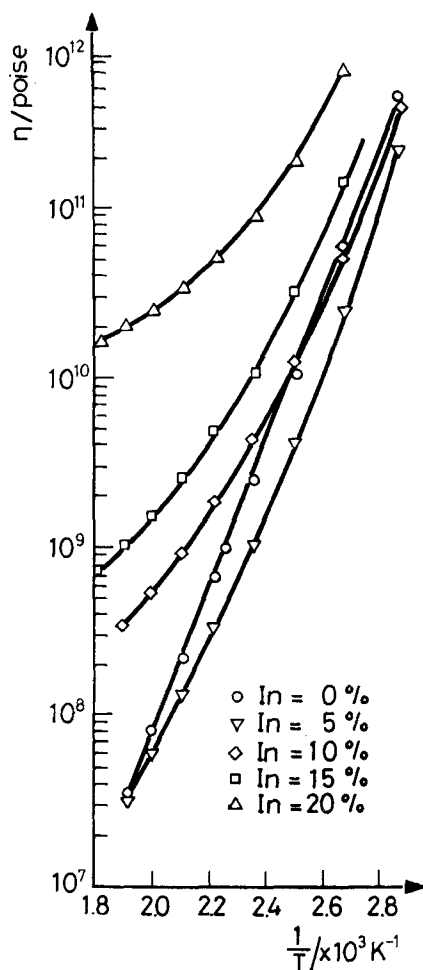
Fig. 7 Variation of viscosity as a function of temperature at $\alpha = 10$ deg·min^{-1} for $(Se_{.7}Te_{.3})_{100-x}In_x$ $(0 \leq x \leq 20)$

$$T_o = (\sqrt{A} T_g - T_p) / (\sqrt{A} - 1) \text{ and } B = E_t/A [T_g - T_o)/T_g]^2$$

where $A = E_t/E_{np} (T_p/T_g)^2$ substituting the values of B and T_o and assuming the viscosity at T_g to be 10^{12} poise, the theoretical curves of viscosity as a function of temperature have been generated and are shown in Fig. 7. The value of viscosity is found to lie in the range 10^7 to 10^{12} poise. It is observed that for the sample containing In≤5 at%, the viscosity is low and increases for samples containing In>5 at%, which is in agreement with the lowering of T_g for samples containing In>5 at% as T_g represents rigidity of the sample.

Conclusion

The effect of In impurity on glass transition temperature, activation energies, growth mechanism and viscosity of $(Se_{.7}Te_{.3})_{100-x}In_x$ $(0 \leq x \leq 20)$ system is found to be different for different In contents. It is observed that the glass transition temperature (T_g) decreases for In$\leq$5 at% and then in creases with further addition of In($>$5 at%). The compositional variation of viscosity is also found to be similar to that observed for T_g. It is found that the bulk nucleation with three dimensional growth for $Se_{.7}Te_{.3}$ changes to two dimensional growth for $(Se_{.7}Te_{.3})_{95}In_5$ and reverts back to three dimensional growth for higher In concentrations.

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Zusammenfassung — Mittels· DTA-Messungen bei verschiedenen Aufheizgeschwindigkeiten $(a=5$ deg/min, 10 deg/min und 20 deg/min) wurde der Effekt von In-Verunreinigungen auf die

Kristallisationskinetik und die Änderungen in der Struktur von (Se_7Te_3) untersucht. Anhand der Abhängigkeit der Werte für T_g, T_c und T_p von der Aufheizgeschwindigkeit wurde die Aktivierungsenergie für die Glasumwandlung (E_t) und für die Kristallisation (E_c) bei verschiedenen Zusammensetzungen von $(Se_7Te_3)_{100-x}In_x$ (mit $0 \le x \le 20$) erhalten. Die Änderung der Viskosität in Abhängigkeit von der Temperatur wurde anhand der Vogel-Tamman-Fulcher-Gleichung ermittelt.

Die Kristallisationsangaben wurden mittels der Näherung von Kissinger und Matusita für nichtisothermische Kristallisation analysiert. Man fand, daß in Proben mit einem Indiumgehalt von 0, 10, 15 und 20 Atom% eine dreidimensionale Keimbildung vorherrscht, während in Proben mit einem Indiumgehalt von 5 Atom% zweidimensionale Keimbildung der vorherrschende Mechanismus ist. Die Abhängigkeit von T_g und der Kristallisationskinetik von der Zusammensetzung wird mit Hilfe der Modifizierung der Struktur des Se–Te-Systems diskutiert.