Journal of Thermal Analysis and Calorimetry, 83 (2006) 2, 401–405

A STUDY OF THERMAL CRYSTALLIZATION IN GLASSY $Se_{80}Te_{20}$ AND $Se_{80}In_{20}$ USING DSC TECHNIQUE

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Different methods have been used by various workers to determine the activation energy of thermal crystallization (E_c) in chalcogenide glasses using non-isothermal DSC data. In the present work, the crystallization kinetics of two important binary alloys $Se_{80}Te_{20}$ and $Se_{80}In_{20}$ is studied using non-isothermal DSC data. DSC scans of these alloys have been taken at five different heating rates. The values of activation energy of crystallization (E_c) have been determined by four different methods, i.e., Kissinger's method, Matusita–Sakka method, Augis–Bennett's method and Ozawa's method, have been used to calculate E_c. The results obtained have been compared with each other to see the effect of using different methods in the determination of E_c.

Keywords: *chalcogenide glasses, differential scanning calorimetry, non-isothermal methods*

Introduction

In the recent years, great attention has been given to chalcogenide glasses mainly due to their wide range of applications in solid state devices both in scientific and technological fields [1–14]. Optical data storage based on laser induced amorphous to crystalline (a–c) phase transformation of chalcogenide glasses is an area with on-going research activity [1–14]. The activation energy of crystallization (E_c) plays an important role in determining the utility of chalcogenide glasses for phase-change recording on compact disks [15].

The a–c transformation in chalcogenide glasses can be investigated by isothermal and non-isothermal methods [16–18]. In isothermal method, the sample is brought near to crystallization temperature very quickly and then any physical quantity which changes drastically is measured as a function of time. In the non-isothermal method, the sample is heated at a fixed rate and the physical quantity is recorded as a function of time or temperature. A shortcoming of the isothermal method is the impossibility of reaching a test temperature instantaneously and during the time, which system needs to stabilize, no measurements are possible. However, the non-isothermal method does not have this drawback [19].

Due to the above mentioned advantages, non-isothermal differential scanning calorimetric (DSC) technique has been widely used in literature [20–24] for the study of the crystallization kinetics. This technique is particular important due to the fact that: (1) it is easy to carry out; (2) it requires little sample preparation; (3) it is quite sensitive and (4) it is relatively independent of the sample geometry. It is interesting to note that different equations have been used by various workers to determine E_c using non-isothermal DSC data emphasizing the suitability of a particular method in their case [20–24].

In the present work, four different methods of analysis (as described in next section) have been used for the determination of activation energy of crystallization for two important binary alloys $Se_{80}Te_{20}$ and $Se_{80}In_{20}$ using non-isothermal DSC data. These binary alloys are found to improve the properties (photosensitivity and thermal stability) of pure glassy Se for many applications.

Using DSC scans of the above glassy alloys at five different heating rates, the values of activation energy of crystallization E_c have been determined by Kissinger's method [25], Matusita–Sakka's method [26, 27], Augis–Bennett's method [28] and Ozawa's method [29]. The results obtained have been compared with each other to see the effect of using different methods in the determination of activation energy of crystallization.

Theoretical basis

The crystallization kinetics of amorphous alloys has been extensively studied using the classical Johnson–Mehl–Avrami (JMA) theoretical model [30–32] in which the extent of crystallization (α) can be described as a function of time (t) according to the formula:

$$\alpha(t)=1-\exp[-(Kt)^n] \qquad (1)$$

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1388–6150/$20.00

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where n is the Avrami exponent and K is the crystallization rate constant which shows the Arrhenius temperature dependence:

$$K=K_0\exp(-E_c/RT) \qquad (2)$$

where E_c is the activation energy of crystallization, R is the universal gas constant and K_0 is the pre-exponential factor of the crystallization rate constant.

Based on JMA model, different authors [25–29] have developed very diverse methods to study a–c transformation of glassy alloys. Given below are the details of four important and useful methods, which have been used in the present study.

Kissinger's method

According to Kissinger [25], the heating rate β, in terms of peak temperature of crystallization T_c, can be expressed as:

$$\ln(\beta/T_c^2) = -E_c/RT_c+\text{constant} \qquad (3)$$

This equation is used to calculate E_c by plotting $\ln\beta/T_c^2$ *vs*. $10^3/T_c$ curve.

Matusita–Sakka's method

The extent of crystallization (α) at a temperature T is well expressed by the expression:

$$\ln(1-\alpha)^{-1} = (C/\beta^n)[(-nE_c)/RT] \qquad (4)$$

The above expression is derived by Matusita and Sakka [26, 27] from the classical JMA equation. Since the values of α are independent of β at $T=T_c$ [33], so at $T=T_c$, the Eq. (4) takes the form:

$$\ln\beta = -E_c/RT_c+\text{constant} \qquad (5)$$

This equation is used to determine the activation energy of crystallization by plotting lnβ *vs*. $10^3/T_c$ curve.

Augis–Bennett's method

The value of E_c can also be calculated by an approximation method developed by Augis and Bennett [28]. The relation used by them is of the form:

$$\ln(\beta/T_c)= -E_c/RT_c+\ln K_0 \qquad (6)$$

Thus, the activation energy of crystallization can be evaluated by this equation using the plots of $\ln\beta/T_c$ *vs*. $10^3/T_c$.

Ozawa's method

Ozawa [29] suggested a method to determine E_c from heating rate dependence of on-set crystallization temperature T_o. According to his method, the relation between heating rate and T_o is given by:

$$\ln\beta = -E_c/RT_o+\text{constant} \qquad (7)$$

The slope obtained from the plot of lnβ *vs*. $10^3/T_o$ gives the value of activation energy of crystallization.

Experimental

Glassy alloys of $Se_{80}Te_{20}$ and $Se_{80}In_{20}$ were prepared by well-known quenching technique. High purity Se, Te and In materials (5N pure) were weighed according to their atomic percentages using an electronic balance (LIBROR, AEG-120) having the least count of 10^{-4} gm. The materials were then sealed in evacuated (10^{-5} Torr) quartz ampoules (length ~5 cm and internal diameter ~8 mm). Each ampoule was kept inside the furnace at an appropriate temperature (where the temperature was raised at a rate of 3–4 K min^{-1}). The ampoules were rocked frequently for 10 h at the maximum temperature to make the melt homogeneous. Quenching was done in ice water and the glassy nature of alloys was checked by X-ray diffraction technique.

The glasses, thus prepared, were ground to make fine powder for DSC studies. For the present measurements, DSC 2910 differential scanning calorimetry (TA instruments, USA) was used for obtaining DSC scans. 10 to 20 mg of each sample was heated at a constant heating rate and the changes in heat flow with respect to an empty pan were measured. Five heating rates (5, 10, 15 and 25 K min^{-1}) were chosen in the present study.

Results and discussion

Figures 1 and 2 show the typical DSC scans of glassy $Se_{80}Te_{20}$ and $Se_{80}In_{20}$ alloys, respectively, at different heating rates. It is clear from these figures that well defined endothermic and exothermic peaks are observed at glass transition temperature (T_g) and crystallization temperature (T_c) respectively. The values of peak crystallization temperature (T_c) and on-set crystallization temperature (T_o) for both the glassy alloys at different heating rates are given in Table 1.

The activation energy of crystallization of the present samples has been calculated by Kissinger's method, Matusita–Sakka's method, Augis–Bennett's method and Ozawa's method. The plots of $\ln(\beta/T_c^2)$ *vs*. $10^3/T_c$, lnβ *vs*. $10^3/T_c$, $\ln(\beta/T_c)$ *vs*. $10^3/T_c$ and lnβ *vs*. $10^3/T_o$ for glassy $Se_{80}Te_{20}$ and $Se_{80}In_{20}$ alloys are shown in Figs 3 and 4, respectively. Curve fitting is done by least square method using Microsoft Excel programming and the square of correlation coefficients

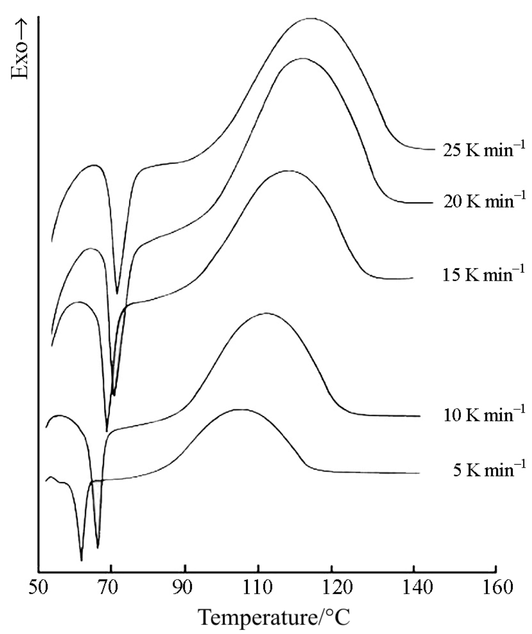

Fig. 1 DSC scans of glassy $Se_{80}Te_{20}$ alloy at different heating rates

(R^2) of each plot is indicated in Figs 3 and 4. From Figs 3 and 4, it is clear that each plot represents a straight line of good correlation coefficient. The values of correlation coefficient (R) for these plots are given in Table 2. This table shows that the correlation coefficient is close to 1 in almost all the cases. This indicates that all the four methods can be applied for the determination of E_c in the present case. The values of E_c obtained for both the samples using the above four meth-

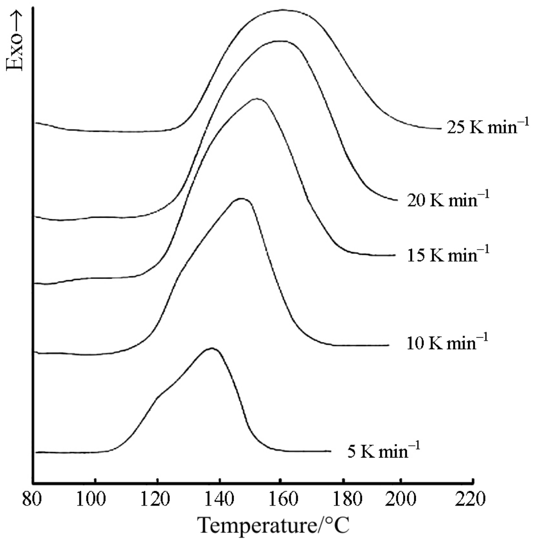

Fig. 2 DSC scans of glassy $Se_{80}In_{20}$ alloy at different heating rates

Table 1 Peak crystallization temperature (T_c) and on-set crystallization temperature (T_o) of glassy $Se_{80}Te_{20}$ and $Se_{80}In_{20}$ alloys

Heating rate, β/K min^{-1}	T_c/K		T_o/K	
	$Se_{80}In_{20}$	$Se_{80}Te_{20}$	$Se_{80}In_{20}$	$Se_{80}Te_{20}$
5	388.00	378.00	363.00	356.00
10	397.00	384.00	371.00	361.00
15	402.00	388.00	373.00	365.50
20	408.00	392.00	380.00	370.50
25	411.00	395.00	383.00	371.00

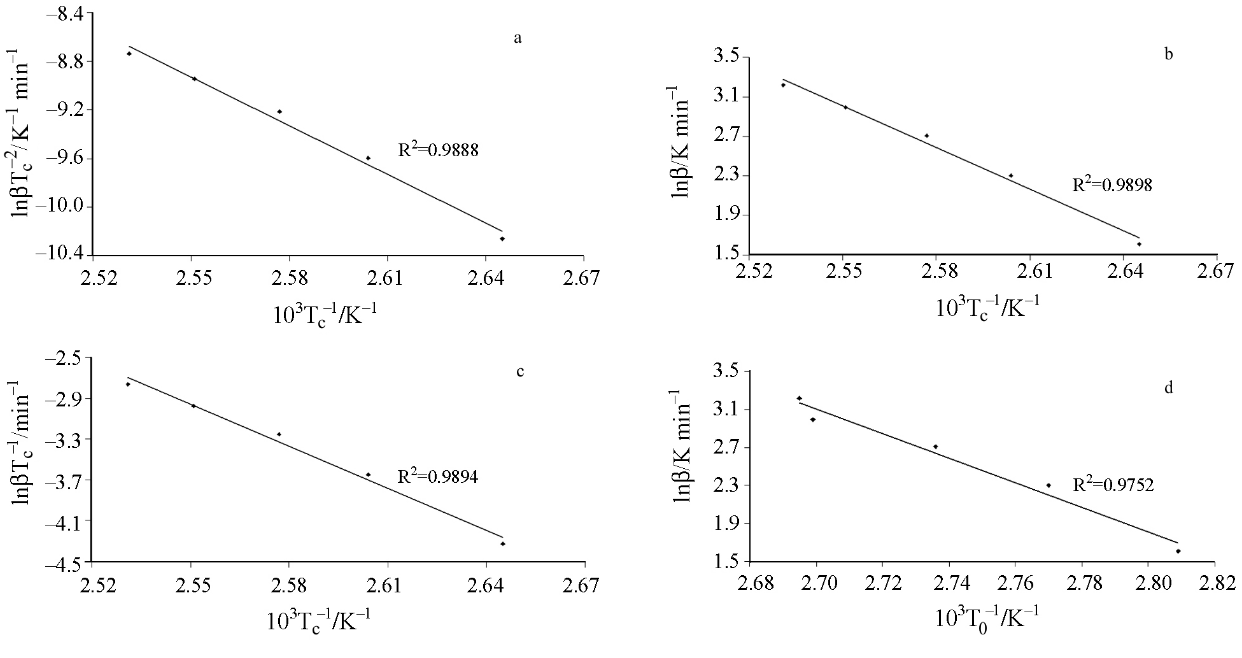

Fig. 3 Plots of a – $\ln(\beta T_c^{-2})$ *vs.* $10^3T_c^{-1}$, b – $\ln\beta$ *vs.* $10^3T_c^{-1}$, c – $\ln(\beta T_c^{-1})$ *vs.* $10^3T_c^{-1}$ and d – $\ln\beta$ *vs.* $10^3T_o^{-1}$ for glassy $Se_{80}Te_{20}$ alloy

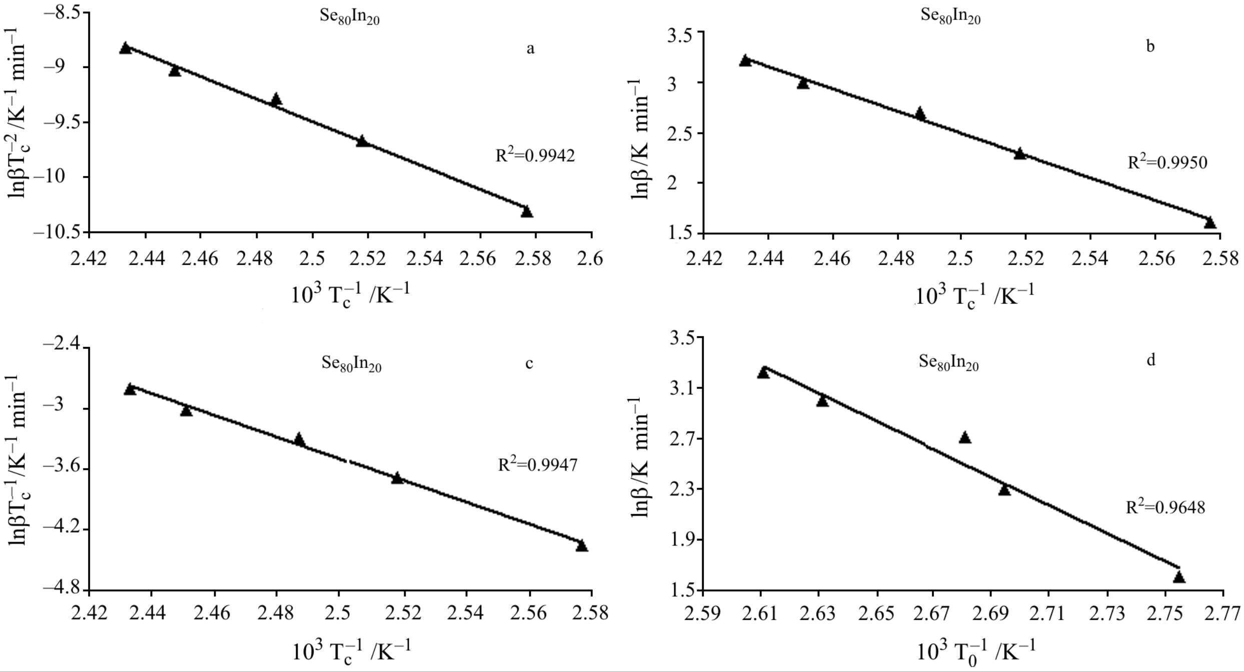

Fig. 4 Plots of a – $\ln(\beta T_c^{-2})$ *vs.* $10^3 T_c^{-1}$, b – $\ln\beta$ *vs.* $10^3 T_c^{-1}$, c – $\ln(\beta T_c^{-1})$ *vs.* $10^3 T_c^{-1}$ and d – $\ln\beta$ *vs.* $10^3 T_o^{-1}$ for glassy Se$_{80}$In$_{20}$ alloy

ods are given in Table 3. Comparison of E_c values of different alloys obtained from Eqs (3), (5)–(7) shows that the values are in good agreement. This means that one can use any of the four equations for the determination of activation energy of crystallization.

Table 2 Correlation coefficient (R) of straight lines obtained for the plots of different non-isothermal methods

Parameter on X-axis	Parameter on Y-axis	R	
		Se$_{80}$In$_{20}$	Se$_{80}$Te$_{20}$
$1000/T_c$	$\ln(\beta/T_c^2)$	0.99	0.99
$1000/T_c$	$\ln\beta$	0.99	0.99
$1000/T_c$	$\ln(\beta/T_c)$	0.99	0.99
$1000/T_o$	$\ln\beta$	0.97	0.98

Table 3 Activation energy of crystallization (E_c) evaluated from different non-isothermal methods

Non-isothermal method	E_c/kJ mol^{-1}	
	Se$_{80}$In$_{20}$	Se$_{80}$Te$_{20}$
Kissinger's method	85.7	110.8
Matusita–Sakka's method	95.4	117.5
Augis–Bennett's method	88.6	113.7
Ozawa's method	91.5	107.9
Average value	90.3	112.5

Conclusions

The activation energy of crystallization (E_c) for thermal crystallization of Se$_{80}$Te$_{20}$ and Se$_{80}$In$_{20}$ glassy alloys has been determined by four different methods under non-isothermal condition. DSC technique has been used for the present study. It has been found that E_c values obtained by all four different methods are in good agreement with each other.

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Received: February 10, 2004
Accepted: September 28, 2005

DOI: 10.1007/s10973-004-6342-8