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Glass transition and crystallization kinetics of $Sb_{14.5}As_{29.5}Se_{53.5}Te_{2.5}$ amorphous solid

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The crystallization kinetics of the quaternary $Sb_{14.5}As_{29.5}Se_{53.5}Te_{2.5}$ glassy alloy was studied under non-isothermal conditions. The method was applied to the experimental data obtained by differential scanning calorimetry (DSC), using continuous-heating techniques. In addition, two approaches are used to analyze the dependence of glass transition temperature (T_g) on the heating rate (β). One is empirical linear relationship between (T_g) and ln (β). The other approach is the use of straight line $\ln (T_g^2/\beta)$ vs. $1/T_g$ for evaluation of the activation energy for glass transition. The phases at which the alloy crystallizes after the thermal process have been identified by X-ray diffraction. The diffractogram of the transformed material shows the presence of some crystallites of As, SbTe, AsSb, As_2Se_3, Sb_2Se_3 and $AsSe_5Te_5$ in the residual amorphous matrix.

1 Introduction

An understanding of the kinetics of crystallization in glasses is important for the manufacturing of glass-ceramics and in preventing devitrification. Nucleation and growth rates are sometimes measured directly in the microscope [1] but this method could not be applied to glasses in which nucleation and crystallization occurred in times below 1 h. Differential scanning calorimetry (DSC) is valuable for the quantitative study of crystallization in different glassy systems. The study of crystallization kinetics has been widely discussed in the literature [2–8]. Different methods were proposed to get crystallization kinetics from the exothermic peaks of the (DSC) curves under non-isothermal conditions. Theoretical models [9–11] proposed for the crystallization process under non-isothermal conditions were applied to calculate crystallization kinetics.

In this work, the glass transition and the crystallization kinetics were studied using DSC with continuous heating of the sample at various uniform heating rates. The characteristic temperatures T_g, T_c, and T_p as well as the activation energy of glass transition and the activation energy for crystallization, E_g and E_c, respectively were determined for $Sb_{14.5}As_{29.5}Se_{53.5}Te_{2.5}$ glassy alloy. Finally, the crystalline phases corresponding to the crystallization process were identified by X-ray diffraction (XRD) measurements.

2 Experimental details

The semiconducting $Sb_{14.5}As_{29.5}Se_{53.5}Te_{2.5}$ glassy alloy was prepared from their components of 99.999% high purity. The proper amount for each material was weighed, and then the weighed materials were introduced into cleaned silica tubes. To avoid the oxidation of the samples the tube was evacuated to 1.33×10^{-3} Pascal, then put into a furnace at around 1250 K for 24 h. During the course of heating the

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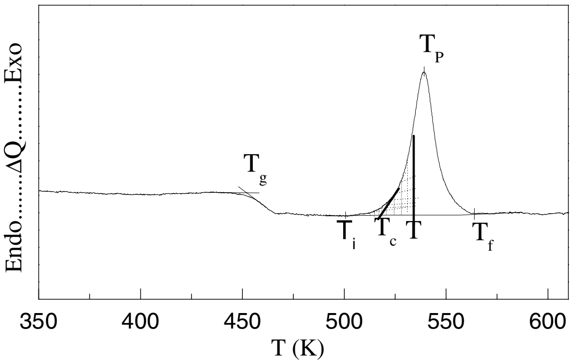

Fig. 1 DSC traces for powdered $Sb_{14.5}As_{29.5}Se_{53.5}Te_{2.5}$ chalcogenide glass at heating rate 5 K min^{-1}. The hatched area shows AT. The area between T_i and T.

ampoule was shaken several times to maintain their uniformity. Finally, the ampoule was quenched into ice cooled water to avoid crystallization.

The amorphous state of the material was confirmed by a diffractometric X-ray scan (Philips diffractometer 1710) using Cu as target and Ni as filter ($\lambda = 1.542$ Å). Energy dispersive X-ray spectroscopy (Link analytical EDS) was used to measure the elemental composition and indicates that the investigated composition is correct up to ±0.2 at%.

The calorimetric measurements were carried out using differential scanning calorimeter Shimadzu 50 with an accuracy of 0.1 K, keeping a constant flow of nitrogen to extract the gases generated during the crystallization reactions, which, is a characteristic of chalcogenide materials. The calorimeter was calibrated, for each heating rate, using the well-known melting temperatures and melting enthalpies of zinc and indium supplied with the instrument [12]. 20 mg powdered samples, crimped into aluminum pans and scanned at continuous heating rates ($\beta = 2.5$, 5, 10, 15, 20, 25 and 30 K min^{-1}). The value of the glass transition temperature, T_g, the crystallization extrapolated onset, T_c and the crystallization peak temperature, T_p, were determined with accuracy ±1 K by using the microprocessor of the thermal analyzer.

The fraction, χ, crystallized at a given temperature, T, is given by $\chi = A_T/A$, where A is the total area of the exotherm between the temperature, T_i, where crystallization is just beginning and temperature, T_f, where the crystallization is completed, A_T is the area between T_i and T, as shown in Fig. 1.

3 Results and discussion

The DSC curve for $Sb_{14.5}As_{29.5}Se_{53.5}Te_{2.5}$ quaternary glass obtained at a heating rate of 5 K min^{-1} as shown in Fig. 1. The glass transition temperature, $T_g = 450.56 \pm 2$ K, the extrapolated onset crystallization temperature, $T_c = 515.8 \pm 2.2$ K, and the peak temperature of crystallization, $T_p = 539.29 \pm 2.5$ K. This DSC trace shows the typical glass crystal transformation. The DSC Data at different heating rates, β, shows that, the characteristic temperatures T_g, T_c, and T_p increase with increasing β, a property which has been reported in the Ref. [13].

3.1 Glass transition

Two approaches are used to analyze the dependence of glass transition temperature on the heating rate. The first is the empirical relationship of the form

$$T_g = A + B \ln \beta , \tag{1}$$

where A and B are constants for a given glass composition [14]. The results shown in Fig. 2 indicate the validity of Eq. (1) for the $Sb_{14.5}As_{29.5}Se_{53.5}Te_{2.5}$ glassy alloy. The empirical relationship for this glass can be written in the form

$$T_g = 441.26 + 5.61 \ln \beta , \tag{2}$$

where a straight regression line has been fitted to the experimental data.

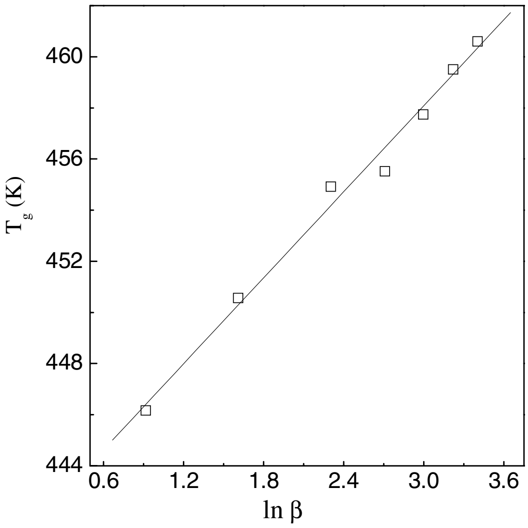

Fig. 2 Glass transition temperature versus ln (β) (β in KS^{-1}) of $Sb_{14.5}As_{29.5}Se_{53.5}Te_{2.5}$ glass.

The other approach is the dependence of the glass transition temperature on the heating rate, β, by using Kissinger's formula [15] in the form [16, 17]

$$\ln (T_g^2/\beta) = -E_g/RT_g + \text{const.}\,, \qquad (3)$$

a straight line between $\ln (T_g^2/\beta)$ and $1/T_g$, whose slope yields a value of E_g and where the subscript g denotes magnitude values corresponding to the glass transition temperature.

Given that the variation of $\ln (T_g^2)$ with β is negligibly small compared with the variation of $\ln (\beta)$, it is possible to write [14, 18]

$$\ln (\beta) = -E_g/RT_g + \text{const.} \qquad (4)$$

Figure 3 shows plots of $\ln (T_g^2/\beta)$, curve (a), and $\ln (\beta)$, curve (b), versus $1/T_g$ for the $Sb_{14.5}As_{29.5}Se_{53.5}Te_{2.5}$ semiconductor glass, displaying the linearity of the used equations. The obtained values of the glass transition activation energy E_g are 293.98 kJ/mol (a) and 300.32 kJ/mol (b), respectively. The average value of E_g is 297.1 ± 4 kJ/mol.

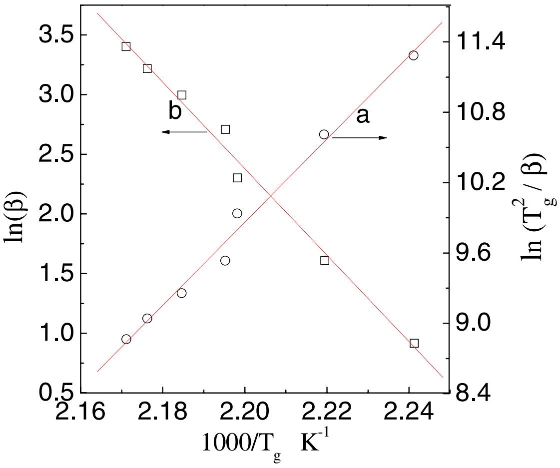

Fig. 3 (online colour at: www. pss-a.com) a) $\ln (T_g^2/\beta)$ vs. $1/T_g$, b) $\ln (\beta)$ vs. $1/T_g$ for $Sb_{14.5}As_{29.5}Se_{53.5}Te_{2.5}$ glass.

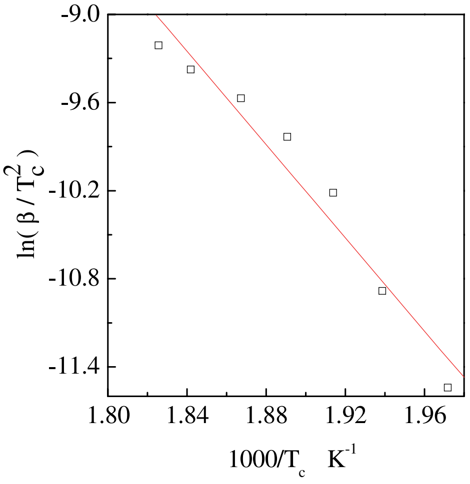

Fig. 4 (online colour at: www.pss-a.com) ln (β/T_c^2) vs. $1/T_c$ for $Sb_{14.5}As_{29.5}Se_{53.5}Te_{2.5}$ glass.

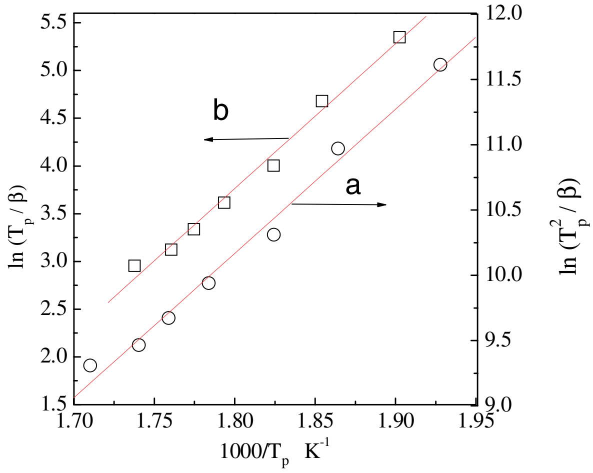

Fig. 5 (online colour at: www.pss-a.com) a) ln (T_p^2/β) vs. $1000/T_p$, b) ln (T_p/β) vs. $1000/T_p$ for $Sb_{14.5}As_{29.5}Se_{53.5}Te_{2.5}$ glass.

3.2 Crystallization

By using Kissinger's formula [15] for the evaluation of the activation energy of glass transition, E_g, for homogeneous crystallization with spherical nuclei, it has been shown that [16, 19] the dependence of T_c on b is given by

$$\ln (\beta/T_c^2) = -E_c/RT_c + \text{const.}\,, \tag{5}$$

where T_c is the onset temperature of crystallization. The relationship between $\ln(\beta/T_c^2)$and $1/T_c$ is shown in Fig. 4. The calculated value of E_c was found to be equal to 132.03 kJ/mol.

For the evaluation of activation energy for crystallization (E_c) from the variation of T_p with β Bansal et al. [1] developed a method for nonisothermal analysis of devitrification as follows:

$$\ln (T_p^2/\beta) = -E_c/RT_p + \ln (E_c/R) - \ln K_0\,, \tag{6}$$

where K_0 is the frequency factor. The plot of $\ln (T_p^2/\beta)$ vs. $1/T_p$ is shown in Fig. 5(a). From the linear dependence E_c was found to be equal 121.41 kJ/mol. Furthermore, from the intercept of this linear relation the frequency factor $K_0 = 6.636 \times 10^8\ \text{s}^{-1}$. The relation between $\ln (T_p/\beta)$ vs. $1/T_p$ is shown in Fig. 5(b) according to the following relation [16, 20]

$$\ln (T_p/\beta) = -E_c/RT_p - \ln K_0\,, \tag{7}$$

from the linear dependence, E_c was found to be equal to 123.69 kJ/mol and the frequency factor $K_0 = 1.02 \times 10^9\ \text{s}^{-1}$.

The area under the DSC curve is directly proportional to the total amount of alloy crystallized. The ratio between the coordinates and the total area of the peak gives the corresponding crystallization rates, which make it is possible plot the curves of the exothermal peaks Fig. 6. It is observed that, the $(dx/dt)_p$ values increases as well as the heating rate, a property which has been widely discussed in the Ref. [9, 21]. In order to form a large number of nuclei the material was reheated up to 470 K (a temperature slightly higher than T_g) for 1 h. It was ascertained by X-ray diffraction that, there is no crystalline peaks were detected after the nucleation treatment.

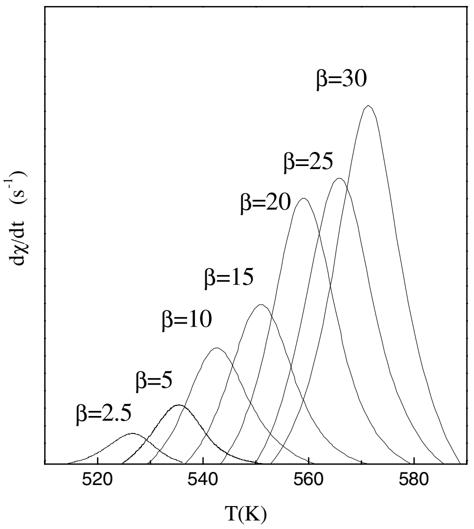

Fig. 6 Crystallization rate versus temperature of the exothermal peaks at different heating rates.

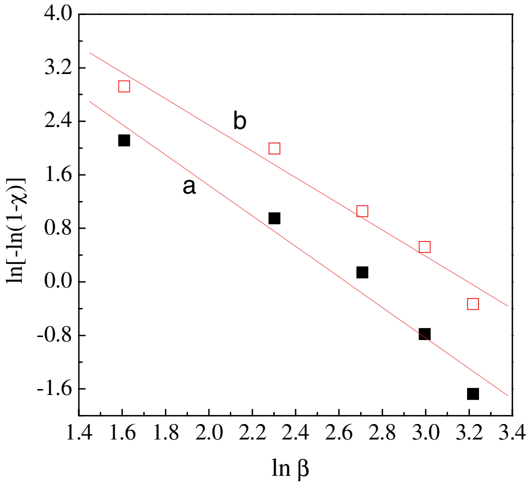

Fig. 7 (online colour at: www.pss-a.com) Variation of ln [–ln (1 – *x*)] with logarithm of heating rate (β in KS^{-1}), a) as quenched glass 560 K, and b) reheating glass 548 K.

For non-isothermal crystallization, the volume fraction χ of crystals precipitated in a glass heated at a uniform rate β is related to E_c by the expression [22, 23]

$$\ln\left[-\ln\left(1-\chi\right)\right] = -n \ln \beta - 1.052(mE_c/RT) + \text{const.} \tag{8}$$

where *m* and *n* are numerical factors depending on the mechanism of nucleation and growth. The plots of ln [–ln (1 – *x*)] versus ln β at different specific temperatures have been drawn, both for the as-quenched glass and the reheated glass. It has been observed that, the correlation coefficients of the corresponding straight regression lines show a maximum value for a given temperature, which was considered as the most adequate one for the calculation of parameter *n*. Figure 6 shows the relation between ln [–ln (1 – *x*)] and ln β for as-quenched glass at fixed temperature 560 K and reheated glass at 548 K. According to Eq. (8), the slopes of these lines give the *n*-values, and it was found that, $n = 2.27$ for the as-quenched glass and $n = 1.96$ for the reheated glass. Allowing for experimental error, both values are close to 2.

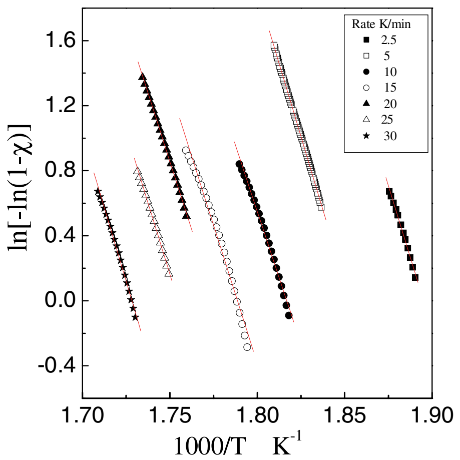

Fig. 8 (online colour at: www.pss-a.com) ln [–ln (1 – *x*)] versus 1/*T* plots calculated from the exothermic peaks at different heating rates for $Sb_{14.5}As_{29.5}Se_{53.5}Te_{2.5}$ glass.

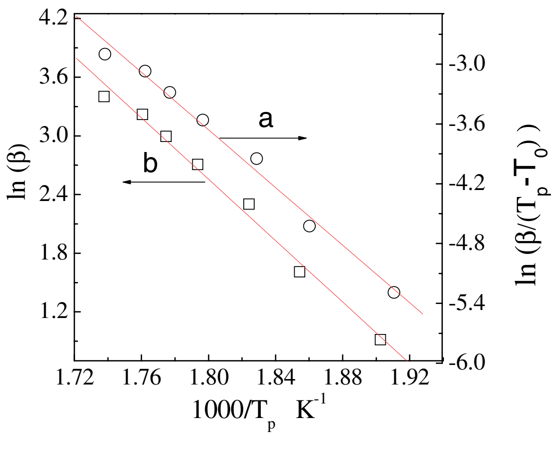

Fig. 9 (online colour at: www.pss-a.com) a) $\ln[\beta/(T_\mathrm{p}-T_0)]$ vs. $1000/T_\mathrm{p}$, b) $\ln(\beta)$ vs. $1000/T_\mathrm{p}$ for $Sb_{14.5}As_{29.5}Se_{53.5}Te_{2.5}$ glass.

This indicates that a large number of nuclei already exists in the material, therefore $m = n = 2$, that is, the crystal particles grow one-dimensionally.

On the other hand, Fig. 8 shows the plots of $\ln[-\ln(1-x)]$ versus $1/T$ for different heating rates (2.5 up to 30 K min^{-1}). From the slopes of these linear relations, the average value of the crystallization activation energy is 130.98 kJ/mol.

Finally, the crystallization activation energy, E_c, can be deduced using the formula suggested by Augis and Bennett [24] as follows

$$\ln[\beta/(T_\mathrm{p}-T_0)] = \ln K_0 - E_\mathrm{c}/RT_\mathrm{p}\,. \tag{9}$$

When $\ln[\beta/(T_\mathrm{p}-T_0)]$ is plotted versus $1/T_\mathrm{p}$ a straight line is obtained whose slope is E_c/R as shown in Fig. 9(a). The value of E_c for $Sb_{14.625}As_{29.5}Se_{53.623}Te_{2.5}$ glass calculated by using this method is 125.72 kJ/mol. For $T_\mathrm{p} \gg T_\mathrm{o}$, the slope of the linear relation between $\ln(\beta)$ versus $1/T_\mathrm{p}$ yields also the crystallization activation energy, E_c, Fig. 9(b). The calculated value of E_c by using this assumption is 130.5 kJ/mol.

4 Identification of the crystalline phases

Taking into account the crystallization exothermal peaks shown by the glassy alloy $Sb_{14.5}As_{30}Se_{53.5}Te_{2.5}$ it is recommended to try to identify the possible phases that crystallize during the thermal treatment applied to the samples by means of XRD. For this purpose, in Fig. 10(a) shows the absence of the peaks which are characteristic of the crystalline phases for the as quenched glass. The diffractogram of the transformed material after the crystallization process (Fig. 10(b)) suggests the presence of some crystal-

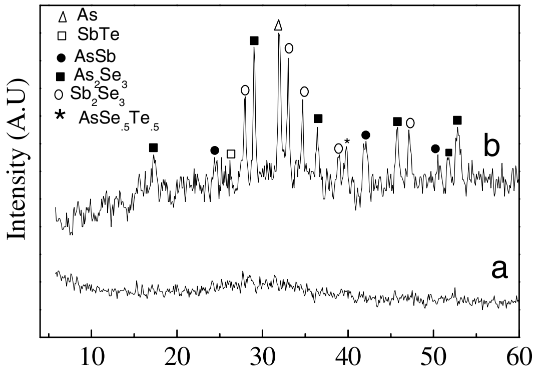

Fig. 10 Diffractogram of $Sb_{14.5}As_{29.5}Se_{53.5}Te_{2.5}$ glass a) as prepared b) after thermal treatment (annealing at T_p for 2 h).

lites of As, SbTe, AsSb, As_2Se_3, Sb_2Se_3 and $AsSe_5Te_5$ indicated with *d* and *I*, respectively, while there remains also a residual amorphous phase.

5 Conclusions

(1) Two approaches were used to analyze the glass transition. One is the linear dependence of the glass transition temperature T_g on the logarithm of the heating rate β. The other is the linear relationship between $\ln(T_g^2/\beta)$ and $1/T_g$.

(2) The numerical factors, *n* and *m* depend on the mechanism of nucleation, growth, and the dimensionality of the crystal. In addition, $n = m + 1$ for as quenched glass containing no nuclei while $n = m$ for a glass containing a sufficiently large number of nuclei. The kinetic parameters were deduced based on the mechanism of crystallization. The value of the kinetic exponent ($n = 2$) for the as quenched glass is consistent with the mechanism of volume nucleation with one dimensional growth.

(3) Finally, the identification of the crystalline phases reveals the existence of some crystallites of As, SbTe, AsSb, As_2Se_3, Sb_2Se_3 and $AsSe_5Te_5$ dispersed in the remaining amorphous matrix.

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