

Kinetics of Amorphous-Crystalline Transformation of Some Se-Te-In Chalcogenide Glasses Using Gao and Wang Model

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The present study reports the assessment of activation energy for crystallization and crystallization reaction order (Avrami exponent n) for the amorphous-crystallization transformation process of $\text{Se}_{85-x}\text{Te}_{15}\text{In}_x$ ($x = 2, 6$ and 10) amorphous alloys using differential scanning calorimetry (DSC) technique under non-isothermal conditions at four different heating rates (5, 10, 15 and 20 °C/min) through Gao and Wang model. The introduction of In to the Se-Te system is found to bring a change in crystallization mechanisms and dimensions of growth.

Keywords: Amorphous materials, DSC, Crystallization activation energy, Avrami exponent.

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1. INTRODUCTION

Chalcogenide glasses have recently emerged as multipurpose materials and have been drawn great attention because of their potential applications in various solid state devices. The physical properties of chalcogenide glasses, being amorphous semiconductors, have attracted much interest due to their wide range of technological applications. Threshold and memory switching are considered as one of the most important technological applications of chalcogenide glasses. It is thought for a long time that memory and threshold behavior of these materials is determined essentially by their crystallization ability. Glasses which do not exhibit a crystallization reaction above the glass transition are suitable for threshold type switches and the glasses which are easily crystallizable are useful in making memory type switches. Thus, crystallization studies may be useful in predicting the switching behavior (threshold or memory type) in chalcogenide glasses. Apart from the technological importance, the knowledge of the crystallization process is important for the better understanding of the short range order. It is difficult to erase a written spot in several hundred nanoseconds if the amorphous-crystalline (a-c) transformation rate of the recording material is not sufficiently high [1, 2]. For this reason, the study of crystallization rate and the factors that influence it are very important for the development of new kinds of erasable phase change (PC) optical materials. The activation energy being an important parameter since it indicates the thermal stability of the glass; its magnitude reflects the nature of transformation and it plays an important role in determining the utility of chalcogenide glasses as recording material [3].

A chalcogenide amorphous alloy results in to crystallization when heated at constant heating rate in DSC or differential thermal analysis (DTA) experiment. Thus, heating of an amorphous glass results into

crystallization phenomenon and studies of crystallization kinetics are always connected with the concept of activation energy. The activation energy in crystallization phenomenon is associated with nucleation and growth processes that dominate the devitrification of most glassy solids. In general, separate activation energies must be identified with individual nucleation and growth processes in a transformation, although they are usually combined into an activation energy representative of the overall crystallization process [4]. The study of crystallization kinetics in amorphous materials by DSC has been extensively discussed in the literature [5, 6].

A large majority of amorphous-crystallization (a-c) transformations are described by a process known as nucleation and growth. Nuclei of the new phase are first formed at a particular rate, followed by the growth of the new phase. The theoretical basis for interpreting the DSC of thermograms is provided by the formal theory developed by Johnson and Mehl [7] and Avrami [8] in which the volume crystallized fraction (χ) can be expressed as the function of time (t) according to the following relation:

$$\chi(t) = 1 - \exp[-(Kt)^n] \quad (1)$$

where $\chi(t)$ is the fraction of the first phase which has transformed into second phase in time t . For a-c transformations, $\chi(t)$ is known as the crystallized volume fraction, t is the time taken for the a-c transformation, n is the Avrami exponent that depends upon the growth mechanism and the dimensionality of the glassy alloy and K is defined as the reaction rate constant assumed to have Arrhenian temperature dependence:

$$K = K_o \exp\left(-\frac{E_c}{RT}\right) \quad (2)$$

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where E_c is the activation energy for the crystallization and K_0 is the frequency factor. Both n and K are useful parameters for kinetic studies. They can be used to explain the nucleation mechanism and rate.

DSC or DTA is a very useful tool for studying the kinetics of crystallization of glass as it is a rapid and convenient means. The appeal of these methods is because of their simplicity and flexibility in selecting heating/cooling rates. Moreover, DTA or DSC technique is on the whole important due to reason that it is easy to carry out, requires little sample preparation, quite sensitive and relatively independent of sample geometry.

In the calorimetric measurements, two basic methods can be used, isothermal and non-isothermal conditions. In the isothermal method, the sample is brought quickly to a temperature above the glass transition temperature (T_g) and the heat evolved during the crystallization process at a constant temperature is recorded as a function of time (t). In the non-isothermal method, the sample is heated from room temperature generally at a fixed heating rate (α) and heat evolved in this case is again recorded as a function of temperature or time. A disadvantage 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.

Due to above mentioned reason, in the present work also, the kinetics of crystallization process of $\text{Se}_{85-x}\text{Te}_{15}\text{In}_x$ ($x = 2, 6$ and 10) amorphous alloys by means of DSC technique under non-isothermal conditions has been discussed and reported through Gao and Wang model [9] with a view to understand nucleation and growth processes and to obtain kinetic parameters viz activation energy, Avrami exponent and rate constant for amorphous-crystallization (a-c) transformation.

The activation energy of crystallization is normally obtained using different theoretical models. The most widely used model is the JMA model for non-isothermal kinetics. This model implies that the Avrami exponent, n , and the activation energy, E_c , should be constant during the transformation process. Generally, the crystallization process is well characterized when the three kinetic parameters, activation energy of crystallization (E_c), Avrami exponent (n) and frequency factor (K_0) are determined. Gao and Wang [9] proposed a slightly different method to analyze DSC curves in terms of the activation energy (E_c), the dimensionality, the rate constant in atomic diffusion, the frequency factor K_0 etc, during the crystallization process. The equations are also derived from Johnson-Mehl-Avrami (JMA) transformation equation and show the relationship between the maximum crystallization rate and the crystallization peak temperature. A method suggested by Gao and Wang uses the following expression to determine the activation energy:

$$\ln\left(\frac{d\chi}{dt}\right)_{T_p} = -\frac{E_c}{RT_p} + \text{const.} \quad (3)$$

where $(d\chi/dt)_{T_p}$ is the rate of transformed volume frac-

tion at the peak of crystallization. To obtain the information about morphology of growth and Avrami exponent, the following relations of Gao and Wang model have been used:

$$K_p = \frac{\alpha E_c}{RT_p^2} \quad (4)$$

$$\left(\frac{d\chi}{dt}\right)_{T_p} = 0.37nK_p \quad (5)$$

where n is Avrami exponent, K_p is the reaction rate constant and other symbols have their usual meanings.

2. EXPERIMENTAL DETAILS

Glassy alloys of $\text{Se}_{85-x}\text{Te}_{15}\text{In}_x$ ($x = 2, 6$ and 10) are prepared using the melt quenching technique. $5N$ pure materials are weighed according to their atomic percentages and sealed in a quartz ampoule (length ~ 5 cm, diameter ~ 12 mm) under a vacuum of $\sim 2 \times 10^{-5}$ mbar. The sealed ampoules have been kept inside a furnace where the temperature is raised to 900°C at a rate of $3-4^\circ\text{C}/\text{min}$. The ampoules are rocked frequently for 10 h at maximum temperature to make the melt homogenous. The quenching is done in the ice cooled water very rapidly. The amorphous nature of the glassy alloys has been verified by X-ray diffraction.

The thermal behavior of the glasses is investigated using Mettler Toledo Star^e DSC system. The temperature accuracy of this equipment is $\pm 0.1^\circ\text{C}$. Approximately, 3-5 mg of sample in powder form is encapsulated in standard aluminum pan in an atmosphere of dry nitrogen at a flow of 40 mL/min and heated at different heating rates from $5-20^\circ\text{C}/\text{min}$ in the range $30-500^\circ\text{C}$. The temperature and enthalpy calibrations are checked with indium ($T_m = 156.6^\circ\text{C}$, $\Delta H_m = 28.55$ J/g) as the standard material.

The values of glass transition temperature (T_g), the peak temperature of crystallization (T_p) and the melting temperature (T_m) are determined by using the microprocessor of the thermal analyzer. Fig. 1 shows the DSC traces of $\text{Se}_{79}\text{Te}_{15}\text{In}_6$ at four different heating rates. Similar trends are also observed for other two samples. It is clear from Fig. 1 that well defined single endothermic and exothermic peaks are obtained at T_g and T_p respectively, which indicates that these glasses exist in single phase. The crystallized fraction (χ) at a given temperature has been calculated using partial area analysis. The crystallized fraction (χ) at a given temperature is given as $\chi = (A_T/A)$, where A is the total area of the exothermic peak between the initial temperature (T_i) where crystallization just begins and the temperature (T_f) where the crystallization is completed. A_T is the area between T_i and T . A best fit for the results is calculated by the least square fitting method for the activation energies.

3. RESULTS AND DISCUSSION

3.1 Activation Energy (E_c)

The activation energy of crystallization can be evaluated by taking the variation of $\ln(d\chi/dt)_{T_p}$ against $1/T_p$

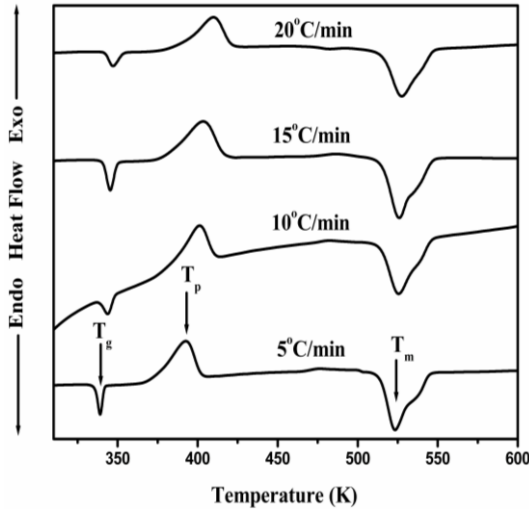


Fig. 1 – DSC plots for $Se_{79}Te_{15}In_6$ at different heating rates

using Eq. (3), whose slope gives the value of E_c/R . The calculated values of E_c using Gao and Wang model for all studied $Se_{85-x}Te_{15}In_x$ samples are listed in Table 1. Fig. 2 shows the variation of $\ln(d\chi/dt)_{T_p}$ against $1/T_p$ for $Se_{79}Te_{15}In_6$. Similar straight line plots have also been observed for other investigated samples. E_c is found to increase with the increase in indium content.

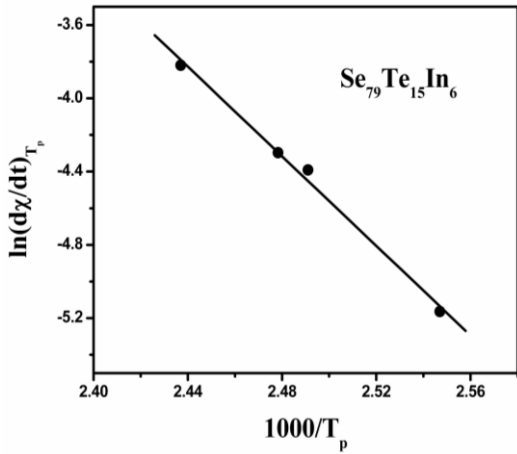


Fig. 2 – $\ln(d\chi/dt)_{T_p}$ versus $1000/T_p$ plot for $Se_{79}Te_{15}In_6$ chalcogenide glass

Moreover, this equation has successfully predicted that the maximum rate of crystallization in DSC increases by the same factor as the heating rate does. Fig. 3 shows the plot of $(d\chi/dt)$ against temperature T at different heating rates for glassy $Se_{75}Te_{15}In_{10}$ alloy. It is clear from Fig. 3 that the peak height increases and shifts towards higher temperature values with the increase in heating rate. This is due to the fact that as the heating rate is increased from 5 to 20°C/min, the rate of crystallization increases and crystallization shifts towards higher temperatures hence, the peak shifts towards higher temperature values. On the other hand, we can say that with this increased rate of crystallization, a greater volume fraction is crystallized in a smaller time as compare to the lower heating rate, which further signifies the increased peak height with increase in heating rate in these curves. The observed

increase in $(d\chi/dt)_{T_p}$ values as the heating rate does has been widely discussed in the literature [9-11].

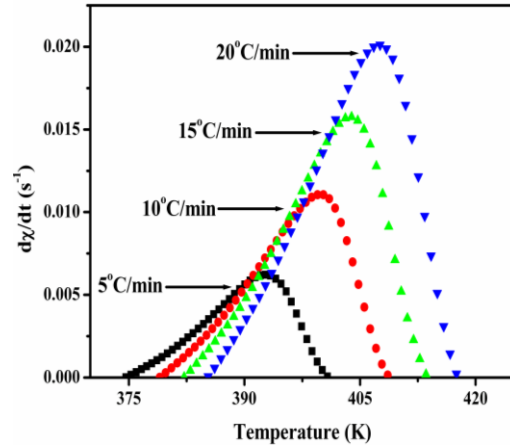


Fig. 3 – Crystallization rate versus temperature of the exothermic peaks at four different heating rates for glassy $Se_{75}Te_{15}In_{10}$ alloy

3.2 Crystallization Reaction Order (n)

The Gao and Wang model is also used to evaluate the Avrami exponent and the values of Avrami exponent using Eq. (5) are listed in Table 1. The values of Avrami exponent using Gao and Wang model are in good agreement with that obtained from Matusita’s method [5]. Mahadevan et al [12] have shown that n may be 4, 3, 2 or 1, which are related to different crystallization mechanisms: $n = 4$, volume nucleation with three-dimensional growth; $n = 3$, volume nucleation with two-dimensional growth; $n = 2$, volume nucleation with one-dimensional growth; $n = 1$, surface nucleation, one-dimensional growth from surface to inside. The calculated values of n are not integers; this means that the crystallization occurs with different mechanisms. From the value of n , it is possible to postulate a crystallization mechanism for the investigated alloys. The average values of the kinetic exponent n show predominantly one-dimensional growth for $Se_{83}Te_{15}In_2$ and $Se_{75}Te_{15}In_{10}$ while two-dimensional growth for $Se_{79}Te_{15}In_6$.

Table 1 – Values of n , K_p , K_0 and effective crystallization activation energy E_c (kJ/mol)

Composition	E_c	n	K_p	K_0
$Se_{83}Te_{15}In_2$	96.14	1.80	0.90	3.54×10^{12}
$Se_{79}Te_{15}In_6$	101.64	2.35	0.93	1.37×10^{13}
$Se_{75}Te_{15}In_{10}$	107.56	2.21	0.99	9.28×10^{13}

3.3 Rate Constant (K_p)

Rate constant at maximum crystallization rate K_p has been evaluated using Eq. (4). It is observed that there is increase in K_p as the In content increases from 2 at. % to 6 and 10 at. % (Table 1). Moreover, a similar trend is also confirmed by the frequency factor (which measures the probability of molecular collisions effective for the formation of the activated complexes in

each case) as the In content increases to 6 and 10 at. % (Table 1). This indicates that the lower concentration indium additive sample ($\text{Se}_{83}\text{Te}_{15}\text{In}_2$) have a higher crystallization tendency as compare to the composition with In = 6 and 10 at. % in the composition range under investigation.

4. CONCLUSIONS

Kinetics of amorphous-crystallization transformation in $\text{Se}_{85-x}\text{Te}_{15}\text{In}_x$ ($x = 2, 6$ and 10) glassy alloys using Gao and Wang model have been reported and

discussed. From the heating rate dependence, the kinetic parameters; the activation energy for the crystallization process, Avrami exponent and rate constant have been deduced and found to be composition dependent. The average value of Avrami index for $x \approx 2$ and 10 indicates the existence of volume nucleation with one-dimensional growth while for $x = 6$, the Avrami index indicates the two-dimensional growth with volume nucleation. Thus, the introduction of indium to the Se-Te system brings about a change in crystallization mechanisms and dimensions of growth.

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