

CRYSTALLIZATION KINETICS OF THE $\text{Se}_{80}\text{Te}_{15}\text{Sb}_5$ GLASS

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Bulk $\text{Se}_{80}\text{Te}_{15}\text{Sb}_5$ glass was prepared using the melt-quench technique. Differential thermal analysis (DTA) curves measured at different heat rates ($5 \text{ K/min} \leq \alpha \leq 40 \text{ K/min}$) and X-ray diffractograms (XRD) are used to characterize the as-quenched glass. The normalized function $z(x)$ has been used as a criterion check whether the JMA model can be or can not be applied for the isochronal crystallization kinetics. The $z(x)$ function attains its maximum limit when x_m lies in the $0.36 \leq x_m \leq 0.46$ range. This range of x_m confirms that the JMA model can not be applied for the isochronal crystallization kinetics of the investigated alloy. The Avrami exponent (n) and the activation energy for crystallization (E_c) of the $\text{Se}_{80}\text{Te}_{15}\text{Sb}_5$ composition are equal 3 and $71.2 \pm 0.6 \text{ kJ/mol}$, respectively. The n -value indicates that only one crystallization (bulk) mechanism can be responsible for the amorphous-crystalline transformations inside the studied glass. Comparing the present isochronal kinetics with those previously reported for the binary $\text{Se}_{80}\text{Te}_{20}$ glass, implies that inserting 5 at. % of Sb on the expense of Te atoms decreases the E_c -value from 105 kJ/mol to 71.2 kJ/mol and increases the Avrami exponent from $n = 2$ up to $n = 3$. The latter n -value means that the mechanism of volume nucleation with two dimensional growth is responsible for the amorphous-crystalline transformations inside the investigated glass.

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1. Introduction

Chalcogenide glasses have gained considerable attention because they combine the characteristic features of the disordered systems in addition to some properties of the crystalline semiconductors. Amorphous to crystalline transformations are used for recording and deleting information in the above mentioned glasses [1]. Thermal analysis (TA) methods such as DTA or DSC are quite popular for crystallization kinetics analysis of amorphous alloys. The crystallization behavior of a glass is necessary to determine the suitable operating temperatures range for a specific technological application. An aspect of considerable importance to kinetic analysis is the determination of the kinetics parameters that reflect the crystallization behaviors. A process which is clearly understood when determining the following three parameters: the Avrami exponent (n), the activation energy of crystallization (E_c) and the frequency factor (K_0). These crystallization kinetics can be deduced using the isothermal or non-isothermal (isochronal) methods. The latter technique has become popular for determination of the crystallization kinetics and thermal stability of the amorphous alloys [2].

Despite being close neighbors on the Periodic Table and having similar electronic structure, Se and Te are totally opposite in terms of their ability to form glassy materials [3–5]. Se based glass are intrinsically good glass formers but are limited in transparency in the long wavelength regime. Te glasses on the other hand are poor glass formers but possess very large

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optical windows. Therefore, an alloy containing Se and Te elements can lead to a good balance between the required properties but ultimately, the low phonons intrinsic to Se vibrations limit the optical window, or the metallic nature of Te limits the glass formation ability. Indeed, Se–Te based alloys are promising materials for many electronic devices using amorphous-crystalline transformations. It was found that [6] the corrosion stability of the Se-Te alloy is much improved in compare with that of the constituent elements. The effect of Sb addition on the crystallization kinetics of the binary Se-Te glasses was studied by Mehra et al. [7]. From the compositional dependence of the glass transition temperature, they found that a small amount of Sb (≤ 4 at %) leads to an increase in the chain length of Se-Te, whereas further increase in Sb content increases the number of Se-Te chains in the alloys.

In the present work, the differential thermal analyses (DTA) of the $\text{Se}_{80}\text{Te}_{15}\text{Sb}_5$ glass are obtained. However, the discussion of the obtained data will be focused only on the crystallization peak in order to specify the crystallization mechanism responsible for the amorphous-crystalline transformations inside the studied glass.

2. Materials and Methods

Bulk $\text{Se}_{80}\text{Te}_{15}\text{Sb}_5$ glass was prepared using the well-known melt-quench technique. High-purity (5N) Se, Te and Sb elements are weighed in atomic proportions and sealed in evacuated (10^{-5} Torr) quartz ampoule. The sealed ampoules are inserted into a controlled programmable Muffle furnace and heated with constant rate of ~ 4 K/min up to 1200 K. The furnace temperature is fixed at the maximum value for 12 h with frequent rocking to ensure homogeneity of the melt. The ampoules are subsequently quenched in iced water to obtain the glass. X-ray diffractometer (Philips Model PW 1710) was employed to check the amorphous state of the quenched material. Copper target was used as a source of x-rays with $\lambda = 1.5418 \text{ \AA}$ ($\text{CuK}\alpha$). The scanning angle (2θ) was varied in the range of $4\text{--}110^\circ$.

Thermal investigation of the quenched glass was made using a Shimadzu differential thermal analysis (DTA) with detector DTG-60H. Thermograms are recorded as the temperature of the sample is increased uniformly up to 450°C using different heating rates ($5 \leq \alpha \leq 40^\circ\text{C}/\text{min}$). The characteristic temperatures of the investigated glasses are determined with precision ± 0.1 K using the microprocessor of thermal analyzer. A best fit of the results is made using the least-square method. Then, the arithmetic means as well as the standard deviations are used for calculation of the crystallization kinetics of the investigated alloys.

3. Results and Discussion

Typical DTA trace of the $\text{Se}_{80}\text{Te}_{15}\text{Sb}_5$ specimen heated at constant rate of $15^\circ\text{C}/\text{min}$ is shown in Fig. 1. Before reaching the glass melting point, three characteristic temperatures are clear in the studied temperatures range. The first one corresponds to the glass transition temperature (T_g), the second to the on-set temperature of crystallization (T_o) and the third one is referred to the peak temperature of crystallization (T_p) of the investigated glass. The small difference of ($T_o - T_g$), as shown in Fig. 1, means that the studied composition has low glass rigidity. But still, its thermal attitude looks like that of the most of the chalcogenide glasses.

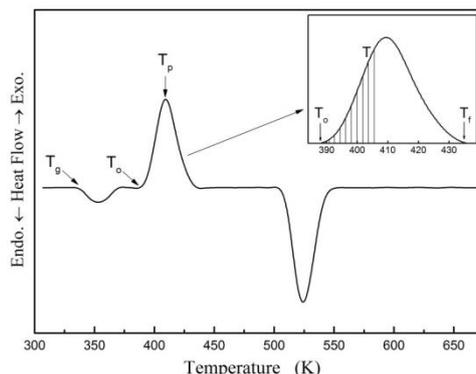


Fig. 1. Typical DTA curve of the $Se_{80}Te_{15}Sb_5$ glass measured at a heating rate of 15 K/min.

The crystallization kinetics of amorphous alloys has been extensively studied in past using the classical Johnson - Mehl - Avrami (JMA) theoretical model [8-10] in which the crystallization fraction (x) can be described as a function of time (t) according to the following formula:

$$x(t) = 1 - \exp[-(Kt)^n] \quad (6)$$

where the factor n (called as Avrami exponent) depends on the nucleation and growth behaviors, and K is a reaction rate constant.

The JMA equation was first derived for transformations under isothermal annealing conditions and even its applicability is restricted to certain assumptions [11-13]. Henderson has pointed out that the validity of the JMA equation can be applied under non-isothermal (isochronal) conditions if the entire nucleation behavior completes at the early stage of the transformation, and it becomes negligible afterwards [11,12]. Thus, the crystallization rate is defined only by temperature and does not depend on the previous thermal history. Based on JMA model, different authors have developed diverse methods to study the amorphous-crystallization transformations inside the glasses.

3.1 Kissinger's Relation

According to Kissinger's formula [14], the peak temperature of crystallization (T_p) depends on the heating rate (α) as follows,

$$\ln\left(\frac{\alpha}{T_p^2}\right) = -E_c/RT_p + \text{constant} \quad (1)$$

Where E_c is the activation energy of crystallization. This equation is used to calculate the activation energy of crystallization from the $\ln\left(\frac{\alpha}{T_p^2}\right)$ versus $10^3/T_p$ plot. The E_c -value, calculated from slope the straight line shown in Fig. (2) and listed in Table (1), of the investigated $Se_{80}Te_{15}Sb_5$ glass equals 67.8 ± 2.9 kJ/mol.

3.2 Augis and Bennett's Approximations

The activation energy of crystallization can also be determined by an approximation method developed by Augis and Bennett [15]. The relation imposed by them has the form

$$\ln(\alpha/T_p) = -(E_c/RT_p) + \ln K_o \quad (2)$$

According to the above equation, the E_c -value can be evaluated from slope of the $\ln(\alpha/T_p)$ against $10^3/T_p$ curve, see the straight line shown in Fig.(2). The E_c -value of the investigated glass, given from Fig. (2) and listed in Table (1), equals 71.2 ± 2.9 kJ/mol.

3.3 Matusita and Sakka's Theory

The extent of crystallization (x) at different (T) is well expressed by the expression

$$\ln(1-x)^{-1} = \left(\frac{c}{\alpha^n}\right) \left(-\frac{nE_c}{RT}\right) \quad (3)$$

For constant temperature, this equation can be written as follows

$$\ln[-\ln(1-x)] = n \ln\alpha + \text{constant} \quad (4)$$

From the above equation, the n -exponent can be calculated by plotting $\ln[-\ln(1-x)]$ versus $\ln\alpha$ curves at different temperatures. The last expression was derived by Matusita and Sakka [16] from the classical JMA equation. Since the value of x are independent of x at $T=T_p$, equation (4) takes the form

$$\ln\alpha = -E_c/RT_p + \text{constant} \quad (5)$$

From slope of the straight $\ln\alpha$ versus $10^3/T_p$ plots, shown in Fig. (2), the activation energy of crystallization is listed in Table (1) and equal to 74.6 ± 2.9 kJ/mol.

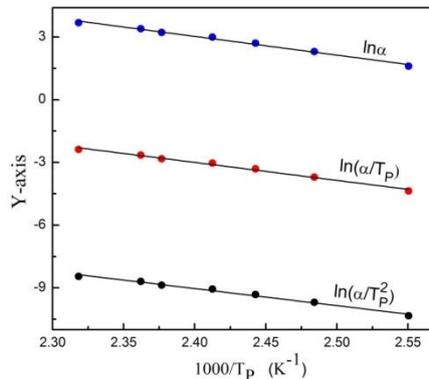


Fig. 2. Three different curves: $\ln(\frac{\alpha}{T_p^2})$ versus $10^3/T_p$, $\ln(\frac{\alpha}{T_p})$ versus $10^3/T_p$ and $\ln\alpha$ versus $10^3/T_p$ plots for the investigated $Se_{80}Te_{15}Sb_5$ glass.

The crystallization fraction (x) has been determined using the partial area technique [17]. The fraction x crystallized at any temperature T is given by $x = (A_T/A)$ at non-isothermal conditions. Here A is the total area of the exothermic peak between temperature T_o on which the crystallization just begins and the temperature T_f at which the crystallization is completed. The hatched portion which represents the partial area (A_T) of the exothermic peak between the temperatures T_o and T , see inset of Fig. (1), can be calculated. Considering all points (temperatures) located inside the exothermic peak, the crystallized fractions as a function of temperature, $x(T)$, are shown in Fig. (3). From this figure, one can calculate $\ln[-\ln(1-x)]$ versus $(10^3/T)$ relations for the x -data lie in the range $15 \leq x \leq 85$ %. These isochronal plots are shown at different heating rates in Fig. 4. The resulting plots are obviously non-linear, suggesting that the JMA model is not valid to the isochronal crystallization kinetics. Certainly, the non-linearity behaviors of the obtained curves could yield inaccurate crystallization parameters.

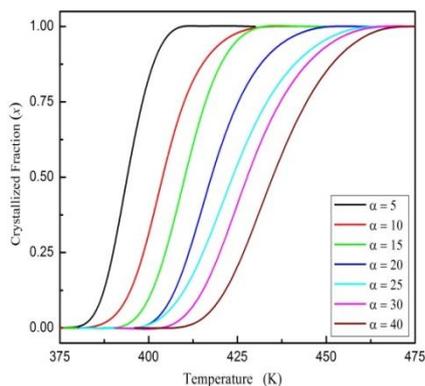


Fig. 3. Temperature dependence of the crystallized fraction (x) of the studied $Se_{80}Te_{15}Sb_5$ glass at different heating rates.

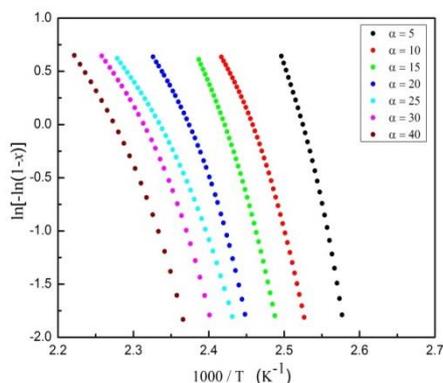


Fig. 4. $\ln[-\ln(1-x)]$ versus $10^3/T$ plots for the $Se_{80}Te_{15}Sb_5$ glass at different heating rates.

In a similar trend, the most popular testing method for isothermal DTA data is an inspection of the linearity of JMA plot $\ln[-\ln(1-x)]$ versus $\ln(t)$. In some cases, the JMA plots show straight lines, but the crystallization kinetics cannot be modeled by JMA equation. Thus, a more practical and reliable test method is needed. A normalized function $z(x)$ was derived to verify the validity of the JMA equation [18]. The check is mainly depending on the value of the crystallized fraction (x_m) at which the function $z(x)$ attains a maximum value. If the values of x_m , giving maximum $z(x)$ function, are almost near 0.632, indicate that the crystallization kinetics can be modeled by JMA equation. However, when the x_m -values are far from the above mentioned one, it implies that JMA model is not valid for the studied crystallization kinetics. According to [17], the normalized function $z(x)$ can be written as

$$z(x) = \Delta H_c K f(x) \tag{7}$$

where $f(x) = n(1-x)[-\ln(1-x)]^{(n-1)/n}$ and K is a reaction rate constant which given by

$$K = K_o \exp(-E_c/RT) \tag{8}$$

where K_o is the pre-exponential coefficient of the effective overall reaction rate and E_c is the effective activation energy describing the overall crystallization process. Figure (5) shows the variation of the normalized $z(x)$ function against the crystallized fraction at different heating rates. It is clear from the above figure that the normalized function attains its maximum limit in the crystalline fraction $0.36 \leq x_m \leq 0.46$ range. It was found previously [18] that the values of x_m , at different isothermal annealing temperatures, are almost constant equal 0.632, which means that the

crystallization process can be modeled by JMA equation. Accordingly, JMA model can not be applied for the isochronal crystallization kinetics of the investigated $\text{Se}_{80}\text{Te}_{15}\text{Sb}_5$ glass.

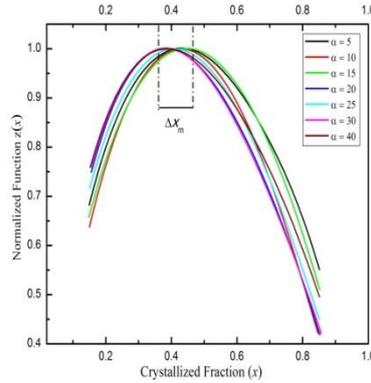


Fig. 5. Variation of the normalized function $z(x)$ with the crystallized fraction (x) of the investigated $\text{Se}_{80}\text{Te}_{15}\text{Sb}_5$ glass at different heating rates.

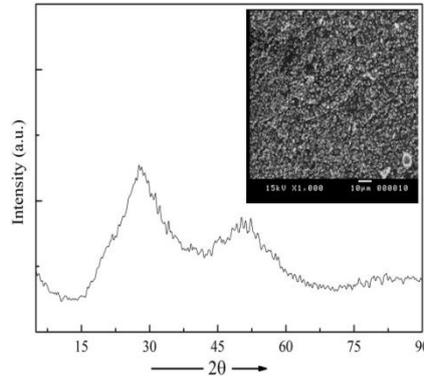


Fig. 6. X-ray diffractogram and Scanning electron micrograph of the the $\text{Se}_{80}\text{Te}_{15}\text{Sb}_5$ glass.

Because of the non-applicability of the JMA model to the crystallization kinetics of the isochronal process, it is necessary to look for some different models which can be appropriate for that type of transformations. Therefore, the thermal kinetics will be obtained using the method specifically suggested by Matusita et al. [19] for non-isothermal conditions. Accordingly, the dependence of the volume fraction of crystals (x) on the crystallization kinetics is given by the expression,

$$\ln[-\ln(1-x)] = -n\ln\alpha - 1.052 \frac{mE_c}{RT} + \text{constant} \quad (9)$$

where n , as defined before, is the Avrami exponent and m another constant which is related in somehow to the exponent n . When the nuclei formed during heating at constant rate are dominate, n is equal to $(m+1)$ and when nuclei formed during any previous heat treatment prior to thermal analysis are dominate, n is equal to m [14,20]. The appearance of tiny peaks in the x-ray diffractogram of the as-prepared alloys, shown in Fig. (6), means that the crystallization nuclei are present prior to DTA process which confirm that the numerical factors n and m are equal. Based on eqn.(9) and at a constant T , $\ln[-\ln(1-x)]$ increases linearly with increasing heating rate of the investigated specimen. Fig. (7) shows straight $\ln[-\ln(1-x)]$ versus $\ln\alpha$ lines, taken at two fixed temperatures, for the investigated glass. From the slopes of the straight lines, one can determine the n -value of the studied specimen. Integer Avrami exponent ($n \approx 3$) indicates that only one mechanism is responsible for the amorphous-crystalline transformations inside the $\text{Se}_{80}\text{Te}_{15}\text{Sb}_5$

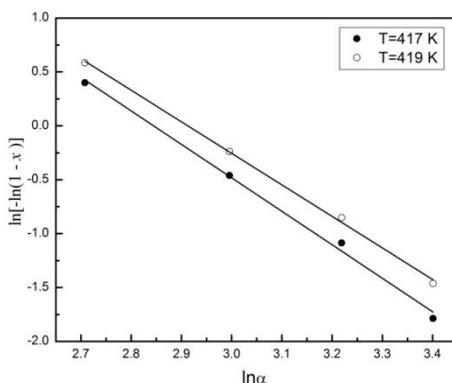


Fig. 7 $\ln[-\ln(1-x)]$ versus $\ln \alpha$ plots for the $\text{Se}_{80}\text{Te}_{15}\text{Sb}_5$ glass at two different temperatures.

glass. It is important to compare the crystallization kinetics of the present results with those previously reported [21] for the $\text{Se}_{80}\text{Te}_{20}$ glass. A comparison which may lead to the role of inserting 5 at.% of Sb instead of Te atoms. For example, inserting 5 at.% of Sb instead of Te atoms reduces the activation energy of crystallization from 105 kJ/mol to 71.2 kJ/mol in case of the present alloy. On the other way, the Avrami exponent equals 3 for the ternary sample while equals 2 for the binary glass.

4. Conclusions

The present results of the differential thermal analyses (DTA) and X-ray diffraction have confirmed the high quality of the as-quenched $\text{Se}_{80}\text{Te}_{15}\text{Sb}_5$ glass. The normalized function $z(x)$ has been used as a criterion to check whether the JMA model can be or can not be applied for the isochronal crystallization kinetics. It is found that the values of x_m lie in the range $0.36 \leq x_m \leq 0.46$ at different heating rates. This range of x_m confirms that the JMA model can not be applied for the isochronal crystallization kinetics of the investigated alloy. The present values of the Avrami exponent (n) and the activation energy for crystallization (E_c) of the $\text{Se}_{80}\text{Te}_{15}\text{Sb}_5$ composition are equal 3 and 71.2 ± 0.6 kJ/mol, respectively. Comparing the isochronal kinetics of the present $\text{Se}_{80}\text{Te}_{15}\text{Sb}_5$ alloy with those previously reported for the binary $\text{Se}_{80}\text{Te}_{20}$ glass, implies that addition of Sb content at the expense of Te atoms decreases the E_c -value from 105 kJ/mol to 71.2 kJ/mol and increases the Avrami exponent (n) from 2 up to 3. The latter n -value means that the mechanism of volume nucleation with two dimensional growth is responsible for the amorphous-crystalline transformations inside the investigated glass. In order to get the crystallization kinetics reported in the present article, one should purchase the Se, Te, and Sb elements with high grade quality. The quenching rate of the molten solution represents a very important factor to control the crystallization kinetics of the investigated glasses. Post-heat treatments of the quenched alloys also introduce significant changes in the thermal characteristics of the studied alloys.

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