Kinetic Analysis of Crystallization Process in Amorphous $\text{Se}_{90-x}\text{Te}_{10}\text{Pb}_x$ Glasses

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The crystallization process of $\text{Se}_{90-x}\text{Te}_{10}\text{Pb}_x$ (where $x = 2.5, 5, 7.5$ and 15 at%) glassy system was studied by differential thermal analysis (DTA) technique under non-isothermal conditions. The crystallization parameters were calculated using different kinetic models. The validity of the Johnson-Mehl-Avrami (JMA) model to describe the crystallization process for the studied compositions was discussed. The results showed that the two-parameter Sestak-Berggren (SB) is the most suitable for quantitative description of the crystallization process for the studied compositions. The results show more complicated crystallization process involving nucleation and growth. The increasing of the Pb content in the Se-Te-Pb system leads to a more complex and accelerated process. The crystalline phases were identified by using x-ray diffraction technique (XRD) and scanning electron microscopy (SEM). [doi:10.2320/matertrans.MC200927]

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1. Introduction

The structural studies of the chalcogenide glasses are very important for better understanding of the transport mechanisms, thermal stability and practical applications.¹⁾ The selection of Selenium is because of its wide commercial applications. It also exhibits a unique property of reversible transformation.²⁾ But its pure state has disadvantages because of the short lifetime and low sensitivity. To overcome these difficulties, Tellurium is used as an additive. The addition of a third element to Se-Te system will create compositional and configurational disorder with respect to the binary system.³⁾

It has been pointed out that the incorporation of Pb element in Se-Te system increases the density of localized states around Fermi level.⁴⁾ Thermal, electrical and optical properties of Se-Te-Pb chalcogenide glasses have been studied by many workers.⁵⁻⁹⁾ Kinetic analysis of crystallization process of Se-Te-Pb glasses are not well covered in literature, from this point of view, the crystallization kinetics taking place under non-isothermal conditions in the Se-Te-Pb glasses is in the center of interest.

The non-isothermal crystallization kinetics of many glassy systems were described by the Johnson-Mehl-Avrami (JMA) nucleation growth model¹⁰⁻¹²⁾ or by the empirical Sestak-Berggren SB(M, N) model.^{13,14)} Generally, the measured heat flow ϕ can be described by the kinetic equation

$$\phi = \Delta H A \exp\left(\frac{-E_c}{RT}\right) f(\alpha) \quad (1)$$

where ΔH is the crystallization enthalpy, A is the pre-exponential factor, E_c is the apparent activation energy, R is the universal gas constant and T is the temperature. The function $f(\alpha)$ is an analytical expression of the kinetic model. For the JMA model, this function is defined as

$$f(\alpha) = n(1 - \alpha)[- \ln(1 - \alpha)]^{1-\frac{1}{n}} \quad (2)$$

where α is the crystallization fraction and n is the kinetic exponent. On the other hand, for the SB(M, N) model the function $f(\alpha)$ is described by^{13,14)}

$$f(\alpha) = \alpha^M (1 - \alpha)^N \quad (3)$$

The values of M and N are characters for a particular crystallization process. The value of M is limited to the interval (0,1). Malek¹⁵⁾ proposed a simple method to test the applicability of the JMA model to describe the crystallization mechanism under non-isothermal conditions using two functions, $y(\alpha)$ and $z(\alpha)$, given by¹⁶⁾

$$y(\alpha) = \phi \exp(E_c/RT) \quad (4)$$

$$z(\alpha) = \phi T^2 \quad (5)$$

The functions $y(\alpha)$ and $z(\alpha)$ are then normalized within the range (0,1). These functions exhibit maxima at α_M and α_P^∞ , respectively. The maximum of $y(\alpha)$ function for the JMA model depends on the value of the kinetic exponent:

$$\alpha_M = 0 \quad \text{for } n \leq 1$$

$$\alpha_M = 1 - \exp(n^{-1} - 1) \quad \text{for } n > 1 \quad (6)$$

The value of α_M is always lower than the maximum of the $z(\alpha)$ function α_P^∞ . The later is a constant for the JMA model

$$\alpha_P^\infty = 0.632 \quad (7)$$

This value is a characteristic fingerprint of the JMA model.¹⁵⁾ Detailed information about $y(\alpha)$, $z(\alpha)$ and their maxima at α_M and α_P^∞ are described in elsewhere.^{15,16)}

The present work is concerned with the study of the crystallization kinetics and deduce the crystallization parameters for $\text{Se}_{90-x}\text{Te}_{10}\text{Pb}_x$ (where $x = 2.5, 5, 7.5$ and 15 at%) glasses by using Differential thermal analysis (DTA) under non-isothermal conditions. The effect of composition on the crystallization mechanism has to be discussed by different kinetic models.

2. Experimental Technique

The bulk materials of $\text{Se}_{90-x}\text{Te}_{10}\text{Pb}_x$ (where $x = 2.5,$

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Fig. 1 A typical DTA thermo-gram at heating rate 20 K/min for $\text{Se}_{90-x}\text{Te}_{10}\text{Pb}_x$ chalcogenide glasses, where T_g is the glass transition temperature, T_c is the onset crystallization temperature, T_p is the peak crystallization temperature and T_m is the melting temperature.

5, 7.5 and 15 at%) were prepared by the usual melt quenching technique. The high pure materials (99.999%) were weighted according to their percentages and sealed in evacuated silica tubes then heated at 950°C for 20 h. During the melt, the tube was frequently rocked to intermix the constituents and to increase the homogenization of the melt. This treatment was followed by fast quenching in ice–water mixture. The glassy nature of the as-prepared as well as the crystalline phase structures for annealed samples was identified using a Philips diffractometer type 1710. DTA experiments were carried out on the as-prepared powder samples by using a Perkin-Elmer DTG-60 under non-isothermal conditions. The values of the glass transition temperature (T_g), the onset crystallization temperature (T_c), the peak crystallization temperature (T_p) and the melting temperature (T_m) were determined with accuracy ± 1 K using the microprocessor of the thermal analyzer. The surface microstructures of the annealed Se-Te-Pb samples were examined using scanning electron microscopy (SEM) type JEOL JSM-T200.

3. Results and Discussion

DTA experiments were performed at different heating rates to investigate the crystallization kinetics of $\text{Se}_{90-x}\text{Te}_{10}\text{Pb}_x$ (where $x = 2.5, 5, 7.5$ and 15 at%). A typical DTA thermogram at heating rate 20 K/min. for $\text{Se}_{90-x}\text{Te}_{10}\text{Pb}_x$ chalcogenide glasses in the temperature range from room temperature to a complete crystallization or even melting temperature are shown in Fig. 1. Two types of crystallization behavior were observed depending on the glass composition. A simple exothermic peak was noticed for the three composition where ($x = 2.5, 5$ and 7.5 at%), while two exothermic peaks appeared for the composition where $x = 15$ as shown in Fig. 1.

The crystalline phase structure of the samples annealed at 385 K for 2 h for all the studied compositions were identified from the XRD patterns shown in Fig. 2(a). The analysis of the XRD patterns for all annealed samples show that the dominant crystalline phase is SePb with cubic crystal structure and lattice parameter $a = 0.61213$ nm according

(a)

(b)

Fig. 2 (a) XRD patterns of the powder samples annealed at 385 K for 2 h. (i) $\text{Se}_{87.5}\text{Te}_{10}\text{Pb}_{2.5}$, (ii) $\text{Se}_{85}\text{Te}_{10}\text{Pb}_5$, (iii) $\text{Se}_{82.5}\text{Te}_{10}\text{Pb}_{7.5}$ and (iv) $\text{Se}_{75}\text{Te}_{10}\text{Pb}_{15}$ (b) Composition dependence of the average particle size for the annealed samples at 385 K for 2 h.

to the ICDS data.¹⁷⁾ The average particle size (D) of the annealed samples was calculated from the XRD patterns according to Scherrer's equation¹⁸⁾

$$D = \frac{k\lambda}{B \cos \theta} \quad (8)$$

Where, k is a constant approximated to unity, its value is related to both the particle shape, θ is the diffraction angle, λ is the wavelength and B is the width at half maximum intensity of the powder reflection peak. The calculated D values using eq. (8) for the annealed samples are shown in Fig. 2(b). It's evident that, the average particle size of the crystallized SePb phase decreases with increasing Pb content.

Figure 3(a)–(d) shows the surface morphology for the studied annealed samples. The surface morphology of the annealed $\text{Se}_{87.5}\text{Te}_{10}\text{Pb}_{2.5}$ sample is shown in Fig. 3(a). It's clear that the crystalline phase embedded in amorphous matrix. In general, further increase of Pb in the the Se-Te-Pb system reveals that the amount of the transformed crystalline phase increases and the crystallized particles decrease in size. These results are in good agreement with the results obtained from the XRD.

Fig. 3 SEM micrographs showing the surface microstructure of the samples annealed at 385 K for 2 h (a) $\text{Se}_{87.5}\text{Te}_{10}\text{Pb}_{2.5}$, (b) $\text{Se}_{85}\text{Te}_{10}\text{Pb}_5$, (c) $\text{Se}_{82.5}\text{Te}_{10}\text{Pb}_{7.5}$ and (d) $\text{Se}_{75}\text{Te}_{10}\text{Pb}_{15}$.

Table 1 The values of T_g , T_c , T_p , T_m , $T_c - T_g$ and K_g for the studied compositions at a heating rate of 20 k/min.

Composition	T_g/K	T_c/K	T_p/K	T_m/K	$T_c - T_g/\text{K}$	K_g
$\text{Se}_{87.5}\text{Te}_{10}\text{Pb}_{2.5}$	335.9	395.0	426.8	516.5	59.1	0.49
$\text{Se}_{85}\text{Te}_{10}\text{Pb}_5$	333.3	388.4	408.6	513.6	55.2	0.44
$\text{Se}_{82.5}\text{Te}_{10}\text{Pb}_{7.5}$	332.8	389.3	410.9	512.6	56.5	0.46
$\text{Se}_{75}\text{Te}_{10}\text{Pb}_{15}$	334.2	364.5	377.5	517.1	30.2	0.20

4. The Glass Transition Region

The glass transition region has been studied in terms of the change in T_g with composition and heating rates. The variation of T_g with composition for $\text{Se}_{90-x}\text{Te}_{10}\text{Pb}_x$ ($x = 2.5, 5, 7.5$ and $15\text{at}\%$) is shown in Table 1. It's observed that there is a small decrease in T_g with increasing Pb content.

The compositional dependence of T_g , T_c , T_p , T_m and $T_c - T_g$ values are listed in Table 1 at a heating rate 20 K/min. The composition dependence of T_c values for these glasses is similar to the dependence of T_p values, which decreases with increasing Pb concentration. Both T_c and $T_c - T_g$ values decrease with increasing Pb content, the $T_c - T_g$ value represents the thermal stability of the glass. Therefore, increasing Pb content in the $\text{Se}_{90-x}\text{Te}_{10}\text{Pb}_x$ glassy system decreases the glass stability,^{2,19} which can be defined as the resistance to crystallization.

The separation between the T_g and T_c indicates the glass forming ability (GFA) of the material. The glass forming factor of a material is given by²⁰

$$K_g = \frac{T_c - T_g}{T_m - T_c} \quad (9)$$

If $K_g \leq 0.1$, the glass is usually difficult to prepare and the glass is good formed if $0.4 \leq K_g$.²¹ The calculated values of K_g for the studied composition are listed in Table 1. In this sense, it can be estimated that the compositions $\text{Se}_{87.5}\text{Te}_{10}\text{Pb}_{2.5}$ and $\text{Se}_{85}\text{Te}_{10}\text{Pb}_5$ have a similar K_g . In general, there is a decrease in K_g as Pb content increases. These results indicate that the crystallization ability increases with increasing Pb content. These results are in good agreement with other experimental results for many chalcogenide glasses.^{19,22,23}

5. Crystallization Kinetics

Based on the JMA equation, the crystallization kinetic parameters, namely the crystallization activation energy (E_c) and the Avrami exponent (n) can be calculated using different approximated methods.^{24–27} The E_c values as well as the Avrami exponent were calculated for the studied composition by using Matusita method.²⁷

$$\ln[-\ln(1 - \alpha)] = -n \ln \beta - 1.052 \frac{mE_c}{RT} + \text{const.} \quad (10)$$

where α the volume fraction crystallized at corresponding temperature, n and m are constants related to the crystallization mechanism and β is the heating rate. As example, a plot of $\ln[-\ln(1 - \alpha)]$ versus $1000/T$ is shown in Fig. 4(a) for the composition $\text{Se}_{85}\text{Te}_{10}\text{Pb}_5$ at different heating rates.

Fig. 4 (a) Plots of $\ln[-\ln(1-\alpha)]$ versus $1000/T$ for composition $\text{Se}_{85}\text{Te}_{10}\text{Pb}_5$ at different heating rates. (b) Plots of $\ln[-\ln(1-\alpha)]$ versus $\ln \beta$ for composition $\text{Se}_{85}\text{Te}_{10}\text{Pb}_5$ at different temperatures.

Table 2 The average values of mE_c , n and E_c obtained by using Matusita equation for the studied compositions.

Composition	Average $mE_c/\text{kJ/mol}$	Average n values	Average $E_c/\text{kJ/mol}$
$\text{Se}_{87.5}\text{Te}_{10}\text{Pb}_{2.5}$	130.47	2.76	43.49
$\text{Se}_{85}\text{Te}_{10}\text{Pb}_5$	210.35	3.09	70.12
$\text{Se}_{82.5}\text{Te}_{10}\text{Pb}_{7.5}$	177.85	2.47	59.28
$\text{Se}_{75}\text{Te}_{10}\text{Pb}_{15}$	297.09	2.64	99.03

The above procedure is used for the other compositions. From the slopes of the straight lines, the mE_c average values are calculated and listed in Table 2 for all the compositions. It's observed that the plots are linear over a wide temperature range. At higher temperatures, a break is seen in the linearity for all the heating rates, this break may be considered due to the saturation of the nucleation sites at the final stage of crystallization.^{28,29)} In addition, to evaluate the E_c values, dimensionality of growth m and n values were calculated from Matusita equation²⁷⁾ for each composition. For as-quenched glass containing no nuclei $n = m + 1$, and for glass containing a sufficiently large number of nuclei $n = m$. The value of n can be obtained by plotting $\ln[-\ln(1-\alpha)]$ versus $\ln \beta$ at specific temperatures. Figure 4(b) shows these plots at three different temperatures for composition $\text{Se}_{85}\text{Te}_{10}\text{Pb}_5$ and the same procedure was used for the other compositions. The average values of n as evaluated from the slopes are listed in Table 2. The calculated n values were not integers, and showed a variation in the range of $2.5 \leq n \leq 3.1$, this means that the crystallization occurs by more than one mechanism.²⁾ These values of n may be accounted for the possibility of a combination of two and three dimensional crystal growth with heterogeneous nucleation.³⁰⁾ From the n value and the average mE_c , the activation energies of the amorphous crystalline transformation for the $\text{Se}_{90-x}\text{Te}_{10}\text{Pb}_x$ (where $x = 2.5, 5, 7.5$ and 15) system were deduced and listed in Table 2.

On the other hand, the activation energy of amorphous-crystalline transformation can be determined by using the iso-conversional methods.^{31–33)} One of these methods is the Friedman method³¹⁾

Fig. 5 The apparent activation energy for crystallization E_c as a function of the fractional conversion α for the studied compositions.

$$\ln \dot{\alpha} = \ln[Af(\alpha)] - \frac{E_c(\alpha)}{RT} \quad (11)$$

This method can be used to calculate the local activation energy of crystallization $E_c(\alpha)$ at specific α using different heating rates. This process can be repeated for various degree of conversion. Figure 5 shows E_c as a function of the fractional conversion for the studied compositions. On the other hand, a more pronounced variation of $E_c(\alpha)$ versus α probably indicated a more complex mechanism of the crystallization process for all studied compositions. In general, the $E_c(\alpha)$ should be practically independent of the fractional conversion in the range of $0.3 \leq \alpha \leq 0.7$, and some changes may be expected for the lower and higher values of α particularly for the faster processes (i.e. higher values of β). These deviations are probably because of the errors in the base line approximations at the peak tails.¹⁵⁾

According to Malek proposal,¹⁵⁾ the validity of the JMA model to describe the crystallization process can be tested by checking the maximum of the $z(\alpha)$ function α_p^∞ . If the maximum falls into the range (0.61–0.65), then the experimental data probably could be presented using the JMA model and if α_p^∞ is shifted to lower values, then the condition of the validity is not fulfilled. This test was checked

Fig. 6 Normalized $y(\alpha)$ and $z(\alpha)$ functions obtained by transformation of non-isothermal data for the crystallization of the $\text{Se}_{85}\text{Te}_{10}\text{Pb}_5$ composition at different heating rates.

Table 3 The average values of E_c , α_M and α_p^∞ for the studied compositions.

Composition	Average E_c /kJ/mol using Friedman's method	Average α_M for different β values	Average α_p^∞ for different β values
$\text{Se}_{87.5}\text{Te}_{10}\text{Pb}_{2.5}$	34.08	0.431	0.58
$\text{Se}_{85}\text{Te}_{10}\text{Pb}_5$	31.14	0.376	0.490
$\text{Se}_{82.5}\text{Te}_{10}\text{Pb}_{7.5}$	46.25	0.327	0.484
$\text{Se}_{75}\text{Te}_{10}\text{Pb}_{15}$	51.24	0.381	0.512

for all the studied compositions. Both $y(\alpha)$ and $z(\alpha)$ functions are calculated according to eqs. (4), (5). The average values of $E_c(\alpha)$ determined by the iso-conversion method of Friedman were used to calculate $y(\alpha)$ functions for all the studied compositions.

As an example, the variations of $y(\alpha)$ and $z(\alpha)$ functions with the fractional conversion are shown in Fig. 6 for the composition $\text{Se}_{85}\text{Te}_{10}\text{Pb}_5$ and the same procedure was followed for the other three compositions. From the plots of $y(\alpha)$ and $z(\alpha)$ versus α , the conversions α_M and α_p^∞ corresponds to their maxima are determined and the average values for each composition at different heating rates are listed in Table 3. The values of α_p^∞ shown in Table 3 are not fulfilling the condition of the JMA applicability test, so the JMA model cannot be used to describe the crystallization behavior of the studied compositions under non-isothermal conditions. The shift of α_p^∞ to lower values than 0.63 indicates a complex and accelerated crystallization process.¹⁵⁾ On the other hand, increasing Pb content generally increases the deviation of α_p^∞ from 0.63 (as shown in Table 3). This implies a more complicated crystallization process. Such behavior of crystallization could be quantitatively described by the empirical SB (M, N) model. The kinetic exponents M and N are parameters that define relative contribution of acceleratory and deceleratory part of the crystallization process.³⁴⁾ These parameters are rather empirical constant, and too much physical significance should not be attached to their numerical values.¹⁵⁾ The M , N parameters can be calculated by using α_M values³⁵⁾ as

Fig. 7 Plots of $\ln[\phi \exp(E_c/RT)]$ versus $\ln[\alpha^{M/N}(1-\alpha)]$ at different heating rates for the composition $\text{Se}_{85}\text{Te}_{10}\text{Pb}_5$.

Table 4 The crystallization enthalpy (ΔH), conversion values corresponding to $y(\alpha)$ and $z(\alpha)$ functions maxima (α_M and α_p^∞ respectively) and the parameters of the SB(M, N) model for the composition $\text{Se}_{85}\text{Te}_{10}\text{Pb}_5$ at different heating rates.

Heating rate/K/min.	ΔH	α_M	α_p^∞	N	M	$\ln A$
10	93.87	0.4084	0.4819	0.9902	0.6835	7.59
15	146.21	0.3761	0.4967	0.9985	0.6019	7.16
20	200.26	0.3573	0.4692	0.9940	0.5525	6.81
25	266.74	0.3731	0.4992	1.0376	0.6175	6.58
30	341.86	0.3628	0.5069	1.0259	0.5842	6.25

$$\frac{M}{N} = \frac{\alpha_M}{1 - \alpha_M} \quad (12)$$

Using the average values of E_c , calculated by Friedman method and M/N values calculated from eq. (12), the N values are calculated by using the dependence³⁵⁾

$$\ln[\phi \exp(E_c/RT)] = \ln(\Delta H A) + N \ln[\alpha^{M/N}(1-\alpha)] \quad (13)$$

This equation is valid in the interval of $0.2 \leq \alpha \leq 0.8$. The values of N could be found from the slopes of the plots of $\ln[\phi \exp(E_c/RT)]$ versus $\ln[\alpha^{M/N}(1-\alpha)]$ and then the M values are calculated using eq. (12). Also the intersections of these plots are used to calculate the values of the pre-exponential factor (A). An example is shown in Fig. 7 for the sample $\text{Se}_{85}\text{Te}_{10}\text{Pb}_5$ and the same procedure was followed for the other three compositions. Table 4 summarizes the parameters M , N , the pre-exponential factor (A) and the enthalpy (ΔH), α_p^∞ and α_M that describe the non-isothermal crystallization of the $\text{Se}_{85}\text{Te}_{10}\text{Pb}_5$ glass. Figure 8 shows the experimental data and the those calculated, according to eqs. (1), (3) by using the parameters in Table 4 and the average E_c value (31.14 kJ/mol), at different heating rates for $\text{Se}_{85}\text{Te}_{10}\text{Pb}_5$ glass. From Fig. 8, a good agreement between the experimental and calculated data is evident. The same procedure was followed for the other three compositions and also a good agreements were obtained, which implies that the empirical SB(M, N) model is most suitable to quantitatively describe the crystallization process in the $\text{Se}_{90-x}\text{Te}_{10}\text{Pb}_x$ (where $x = 2.5, 5, 7.5$ and 15 at%) glasses.

Fig. 8 Non-isothermal crystallization of $\text{Se}_{85}\text{Te}_{10}\text{Pb}_5$ powder samples for different heating rates compared with the calculated dependences (solid lines) using SB model.

6. Conclusions

The presented results for the $\text{Se}_{90-x}\text{Te}_{10}\text{Pb}_x$ ($x = 2.5, 5, 7.5$ and 15 at%) glasses indicate that:

- (1) The glass forming factor (K_g) decreases with increasing Pb content.
- (2) The average particle size of the crystallized PbSe phase formed in the samples annealed at 385 K for two hours decreases with increasing Pb content.
- (3) More complex crystallization behavior was observed under non-isothermal conditions for the studied compositions. In this case, the JMA model cannot be applied.
- (4) The empirical two parameters SB (M, N) model was found to be the suitable model that can be used to quantitatively describe the crystallization process under non-isothermal conditions for the studied compositions.
- (5) Increasing the Pb content in the Se-Te-Pb leads to a more complex and accelerated process.

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