Glass transition and crystallization kinetics of a new chalcogenide-alkali metal $\text{Se}_{80}\text{Te}_8(\text{NaCl})_{12}$ alloy

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Abstract. A new chalcogenide-alkali metal alloy of $\text{Se}_{80}\text{Te}_8(\text{NaCl})_{12}$ has been prepared by a melt-quench technique. The crystallized phases due to the thermal annealing are observed by X-ray diffraction of the powdered sample. The glass transition and kinetics of crystallization in the $\text{Se}_{80}\text{Te}_8(\text{NaCl})_{12}$ alloy are studied using the differential scanning calorimetric technique under non-isothermal conditions. The activation energy of the glass transition is evaluated by Kissinger and Mahadevan methods. The crystallization activation energy (E_c) is calculated by isoconversion Friedman methods. The decrease of E_c with increasing crystallization conversion is attributed to the complex mechanism of the crystallization process. Based on the shape of the characteristic kinetic function, the crystallization growth is found to be a three-dimensional growth from the bulk nuclei. The results show that the conditions of the Sestak–Berggren model are satisfied for describing the crystallization process of the studied $\text{Se}_{80}\text{Te}_8(\text{NaCl})_{12}$ alloy. The parameters M and N involved in this model are calculated and related to the crystallization process.

Keywords. Chalcogenide; alkali metal; glass transition; crystallization kinetics.

1. Introduction

Selenium–tellurium-based chalcogenide materials are the subject of intensive studies because of their use in technological applications, such as sensors, solar cells, infrared detectors and xerography [1–4]. Incorporating an alkali metal, such as sodium in a chalcogenide matrix has a beneficial effect on photovoltaic properties by increasing the fill-factor and hole density [5]. The inclusion of Na also improves the power, conversion efficiency of solar cells [6].

The crystallization mechanism in chalcogenide glass is important from the point of view of applications, such as xerography and optical recording. The crystallization kinetics can be described by the thermal analysis which is considered as a rapid and convenient tool. The determination of kinetic parameters of many glassy systems were determined by the nucleation growth model suggested by Johnson–Mehl–Avrami (JMA) model [7,8] or by the empirical Sestak–Berggren (SB) model [9]. The heat flow (ϕ) evaluated during the crystal growth can be expressed by

$$\phi = \Delta H_c A \exp(-E_c/RT) f(\alpha), \quad (1)$$

where ΔH_c is the heat of crystallization, A the pre-exponential frequency factor, E_c the activation energy for crystallization, R the universal gas constant, T absolute temperature and α the degree of crystallization or conversion. For JMA, the function $f(\alpha)$ defined as [7,10]

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

where the exponent n is related to the nucleation and crystal growth mechanisms. For the SB model, the function $f(\alpha)$ is defined as [11]

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

where M and N are kinetic parameters and denote the relative contribution of acceleratory and decaying regions of the transformation process, respectively.

The validity of either JMA model or SB one for describing the crystallization process is based on two proposed functions $y(\alpha)$ and $z(\alpha)$, which are [12]

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

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

The JMA model is not appropriate to describe the crystallization process unless the maximum α_p of the $z(\alpha)$ function falls into the range of 0.61–0.65 [13]. While SB model can be used to describe the thermal analyses if $0 < \alpha_m < \alpha_p$, where α_m is maximum of the $y(\alpha)$ function [9].

This work aims to study the glass and crystallization transformations of bulk $\text{Se}_{80}\text{Te}_8(\text{NaCl})_{12}$ alloy under non-isothermal conditions. We also intend to determine the kinetics and mechanism of the crystallization process. This work belongs to a few papers studying the crystallization kinetics in chalcogenide–alkali metal alloys. Our previous work is the only study that concerned $\text{Se}_{80}\text{Te}_8(\text{NaCl})_{12}$ thin

Figure 1. Spectral distribution of constituent elements of $\text{Se}_{80}\text{Te}_8(\text{NaCl})_{12}$ alloy.

film alloy, in which, the effect of the film thickness on the optical properties has been reported [14].

2. Experimental

The bulk of $\text{Se}_{80}\text{Te}_8(\text{NaCl})_{12}$ chalcogenide–alkali metal alloys was fabricated from a mixture of Se, Te elements and NaCl salt (Aldrich Chem. Co., USA) by the melt-quench technique. The constituent elements of 99.999% purity were weighed as per atomic percentages and sealed in evacuated quartz ampoules. The ampoules were heated in a rocking furnace up to 700°C at a heating rate of $2\text{--}3^\circ\text{C min}^{-1}$. The ampoules were rocked at a constant rate to ensure homogeneity of the mixture. The samples were maintained at 700°C for 24 h and then quenched in ice cold water. The investigation of the nature of the bulk samples structure by X-ray diffraction (XRD) and the thermal behaviour by differential scanning calorimetry (DSC) were discussed in our previous works [14,15].

3. Results and discussion

3.1 Elemental analysis

The quantitative analysis of the prepared bulk alloy was carried out using energy-dispersive X-ray spectroscopy technique. Figure 1 shows the typical spectral distribution of constituent elements of the studied alloy. The atomic percentage ratios of Se, Te, Na and Cl were found as shown in the inset table of figure 1. This composition is very close to the target composition which is $\text{Se}_{80}\text{Te}_8(\text{NaCl})_{12}$.

Figure 2. XRD patterns of $\text{Se}_{80}\text{Te}_8(\text{NaCl})_{12}$ alloy after annealing at three different temperatures for 0.5 h.

3.2 Crystalline phases

The XRD patterns of the powdered $\text{Se}_{80}\text{Te}_8(\text{NaCl})_{12}$ annealed at temperatures 353, 373 and 393 K for 0.5 h is shown in figure 2. Based on the DSC feature, these annealing temperatures represent the temperature range in which the crystallization process occurs. It can be noticed that the sample is crystallized in preferential orientations indicated with strong peaks depending on the annealing temperature. These orientations are along the (600) plane corresponding to Na_2TeSe_3 phase for annealing at 353 K, and (100) and (221) planes correspond to Se phases for annealing at 373 K. The strong XRD

Table 1. Observed and standard ASTM values for diffractograms and calculated particle size (D) for the bulk $\text{Se}_{80}\text{Te}_8(\text{NaCl})_{12}$ alloy at different annealing temperatures.

Annealed (K) temp.	$2\theta_{\text{exp.}}$ (°)	$2\theta_{\text{stand.}}$ (°)	$d_{\text{exp.}}$ (Å)	$d_{\text{stand.}}$ (Å)	hkl	Phase	D (nm)
353	22.710	22.723	3.916	3.913	2 0 2	Na_2Se_4	9.2
	25.169	25.117	3.538	3.545	1 0 3	Se	6.3
	28.787	28.774	3.101	3.103	6 0 0	Na_2TeSe_3	11.7
	31.000	31.058	2.885	2.879	1 0 1	Se	12.1
	40.540	40.536	2.225	2.226	0 4 1	Se	4.5
	42.441	42.452	2.130	2.129	$-3\ 2\ 3$	$\text{Se}_{7.68}\text{Te}_{0.32}$	8.3
	44.500	44.511	2.036	2.036	1 3 4	Se	4.9
	50.740	50.734	1.799	1.799	8 0 2	Na_2TeSe_3	4.4
	54.160	54.132	1.693	1.694	8 2 1	Na_2TeSe_3	7.3
	60.460	60.442	1.531	1.532	1 2 7	Se	5.4
	64.480	64.467	1.445	1.445	1 1 -3	Te	6.5
	71.980	71.910	1.312	1.313	5 1 1	Na_2Se	11.5
373	22.911	22.961	3.882	3.873	4 1 1	SeCl_4	9.1
	25.370	25.382	3.511	3.509	1 0 0	Se	5.9
	28.962	28.990	3.083	3.080	2 2 1	Se	13.0
	31.240	31.233	2.863	2.864	3 1 0	Se_8	19.9
	40.720	40.700	2.216	2.217	3 1 4	Na_2Se_4	4.7
	44.620	44.652	2.031	2.029	$-1\ 2\ 5$	$\text{Se}_{7.68}\text{Te}_{0.32}$	2.8
	50.920	50.880	1.793	1.795	$-9\ 1\ 6$	Na_2TeSe_3	5.4
	60.520	60.318	1.530	1.535	$-9\ 3\ 2$	Na_2TeSe_3	4.2
	72.220	72.269	1.308	1.307	7 3 2	Na_2Se_4	12.4
393	22.875	22.723	3.888	3.913	2 0 2	Na_2Se_4	11.2
	28.955	28.969	3.084	3.082	2 2 1	Se_8	13.6
	31.287	31.253	2.859	2.862	3 1 0	Se	18.4
	40.679	40.641	2.218	2.219	1 1 4	Na_2TeSe_3	8.7
	42.620	42.616	2.121	2.122	$-4\ 2\ 4$	Na_2TeSe_3	10.2
	44.631	50.827	2.030	1.796	3 4 1	$\text{Se}_{7.68}\text{Te}_{0.32}$	5.7
	50.871	54.924	1.795	1.672	2 5 1	$\text{Se}_{7.68}\text{Te}_{0.32}$	9.1
	54.940	54.949	1.671	1.671	2 0 0	Se	5.5
	60.580	60.590	1.528	1.528	2 3 6	Se	3.4
	64.240	64.278	1.450	1.449	1 1 -3	Te	3.9
	70.180	70.187	1.341	1.341	2 1 1	Te	7.9

peaks for annealing at 393 K indicate (202) and (221) planes corresponding to the Na_2Se_4 and Se_8 phases. The other orientations with their corresponding phases are listed in table 1. The assignment of the phases is determined on the basis of the best agreement between the experimentally observed $2\theta_{\text{exp.}}$ and inter-planar spacing, $d_{\text{exp.}}$, with those of American Society for Testing and Materials (ASTM), $2\theta_{\text{stand.}}$ and $d_{\text{stand.}}$ as presented in table 1.

The crystallite sizes (D) are calculated using the well-known Scherrer formula:

$$D = \frac{0.94\lambda}{\gamma \cos \theta}, \quad (6)$$

where λ in nm is the X-ray wavelength, γ in radian is the width of the diffraction peak and θ in radian is the diffraction angle. The calculated D values for observed crystalline phases are

listed in table 1. The average particle size of the crystalline phases increases to 7.68, 8.60 and 8.87 nm when the annealing temperature increases to 353, 373 and 393 K, respectively.

3.3 Thermal analysis

DSC of the powdered $\text{Se}_{80}\text{Te}_8(\text{NaCl})_{12}$ at different heating rates (β) ranging from 5 to 30 K min⁻¹ is shown in figure 3. Four characteristic events are resolved in the DSC thermograms. For example, at $\beta = 15$ K min⁻¹, the first event is an endothermic peak at $T = 337$ K corresponding to the glass transition temperature, T_g . The second and third events are the onset and the peak of an exothermic curve corresponding to the onset and the crystallization peak temperature T_c and T_p at $T = 359$ and 382 K, respectively. The last characteristic event is an endothermic peak centred at $T = 513$ K corresponding to the melting peak temperature, T_m . The positions of T_g , T_c

and T_p shift to higher temperatures with increasing β , while T_m as a thermodynamic parameter is almost kept constant as β increases.

The thermal stability of glass against crystallization can be estimated using two common stability criteria which are $\Delta T = T_c - T_g$ and $W_s = \Delta T/T_g$. The value of ΔT is proportional to thermal stability of the glass; while W_s expresses the weight of stability [16,17]. As heating rate β is increased from 5 to 30 K min⁻¹, ΔT increases as reported in table 2. Therefore, the glass thermal stability against crystallization is improved with increasing β . The value of W_s irregularly changes with β . It has a maximum value at β of 10 K min⁻¹ reflecting the most weight of stability at this heating rate.

The enthalpy increases when one mole of a substance is transformed into its crystalline state at constant pressure. The delta enthalpy (ΔH_c) for the crystallization process of the investigated chalcogenide Se₈₀Te₈(NaCl)₁₂ is obtained from the computer program involved in the DSC apparatus and listed in table 2. It is found that ΔH_c is independent of β . The enthalpy release is related to the metastability of glass. That is, the least stable glass is supposed to have maximum ΔH_c . From table 2, it is clear that ΔH_c has the lowest value at

$\beta = 10$ K min⁻¹. Hence, the crystallization state at this rate is the most stable among the whole heating rates.

3.4 Glass transition

The activation energy (E_g) of the glass transition can be determined by different methods. For instance, Kissinger and Mahadevan methods evaluate E_g from the dependence of glass transition T_g on the heating rate β [18,19]. According to Kissinger approach, E_g can be calculated using the relation [18]

$$\ln \left(\frac{\beta}{T_g^2} \right) = - \left(\frac{E_g}{R} \right) \frac{1}{T_g} + \text{const.}, \quad (7)$$

where R is the universal gas constant. The plot of $\ln(\beta/T_g^2)$ vs. $1000/T_g$ is shown in figure 4a. The obtained value of the activation energy for glass transition of Se₈₀Te₈(NaCl)₁₂ glass is 455.98 kJ mol⁻¹. The heating rate dependence of T_g can be also employed to evaluate E_g using the method of Mahadevan [19]:

$$\ln \beta = - \left(\frac{E_g}{R} \right) \frac{1}{T_g} + \text{const.} \quad (8)$$

Figure 4b shows the plot of $\ln \beta$ vs. $1000/T_g$, from which E_g is calculated as 461.56 kJ mol⁻¹. This value of activation energy is almost in agreement with that obtained by using Kissinger's method.

The small difference in E_g evaluated from the Kissinger equation is because this equation has less dependence on the thermal history. While the Mahadevan method is an approximation of the Kissinger equation, where the temperature affects kinetic parameters as low heating rates can cause an error; for example 1 K can cause error 5% in E_g .

3.5 Crystallization kinetics

The crystallization temperature appeared in DSC trace when a temperature matching the fraction of crystallization α as a result of an immediate change in specific heat of the material. At any temperature, the fraction of crystallization is given as $\alpha_T = \sigma_T/\sigma$, where σ_T is the area of a selected portion

Figure 3. DSC traces for Se₈₀Te₈(NaCl)₁₂ alloy at different heating rates.

Table 2. Glass and crystallization transition temperatures, stability criteria and enthalpy of crystallization of Se₈₀Te₈(NaCl)₁₂ alloy at different heating rates.

β (K min ⁻¹)	T_g (K)	T_c (K)	T_p (K)	ΔT (K)	W_s	ΔH_c (J g ⁻¹)
5	332	354	372	22	0.066	26.53
10	335	360	380	25	0.074	23.77
15	337	359	382	22	0.065	31.65
20	338	362	387	24	0.071	25.61
30	341	366	389	25	0.073	28.19

Figure 4. Plots of $\ln(\beta/T_g^2)$ and $\ln \beta$ vs. $(1000/T)$ for $\text{Se}_{80}\text{Te}_8(\text{NaCl})_{12}$.

Figure 5. Extent of crystallization (α) for $\text{Se}_{80}\text{Te}_8(\text{NaCl})_{12}$ alloy as a function of temperature at different heating rates.

within the exothermic crystallization peak and σ is the total area under the crystallization peak between T_c and the temperature at which the crystallization process is completed. The extent α as a function of temperature at different heating rates β is shown in figure 5. All curves are sigmoidal in shape. For a given heating rate, a slow rate of crystallization is observed at the starting temperature. The rate then increases due to the growth of nuclei. Finally, the crystallization rate decreases again because of colliding of crystallites. However, the increase in heating rate decreases the crystallization fraction as a result of decreasing the incubation time which is required for the nucleation process.

The activation energy of crystallization (E_c) can be calculated without assuming any kinetic model by using the transformation rate isoconversional methods [20,21]. E_c is then calculated as a function of the fractional conversion α . Friedman method is a good reliable isoconversion method

Figure 6. Plots of $\ln(\phi)$ vs. $1000/T$ at specific degree of crystallization (α) for different heating rates.

Figure 7. Activation energy of crystallization (E_c) for $\text{Se}_{80}\text{Te}_8(\text{NaCl})_{12}$ alloy as a function of fraction of crystallization (α).

because it has no approximations. This method is represented by the equation [20]:

$$\ln(\varphi) = \ln(\Delta H_c A) - \frac{E_c}{RT} + \ln[f(\alpha)], \quad (9)$$

where A is a pre-exponential. For a constant α ,

$$\left[\frac{d[\ln(\varphi)]}{d(1/T)} \right]_{\alpha} = -\frac{E_c}{R}. \quad (10)$$

So, for each value of α , there will be a corresponding value of E_c . Figure 6 shows the plots of $\ln(\beta)$ vs. $1000/T$ at a specific degree of crystallization α for different heating rates. By applying the value of T_{α} at different transformation stages, the variation of $E_c(\alpha)$ can be obtained. The deduced value

of E_c as a function of α is shown in figure 7. The remarkable variation as the decrease in E_c with increasing α indicates a more complex mechanism of the crystallization process.

Figure 8 shows the variation of E_c as a function of crystallization temperature T at different heating. The observed decrease in E_c with increase in T indicates that the crystallization rate increases with increasing temperature. In addition, this dependence of E_c on T suggests that the amorphous to crystalline transformation in the studied system is not obeying the crystallization mechanism of a single step. Therefore, the simplified mechanism based on constant E_c is not suitable to describe the present crystallization process. Instead, the crystallization mechanism may be expressed in terms of

Figure 8. Activation energy of crystallization (E_c) for $\text{Se}_{80}\text{Te}_8(\text{NaCl})_{12}$ alloy as a function of crystallization temperature (T) at different heating rates.

the nucleation theory based on the existence of rates of two processes, nucleation and diffusion [22].

The heat flow ϕ can be expressed by two characteristic kinetic functions $y(\alpha)$ and $z(\alpha)$ which are calculated according to equations (4 and 5) using the average value of E_c ($91.94 \text{ kJ mol}^{-1}$) deduced from equation (9). The dependence of both normalized functions on the fractional conversion is shown in figure 9. Both functions show similar shapes for the dependence on the heating rate β . This behaviour of $y(\alpha)$ and $z(\alpha)$ curves with varying of β indicates the characteristic of complex kinetic crystallization [23]. The $y(\alpha)$ function shows an obvious high- α side shoulder suggesting the growth of crystallization is three-dimensional growth from bulk nuclei [24]. The shoulder indicates steadily increasing participation of the bulk mechanism depending on the ratio between the number of surface defects and bulk crystallization centres [25]. For high values of α , $y(\alpha)$ curves depend on the heating rate β . At low values of β , there is a relatively sufficient time for forming a large number of volume crystallization centres reaching the maximum nucleation rate. As a result, the volume crystallization becomes considerably more. For high heating rates, there is not enough time for growing the volume nuclei because of probably insufficient nucleation time. Accordingly, the volume crystallization occurs to some extent.

3.6 Determination of crystallization process model

The set of crystallization parameters for a given glass depends on the crystallization mechanism as represented by equation (1). For best model describing the thermal analyses data, the evaluated E_c without assuming any kinetic model is used to calculate the functions of $y(\alpha)$ and $z(\alpha)$. These functions can then be employed to determine a suitable mechanism describing the crystallization process. From the plots of $y(\alpha)$ and $z(\alpha)$ vs. α , the values of α_m and α_p at which $y(\alpha)$ and $z(\alpha)$

Figure 9. Plots of the normalized $y(\alpha)$ and $z(\alpha)$ functions vs. the fraction of crystallization (α) for $\text{Se}_{80}\text{Te}_8(\text{NaCl})_{12}$ alloy at different heating rates.

Table 3. The maxima α_m and α_p of $y(\alpha)$ and $z(\alpha)$ functions, the pre-exponential A and the parameters M and N of the SB model at different heating rates.

β (K min ⁻¹)	α_m	α_p	$A \times 10^{11}$ (min ⁻¹)	N	P	M
5	0.499	0.234	6.0304	1.51	0.31	0.46
10	0.463	0.179	5.4996	1.80	0.22	0.39
15	0.508	0.168	5.8443	1.49	0.20	0.31
20	0.469	0.152	5.2329	1.81	0.18	0.32
30	0.486	0.161	6.2343	1.59	0.19	0.31

Figure 10. Dependence of $\ln[\phi \exp(E_c/RT)]$ on $\ln[\alpha^P(1-\alpha)]$ for $\text{Se}_{80}\text{Te}_8(\text{NaCl})_{12}$ alloy at different heating rates.

reaching its maximum are deduced for the different heating rates and listed in table 3. The results in figure 10 and table 3 show the DSC peak which varies within the interval $0.152 < \alpha_p < 0.234$ which is considerably smaller than the fingerprint ($\alpha_p = 0.632$) of the JMA model. Therefore, α_m and α_p satisfy the relation $0 < \alpha_m < \alpha_p$ and α_p does not fall into the range of 0.61–0.65 for any heating rate. These results satisfy the condition of SB model which then can be used to describe the crystallization mechanism of the studied $\text{Se}_{80}\text{Te}_8(\text{NaCl})_{12}$ composition.

The kinetic parameters of SB model are the exponents M and N which express the relative contribution of acceleratory and deceleratory parts, respectively, of the crystallization process. The value of N can be calculated using the average values of E_c according to the following relation [26]

$$\ln \left[\phi \exp \left(\frac{E_c}{RT} \right) \right] = \ln(\Delta H_c A) + N \ln[\alpha^{M/N}(1-\alpha)], \quad (11)$$

where A is a pre-exponential. Figure 10 shows the dependence of $\ln[\phi \exp(E_c/RT)]$ on $\ln[\alpha^P(1-\alpha)]$ which is valid

in the interval $0.2 \leq \alpha \leq 0.8$. The parameters N and A are determined from the slope and the intercept of y-axis of this relation, respectively. Then, the parameter M can be deduced using the following equation [27]:

$$P = \frac{M}{N} = \frac{\alpha_m}{1 - \alpha_m}. \quad (12)$$

The calculated values of the pre-exponential A , ratio P and parameters M and N for the different heating rates are listed in table 3. It can be seen from table 3 that the values of M are smaller than those of N for all the values of β . The relative high value of the kinetic parameter M indicates a more significant role of the precipitated phase on the whole kinetics, while the parameter N having the values of $N > 1$ indicates the increasing complexity of crystallization [28].

4. Conclusions

The chalcogenide–alkali metal $\text{Se}_{80}\text{Te}_8(\text{NaCl})_{12}$ bulk alloy is prepared by a melt-quench technique. The crystallization process in the as-prepared alloy is induced by DSC. The relevant crystalline phases due to the thermal annealing are assigned using XRD. The E_c is calculated using the isoconversion Friedman method depending on the transformed crystallization fraction (α). It is found that E_c decreases as α increases indicating the complexity of crystallization mechanism. The characteristic kinetic functions reveal that the crystallization growth is a three-dimensional growth from the bulk nuclei. The SB model with the parameters M and N is employed to describe the crystallization process. The values of these parameters indicate a significant role of the precipitated phase and complexity of the crystallization process.

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