

CRYSTALLIZATION KINETICS OF $\text{Zn}_{10}\text{Se}_{90}$ CHALCOGENIDE GLASSY ALLOYS USING NON-ISOTHERMAL METHODS

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This work is an attempt to quantitatively investigate the non-isothermal crystallization kinetics of $\text{Zn}_{10}\text{Se}_{90}$ chalcogenide. The behavior of kinetics parameters suggested that it is appropriate to conduct the investigation in three different heating regimes [(1) $\beta = 3-15$, (2) $\beta = 20-50$, and (3) $\beta = 60-99 \text{ K min}^{-1}$]. Quantitative methods based on the Friedman and Starink models were utilized to evaluate variation in activation energy as a function of reaction progress and temperature. Both models showed the same trend, with a small variation which might have been due to the approximation approach. The variation in activation energy suggested that the chalcogenide responded differently in each heating-rate regime. This behavior was observed for the results obtained from the two models. Avrami's equation and Matusita analysis were used to evaluate Avrami's exponents. The results showed good agreement, indicating the reliability of both approaches.

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1. Introduction

Selenium (Se) is an element that has found its way into commercial applications in various fields, including digital x-ray imaging, memory devices, etc.[1]. However, an inherent shortcoming of Se is its short lifetime and low photosensitivity. To minimize these drawbacks and enhance its physical properties, Se, chalcogen elements, is mixed with different elements such as zinc (Zn), tin (Sn), silicon (Si), germanium (Ge), etc. Zn, in particular, attracted many researchers' interests as being the appropriate additive due to the interesting features of the ZnSe binary, such as a wide-bandgap (2.8 eV) II-VI semiconductor [2][3]. Throughout the last decade, various researchers investigated thermal studies of ZnSe chalcogenide [4]. The interesting optical, mechanical, and electrical properties of ZnSe chalcogenide paved its way for use in a variety of applications, such as optical recording media, laser printing infrared spectroscopy, laser fiber, thin film transistors, photodiodes, solar cells, sensors, and photocatalysis, etc.[5][6][7][8][9].

Abdel-Rahim et al. [10] investigated the transformation of amorphous $\text{Zn}_{10}\text{Se}_{90}$ to crystalline phases using differential thermal analysis (DTA) complemented with XRD analysis. Their findings suggested the coexistence of micro-crystallites ZnSe and Se within the amorphous matrix of ZnSe. The activation energy obtained using Kissinger's and Matusita's model was comparable.

The effect of Zn content on the crystallization temperature of $\text{Zn}_x\text{Se}_{100-x}$ thin films was investigated using DTA and reported in [11]. Lamia Heireche et al. [12] reported the effect of adding Sb with different ratios to the glass transition and the crystallization behavior of ZnSe alloy using different models. Abhay Kumar [13] used DSC to investigate the rule of carbon nanotube and graphene on the thermal behavior of Se-Zn-Sb composite. The outcomes of their study revealed that thermal stability was improved through incorporation of the nanotube compared to the inclusion of graphene. Sphoorti Srivastava et al.[14] investigated the kinetics of crystallization of $\text{Se}_{70}\text{Te}_{30-x}\text{Zn}_x$. Incorporating Zn up to 4 at % was found to enhance the activation energy of

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crystallization. A further increase of Zn showed a decrease in crystallization energy. Naqvi et al. [15] attributed the thermal stability of $\text{Se}_{80-x}\text{Te}_{20}\text{Zn}_x$ as Zn content increased to the increase in Zn-Zn bonds. This stability was clearly observed in DSC studies under non-isothermal conditions. Shamshad et al. [16] prepared $\text{a-Bi}_{0.5}\text{Se}_{99.5-x}\text{Zn}_x$ ($x = 0, 0.1, 0.2, 0.5, \text{ and } 1$) glasses. The isothermal method was employed to investigate the thermal stability of the prepared chalcogenide as a function of Zn content. The activation energy was found to increase as Zn content increased. Another interesting finding that showed a promising feature of ZnSe was the energy storage system; a gain in capacity was observed as SeZn was incorporated as a negative electrode [17].

A proper understanding of the crystallization process of ZnSe provides valuable information for determining the material's appropriate application. This work is an attempt to understand the crystallization mechanism of $\text{Zn}_{10}\text{Se}_{90}$ by calculating the relevant thermal parameters such as activation energy, the Avrami exponent, and crystallization half-time through a wide range of heating rates.

2. Experimental

Samples with the desired composition were prepared using the conventional melt-quench procedure. Zn and Se of high purity (99.999% pure) were purchased from Aldrich UK. Clean quartz ampoules were charged with constituent elements and sealed after removal of the residual gases to a pressure of 10^{-5} Torr. The ampoules were physically shaken to ensure physical mixing, then placed in a furnace (type R07115) and heated to 700 K for 24 hours. To ensure homogeneity of the melt, the ampoule was manually stirred several times. Finally, to obtain $\text{Zn}_{10}\text{Se}_{90}$ in glass state, the ampoule was rapidly quenched in ice-cooled water.

The non-isothermal crystallization experiments were performed using a differential scanning calorimeter (DSC) [TA instruments DSC-Q 2000]. Samples of approximately 5 to 8 mg were accurately weighed. The samples were heated from room temperature to 500 K at a constant heating rate (β) of 3, 4, 5, 7, 10, 12, 15, 20, 25, 30, 40, 50, 60, 70, 80, 90, and 99 K per minute, respectively. All the experiments were carried out under nitrogen atmosphere (50 ml/min.). To determine the kinetics parameters, the obtained DSC thermograph was analyzed using the advanced thermokinetics software package, AKTS-Thermokinetics, Ver. 4.15 (Advanced Kinetics and Technology Solutions, <http://www.akts.com>). Because the baseline can significantly influence the values of the kinetic parameters determined for the reaction, this study used the tangential baseline to analyze the DSC, as it is more accurate than the linear baseline. This allows temperature changes to be taken into account [18].

3. Results and discussions

Fig. 1 presents the crystallization thermographs of $\text{Zn}_{10}\text{Se}_{90}$ alloy heated at room temperature to 500 K at different heating rates of 3–99 K min^{-1} . These thermographs show one well-defined exothermic peak for each heating rate. The exothermic peaks shown in Fig. 1 can be attributed to amorphous-crystalline transformation. Moreover, the single crystallization peak indicates the single phase formation while transforming from the amorphous phases to the crystalline ones. A quick analysis of Fig. 1 shows that increasing the heating rate generally increases the crystallization temperatures and the broadening of these peaks. Crystallization in chalcogenides occurs as a result of the nucleation and growth process. The first happens at low temperatures whereas the second takes place at higher temperatures. As a result, T_p increases as β increases. The observed increase of T_p with the increase in heating rate can be attributed to the fact that when β is large, the sample does not get sufficient time for nucleation and crystallization [19]. Consequently, by the time crystallization starts, the temperature will have increased because of the higher heating rates. The bulk of the crystallization occurs between $0.2 < \alpha < 0.8$. The activation energy of nucleation and growth is defined as the energy evolved in transformation from

the amorphous to the crystalline state. Because the peak temperature varies with the heating rate, several mathematical methods have been proposed to calculate the effective activation energy. The Friedman [20] and Starink [21] models were utilized to quantitatively investigate the non-isothermal crystallization kinetics. Before proceeding further, it would be appropriate to review the basis of these two models. The Friedman model can be expressed as follows:

$$\ln \left(\frac{d\alpha}{dt} \right)_{\alpha,i} = \text{constant} - \frac{E_{\alpha}}{RT_{\alpha,i}} \quad (1)$$

where $d\alpha/dt$ is the instantaneous crystallization rate, E_{α} the activation energy, T the temperature, i heating rate, α the conversion fraction representing the volume of the crystallized fraction, and R the universal gas constant. Equation 1 can be used for any heating system because, for each value of α , the activation energy can be deduced by plotting $\ln (d\alpha/dt)_{\alpha,i}$ with respect to $(1/T)_{\alpha,i}$ a straight line must be obtained with a slope equal to E_{α}/R .

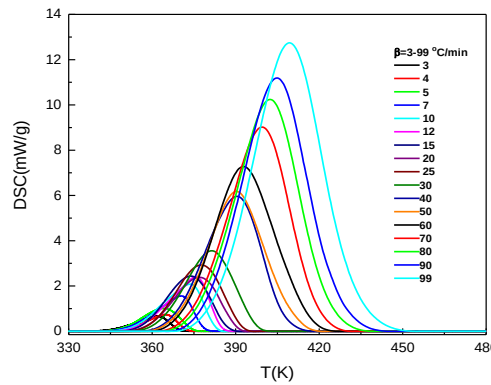


Fig. 1. Crystallization exotherms showing the effect of heating rate on the crystallization of $\text{Zn}_{10}\text{Se}_{90}$.

The Starink method can be expressed by equation 2

$$\ln \frac{\beta}{T_{\alpha}^{1.92}} = C - 1.0008 \left(\frac{E_{\alpha}}{RT_{\alpha}} \right) \quad (2)$$

where C is the constant and α is the conversion fraction.

Using the Starink method, the activation energy can be obtained by the linear fitted function of $\ln(\beta/T_{\alpha}^{1.92})$ versus $1/T$ (Eq. 2), for a constant crystallized fraction.

Our preliminary analysis and calculations of the activation energy suggested that the behavior of the crystallization activation energy depends on the range of heating rates. Therefore, the thermal behavior can be studied in three different regimes, i.e., 3-15, 20-50, and 60-99 K min^{-1} , as reflected in Fig. 2. Fig. 2 depicts the relationship between $\beta/T_p^{1.92}$ versus $10^3/T_p$ for the three regimes. The slope of each line corresponds to the activation energy within the specified heating-rate regime. From the slope of the three lines corresponding to the three heating regimes, it can be clearly seen that the activation energy decreased as the heating rate increased. It was found that as the heating rate increased, a remarkable decrease in the activation energy was observed, for $\beta = 3-15 \text{ K min}^{-1}$, E in the order of $116.4 \text{ kJ mole}^{-1}$, for $\beta = 20-50 \text{ K min}^{-1}$, E in the order of $56.6 \text{ kJ mole}^{-1}$, and for $\beta = 60-99 \text{ K min}^{-1}$, E in the order of $37.6 \text{ kJ mole}^{-1}$. The activation energy obtained considering the heating rates from $\beta = 3-99 \text{ K min}^{-1}$ was 80 kJ mole^{-1} . This behavior is consistent with the one observed [10]. It is well known that the crystallization kinetics of

chalcogenide materials including ZnSe are described in terms of the activation energies of amorphous and crystalline transformation [22]. Fig. 3 presents the variation of the effective crystallization activation energy as a function of the extent of relative crystallization for ZnSe. These values were obtained on the basis of the above two isoconversional methods. Several observations can be drawn from Fig. 3: (1) for the three aforementioned regimes, the activation energy obtained using the Friedman method is always lower than that obtained using the Starink method. Such differences between the two models can be attributed to the approximation adopted in the integral form (Starink). The sensitivity of the rate of conversion ($d\alpha/dt$) in the Friedman method might be another reason to make such a difference, which leads to imprecision in the kinetic analysis [23]; (2) the calculated activation energy depends on the heating rate range. The average of activation energy is the highest for regime 1, indicating the potential for crystallization [24]. However, as the heating rate increases in regimes 2 and 3, a remarkable drop in the average activation energy is observed. This might be due to the decrease in viscosity of the medium at a high heating rate; and (3) all the processes have the same tendency, and it can be seen that the two methods yield a decrease in the activation energy with increasing α . However, the decrease is more pronounced in regime 1. Such a remarkable decrease signifies that the different behavior in crystallization also indicates the crystallization behavior of the first regime. Changes in the conversion fraction do not appear to appreciably alter regime 3. Fig. 4 shows the variation in the activation energy as a function of temperature obtained using the Starink method. For regime 1, activation energy decreases from 130 to 107 kJ/mole. In regime 2, the activation energy drops from 70 to 47. However, the variation in the activation energy in regime 3 is the minimum. This variation in the activation energy suggests that the crystallization process occurs in a multi-step process involving different growth mechanisms. In fact, nucleation and diffusion take place where the activation energy for both differs [25]. Fig. 5 shows the predicted isothermal relative degree of crystallinity (or fractional crystallization) as a function of time. These curves were obtained based on the non-isothermal crystallization plots of the ZnSe samples at different heating rates of regime 1. The crystallization curves relative to time have a sigmoidal shape. The sigmoidal shape suggests that the heating rate has a lagging effect relative to the crystallization process. The reliability of such prediction using AKTS package has been reported elsewhere [26, 27].

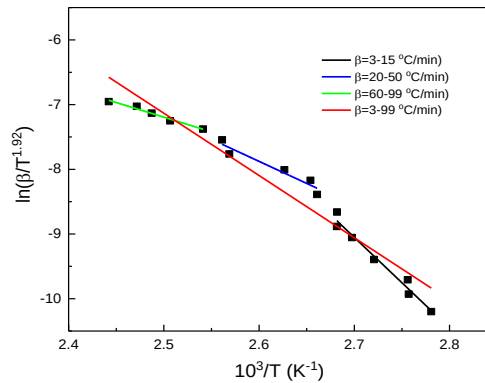


Fig. 2. Starink plot from which the activation energy was calculated.

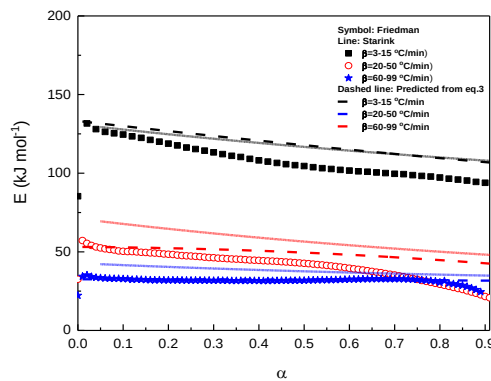


Fig. 3. Variation of the activation energy with α as obtained by Friedman (symbols) and Starink (lines) for the three heating-rates regimes.

In the isothermal model, the activation energy of crystallization can be deduced using the Arrhenius equation, in which the time required for a given crystallized fraction and temperature is related as follows:

$$k = A \exp\left(\frac{E_{\alpha}}{RT_{\alpha}}\right) \quad (3)$$

where k is the reaction rate constant (1/s), A a constant, E_{α} the activation energy, R the universal gas constant, and T is the temperature. Another approach can be used to calculate the activation energy based on the isothermal prediction as follows:

$$t(\alpha) = t_0 \exp\left(-\frac{E_{\alpha}}{RT_{\alpha}}\right) \quad (4)$$

Variation in activation energy as the crystallization progress using equation 3 and 4 are also reflected in Fig. 3. However, the activation energy at $\alpha = 0.5$ is shown in Table 1. The values are very comparable, suggesting that the crystallization process for non-isothermal and isothermal follows a very similar phase transformation mechanism. Also, such good agreement indicates the AKTS package's accuracy in predicting the isothermal parameters.

Table 1. Crystallization activation obtained using the Starink and Arrhenius equation.

Heating-rate regime	Starink model (kJ mol ⁻¹)	E (from prediction) (kJ mol ⁻¹)	Arrhenius equation (kJ mol ⁻¹)
3-15	116.4	116	113.9
20-50	56.6	50	47.7
60-99	37.6	32	32.3

The Johnson-Mehl-Avrami (JMA) method [28-30], from which the isothermal crystallization kinetics can be analyzed, is usually written in a double logarithmic form as follows:

$$\ln[-\ln(1 - \alpha_t)] = n \ln k + n \ln t \quad (5)$$

where n is the Avrami exponent and k the overall kinetic rate constant. Both k and n depend on the mechanism of nucleation as well as the growth geometry. The plotting of $\ln[-\ln(1-\alpha_t)]$ against $\ln t$ at a certain temperature (isothermally) yields straight lines; the slope and the intercept of these lines give n and $\ln k$, respectively. Fig. 6 represents such a plot for regime 1. The linearity of the obtained data validates this approach's applicability. Fig. 7 shows the variation of Avrami's exponents as a function of temperature for the three heating-rate regimes. The average n for regime 1 is 1.4, indicating the one-dimensional crystallization process. However, for regime 2, a two-dimensional growth is indicated, as the average n is 2.1. In both regimes, a decrease in n values is observed as a function of temperature. Interestingly, n values are independent of temperature for regime 3.

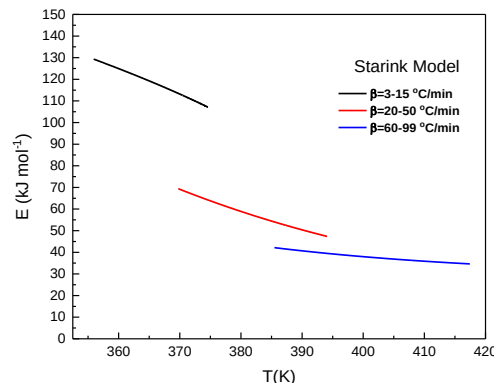


Fig. 4. The temperature dependence of the effective activation energy calculated using the Starink model.

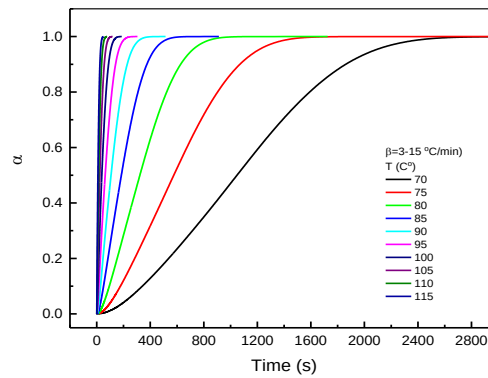


Fig. 5. Variation of the crystallization fraction over time (isothermally) calculated at 10 different temperatures of ZnSe using the AKTS software package.

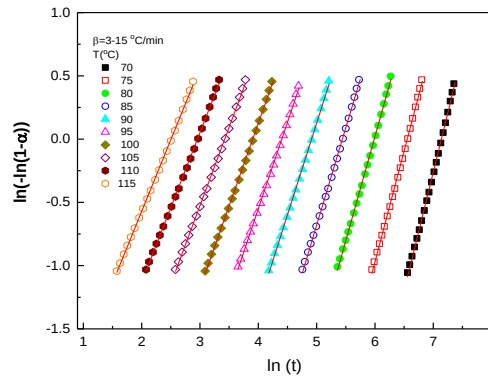


Fig. 6. The plot of $\ln[-\ln(1-\alpha)]$ versus $\ln t$ obtained for regime 1 at the temperatures shown in Fig. 5. Symbols are the predicted values and lines are the linear fit.

To validate the calculated Avrami's exponents obtained by the isothermal prediction approach, Matusita's analysis [29] was utilized to calculate these values according to equation 6. To obtain n numbers using Matusita's approach, experimental data are necessary to determine pertinent kinetic parameters.

$$n = - \frac{d \{ \ln[-\ln(1-\alpha)] \}}{d(\ln \beta)} \bigg|_T \quad (6)$$

The calculated n for the three regimes are also included in Fig. 7. It is readily evident from Fig. 7 that the calculated data agree well with those obtained from the prediction, indicating that the isothermal analysis can be used adequately to obtain n under non-isothermal conditions [19]. Fig. 8 depicts the variation in the reaction rate constant for each heating rate regime.

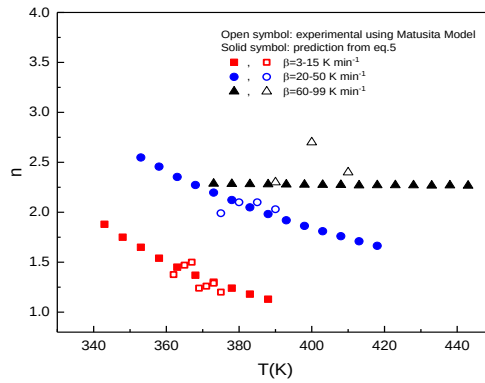


Fig. 7. Variation of the Avrami exponent n as a function of temperature for the three heating-rates regimes. n was obtained using the Matusita (open symbols) and Avrami equations (solid symbols).

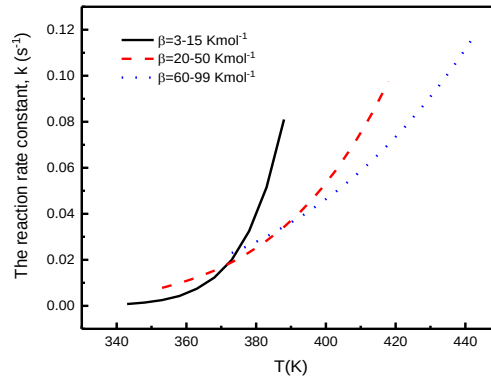


Fig. 8. Variation in the reaction rate constant as a function of temperature for the three heating rate regimes.

The time needed for the relative crystallinity of the sample to reach 50% of the total crystallization is defined as the crystallization half-time $t_{1/2}$ and can be calculated using [30]:

$$t_{1/2} = \left(\frac{\ln 2}{k} \right)^{\frac{1}{n}} \quad (7)$$

Fig. 9 compared $t_{1/2}$ obtained for the three regimes as a function of temperature. As the figure indicates, the half-time get smaller as the temperature increases, suggesting that the crystallization process is enhanced at higher temperatures. The $t_{1/2}$ value of regime 1 is higher relative to regimes 2 and 3. However, the values drastically decrease as the temperature increases. The small values of $t_{1/2}$ indicate faster crystallization rates.

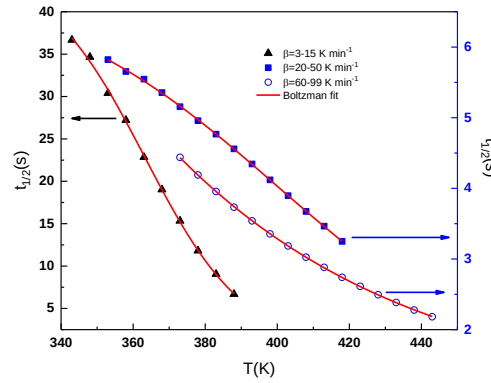


Fig. 9. Half-time of crystallization as a function of temperature for the three heating-rate regimes.

4. Conclusions

The non-isothermal approach was adopted to obtain the kinetic parameters, including the activation energy, Avrami exponent, and crystallization half-time. DSC exotherms show one pronounced peak for all heating rates, indicating a single phase formation while crystallization occurs. The results showed that the response of the ZnSe chalcogenide varied based on the heating rate range. Accordingly, we have performed the calculation on three different heating regimes ($\beta = 3-15$, $20-50$, and $60-99 \text{ K min}^{-1}$).

For the activation energy calculation rate, the Friedman and Starink models were used. The trend of the activation energy in the three heating rate regimes was similar with a small drop in the values although $E_1 > E_2 > E_3$, which might be attributed to the approximation methods. Our study showed that the values of the activation energy obtained in the non-isothermal condition (Starink) and that were deduced through the isothermal condition (Arrhenius equation) were very close, suggesting that the crystallization process on non-isothermal and isothermal conditions obey a very similar phase transformation mechanism. In general and for both models, a slight decrease was observed in the activation energy as a function of the crystallization fraction. Such phenomena can be attributed to the fact that as crystallization progresses, the energy required for nucleation decreases. Therefore, the activation energy's value is lower.

The average value of the Avrami exponent was 1.4 for regime 1 and 2.1 for regime 2. These values assume one and two-dimensional growth, respectively. The Avrami exponent deduced through the Matusita model yielded very similar results.

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