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Crystallization process analysis for $Se_{0.95}In_{0.05}$ and $Se_{0.90}In_{0.10}$ chalcogenide glasses using the contemporary isoconversional models

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Abstract Carrying out crystallization studies for both $Se_{0.95}In_{0.05}$ and $Se_{0.90}In_{0.10}$ chalcogenide glasses under non-isothermal conditions at different heating rates, it was realized that a rate controlling process occurs where random nucleation of one- to two-dimensional growth is accompanied with the introduction of up to 10 at% In into glassy Se matrix. The crystallization kinetics together with its dimensionality has been studied using the four currently used isoconversional models (Kissinger–Akahira–Sunose, Ozawa–Flynn–Wall, Tang, and Starink). The activation energy of crystallization (E_c) has been determined using these indicated four models where a satisfactory concurrence is achieved. The value of E_c shows a decrease while increasing both the In-content as well as the extent of crystallization.

Keywords Thermal analysis · Differential thermal analysis (DTA) · Isoconversion methods · Crystallization kinetics · Non-crystalline semiconductors · Chalcogenide glasses · III–VI semiconductors · Selenium–Indium (Se–In)

Introduction

The recognizable substantial interest of research workers in chalcogenide glasses is attributed to the likelihood of their various applications in different fields of electronics based on the nature of the non-crystalline to crystalline phase transformation criteria and its influenced change on the corresponding optical as well as electrical properties. 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 or threshold behavior of these materials is determined basically by their crystallization ability. Those which are prone to easy devitrification show memory and stable glasses exhibited threshold behavior. Kinematical studies give important conclusions for the suitable usage of a chalcogenide glass in the proper application field [1–4].

Binary selenium–indium (Se–In) alloys are turning out to be more attractive materials for their potential applications. Se–In alloys with the general formula $A^{III}B^{VI}$, possess layered structure. Such structure allows for intercalation of atoms or molecules, so that their physical properties can be changed without destroying the initial structure (c.f. [5] and references cited therein). This characteristic feature has been utilized to assemble batteries. The fundamental technologies of electronics are used for low-cost and simple photo-converters with exactly predicted properties. Besides, it is also found that the optical band gap of Se–In alloys is of the order of 1.3 eV at 300 K, which is adjacent to the theoretical optimum value for solar energy conversion. Subsequently, glassy Se–In alloys have drawn great attention because of their potential applications in solar cells (c.f. [6] and references cited therein). Despite this reality, these alloys are still found to have low glass transition and crystallization temperatures, and hence their physical properties may deteriorate with temperature changes and over time during the operation.

Traditional studies of glass transition and/or crystallization kinetics are often limited to idealized conditions, in

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which the parameters of state (temperature, pressure, … etc.) are constant. Meanwhile, and in real circumstances, the external conditions change continuously, thus causing the kinetics of the transformation process to be dependent on instantaneous conditions, as well as on the rate of change. In a previous paper [7], a non-isothermal glass transition kinetics has been studied for the two $Se_{0.95}In_{0.05}$ and $Se_{0.90}In_{0.10}$ chalcogenide semiconductor glasses. The specific selection for these two Se–In compositions is critically reviewed elsewhere [7]. This study came up with the fact that the increase of glass transition temperature (T_g) with increasing the introduction of In-content (up to 10%) has a positive impact on different calculated stability parameters of glassy selenium (g-Se). Moreover, it exemplified that the glass transition activation energy (E_g) showed a decrease with In-content in the g-Se matrix. In fact, the usage of isoconversion methods is a trustworthy technique for obtaining reliable and consistent kinetic information from non-isothermal data. Hence, the complexity of multiple reactions can be ascribed due to dependence of the activation energy on the extent of conversion. The present work aims at studying the crystallization process for these two Se–In chalcogenide glassy compositions using different isoconversion methods under non-isothermal condition.

Experimental

Binary chalcogenide glasses of the compositions $Se_{0.95}In_{0.05}$ and $Se_{0.90}In_{0.10}$ were prepared by the melt quenching technique. Details of the materials purity and preparation conditions have been described elsewhere [7]. The amorphous nature of the quenched ingots has been confirmed using X-ray diffraction recorded by Philip's computerized diffractometer of type XPERT-MPDUC PW 3040 with CuK_α radiation source $\lambda = 0.15406$ nm, at power of 1600 W (40 kV and 40 mA). The freshly as-prepared materials were grounded to formulate fine powder forms for differential thermal analysis (DTA) studies. The DTA measurements were carried out using Thermo-System of model: Mettler Hot-Stage FP80. For each DTA scan, whereby 20 mg of the powder was heated starting from room temperature at different heating rates, namely 1, 5, 10, 15, and 20 °C/min.

Results and discussion

Table 1 Heating rate dependence of the characteristic transition temperatures as a function of heating rate scans for the two Se–In quenched glasses investigated

β/°C/min	$Se_{0.95}In_{0.05}$				$Se_{0.90}In_{0.10}$			
	T_g/°C	T_0/°C	T_c/°C	T_m/°C	T_g/°C	T_0/°C	T_c/°C	T_m/°C
1	42	75	82	220	43	80.5	90	221
5	45	74	94.5	220	47	87	102	221
10	47	76	97.5	220	48.5	88	107.5	221
15	49	81	106.5	220	51.5	94	116	221
20	51	81	108.5	220	52.5	96	118	221

The DTA curves for the as-prepared $Se_{0.95}In_{0.05}$ and $Se_{0.90}In_{0.10}$ chalcogenide compositions have been automatically recorded at different heating rates in the range of 1:20 °C/min. These DTA curves are given elsewhere [7]. Each curve, of which, is characterized by an endothermic step corresponding to glass transition at temperature T_g, an exothermic peak due to crystallization with onset temperature T_0 and maximum rate of crystallization at T_c, and a well-defined endothermic peak due to melting at T_m. Table 1 summarizes these temperature transitions as a function of composition. The table indicates a shift to higher temperatures with increasing the heating rate for both $Se_{0.95}In_{0.05}$ and $Se_{0.90}In_{0.10}$ compositions.

Analysis of the exothermic peaks

As being acknowledged, the process of crystallization is usually preceded with two different temperature-dependent stages. These are: nucleation of fine crystalline centers and crystal growth of these nuclei. This could be achievable through an isothermal or continuous heating (non-isothermal) fashion. In the case of non-isothermal study, one of the very useful techniques is that correlated to the DTA (or DSC). The exothermic peak that is observed in the DTA scan of a glassy material is generally applied for the sake of studying the crystallization process in such a glass.

The fraction α crystallized at any temperature, T, can be calculated from the DTA exothermic peak using the relation $\alpha(T) = A_T/A$, where A_T is the partial area at the temperature interval ΔT, and A is the total area of the exothermic peak, i.e., the area between the onset crystallization T_0, where crystallization just commences, and the end temperature of crystallization. Figure 1 illustrates the variation of α with temperature for both $Se_{0.95}In_{0.05}$ and $Se_{0.90}In_{0.10}$ glasses at the different heating rates investigated.

In fact, the crystallization kinetics has been extensively scrutinized using the classical Jonson–Mehl–Avrami (JMA) equation [8] in which the crystallized fraction (α) is expressed as a function of time (t) as

$$\alpha(t) = 1 - \exp(-Kt^n), \qquad (1)$$

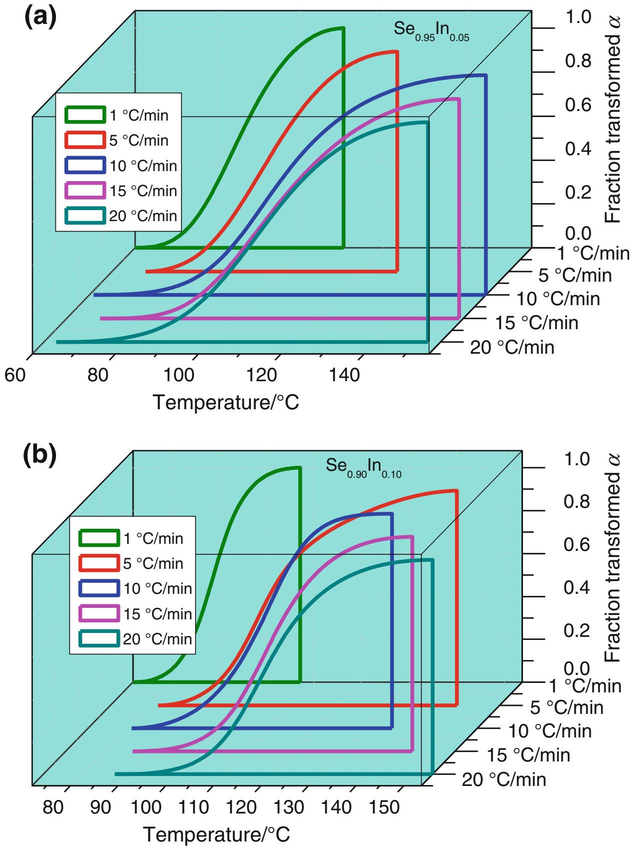

Fig. 1 Temperature dependence of fraction crystallized for **a** $Se_{0.95}In_{0.05}$ and **b** $Se_{0.90}In_{0.10}$ glasses as-scanned at different heating rates

where K is defined as an effective reaction rate constant and n is known as Avrami exponent that relies on the mechanism of growth and dimensionality of the process. Equation 1 is based on three basic assumptions: (i) isothermal transformation conditions; (ii) spatially random nucleation; and (iii) the growth rate of the new phase is dependent only on temperature and not on time. In this respect, Evans's theoretical principle suggests linear change of the number of nuclei with time (i.e., linear growth kinetics). With an increase in the rate of increase of nuclei, the exponent n can attain increasing values; i.e., n can acquire continuous values up to 4 instead of 3 obtained in case of sporadic three-dimensional growth. In case of predetermined processes, n can get only three integer values, 1, 2, or 3, depending on whether it is one-, two-, or three-dimensional growth, respectively [9]. However, Hay [10], taking into account the experimental data obtained for polymer crystallization, had proved the possibility of half-integer values for n in case of lateral growth and in case of growth controlled by diffusion.

The rate constant K of JMA equation is given by an Arrhenius formula as

$$K = K_0 \exp\left(-\frac{E_c}{RT}\right), \tag{2}$$

where E_c is the activation energy for crystallization and R is the universal gas constant. The pre-exponential factor K_0 is considered to be constant with respect to temperature and most often called the frequency factor, as is a measure of the probability that a molecule having energy E_c will participate in a reaction.

Three decades ago, Henderson [11] explained that the JMA equation can be broadly applied to cover non-isothermal conditions if the entire nucleation process takes place during the early stages of the transformation process, however, it becomes negligible afterwards. This case has been referred in literature to as *site saturation* (c.f. [12] and references cited therein). Here, the crystallization rate is defined only by temperature and is not contingent on the previous thermal history of the material investigated. In other words, to apply the JMA equation under non-isothermal conditions, sufficient randomly distributed nuclei must be presented at the initiation of the crystallization process. Whilst the additional nucleation is possibly activated during the crystallization process having a negligible impact on the overall crystallization kinetics [13].

Obtaining the correct reaction mechanism by non-isothermal techniques, the isothermal transformation rate ($\mathrm{d}\alpha/\mathrm{d}t$), can be easily determined from Eq. 1 after its differentiation with respect to time to yield

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = nK(1-\alpha)[-\ln(1-\alpha)]^{(n-1)/n} \tag{3}$$

In order to determine the solid state transformation mechanism using non-isothermal techniques, it is obligatory to use the assumption of isothermal conditions where the transformation rate of a solid–state reaction is the product of two functions: one dependent on (T) and the other dependent on (α), [14]. Accordingly, Eq. 3 can be written as

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = K(T)f(\alpha) = K_0 f(\alpha)\exp\left(-\frac{E_c}{RT}\right), \tag{4}$$

where $f(\alpha)$ is a dependent kinetic model function. For non-isothermal condition, when the temperature varies with time with a constant heating rate $\beta = \mathrm{d}T/\mathrm{d}t$, Eq. 4 is modified to be

$$\beta\frac{\mathrm{d}\alpha}{\mathrm{d}T} = f(\alpha)K_0\exp\left(-\frac{E_c}{RT}\right) \tag{5}$$

This last equation can be integrated by the separation of variables to be

$$g(\alpha) = \int_0^{\alpha}\frac{\mathrm{d}\alpha}{f(\alpha)} = \frac{K_0}{\beta}\int_{T_0}^{T}\exp\left(-\frac{E_c}{RT}\right)\mathrm{d}T, \tag{6}$$

where g(α) is the integral form of the reaction model and T_0 is the initial temperature. If it is assumed that $T_0 \ll T$, so the upper limit of the integral can be approximated to be infinity; i.e.,

$$g(\alpha) \approx \frac{K_0 E_c}{\beta R} \int_x^{\infty} \frac{\exp(-x)}{x^2} \mathrm{d}x = \frac{K_0 E_c}{\beta R} p(x) \tag{7}$$

Here, $p(x)$ is the temperature integral, where $x = E_c/RT$, which does not have analytical solution. Hence, the logarithmic form of Eq. 7 can be expressed as

$$\ln[g(\alpha)] = \ln \frac{K_0 E_c}{\beta R} + \ln[p(x)] \tag{8}$$

The function $p(x)$ is not integrable in closed form and the authors Lopez-Alemany et al. [12] have developed a method to evaluate it by an alternating series, resulting

$$\begin{aligned} p(x) &= \left[-\frac{\mathrm{e}^{-x}}{x^2} \sum_{r=0}^{\infty} \frac{(-1)^r (r+1)!}{x^r} \right]_x^{\infty} \\ &= -\frac{\mathrm{e}^{-x}}{x^2} \sum_{r=0}^{\infty} \frac{(-1)^r (r+1)!}{x^r} \end{aligned} \tag{9}$$

The expression $\ln[p(x)]$, to a first approximation, is a linear function of $1/T$, if x is sufficiently large. Therefore, in the range of $20 < x < 60$, the function $\ln[p(x)]$ with $r = 0$, can be fitted very satisfactorily by the following linear approximation:

$$\ln[p(x)] \cong -5.1202 - 1.052x \tag{10}$$

In this consensus, it should be noted that, the term $\ln \frac{K_0 E_c}{\beta R}$, in Eq. 8, is independent of temperature. Thus, considering Eq. 8 as well as the above mentioned fact that $\ln[g(\alpha)]$ is a linear function of $1/T$, the relation between $\ln[g(\alpha)]$ and $1/T$ should be linear. Plotting the calculated values of $\ln[g(\alpha)]$ for various rate processes, using DTA (or DSC) technique, versus the corresponding $1/T$ values ought to give a straight line only for the rate process which can be designated as the most probable one. The others, for which this plot is not linear, can be refused. In other words, $g(\alpha)$ is determined by comparing the experimental data with different kinetic equations. In Fig. 2, $\ln[g(\alpha)]$ is plotted versus $1/T$ for different rate-controlling processes that calculated from the DTA exothermic peaks for the two considered binary Se–In glassy compositions recorded at $\beta = 1$ °C/min, with the functions labeled according to the symbols given by Sharp et al. [15]. Figure 2a for $Se_{0.95}In_{0.05}$ shows that the function $F_1(\alpha)$, $n = 1$, where $\ln(1 - \alpha) = Kt$, is in full agreement with the experimental calculations executed over the maximum range of α (90%). A least-squares fit to the experimental points indicates that deviations from linearity are comparatively very small for the functions $A_2(\alpha)$ and $A_3(\alpha)$, where the fitting region is of 80–85%. For $Se_{0.90}In_{0.10}$ (Fig. 2b), however, the experimental calculation is critically fitted to the function: $A_2(\alpha)$, $n = 2$, where $[-\ln(1 - \alpha)]^{1/2} = Kt$. Also, fitting can be achieved with the two functions $F_1(\alpha)$ and $A_3(\alpha)$, but only in narrower region of α; but, a rather poor fit can be seen for the rest of the other rate-controlling processes, where the linearity is only partially obeyed in a narrow range of α. Both functions, $F_1(\alpha)$ and $A_2(\alpha)$, indicate a random nucleation process in which the growth is diffusion controlled for the two Se–In glassy alloys investigated. Here, it is worth emphasizing that the accurate knowledge of the value of n is crucial for determining the kinetic parameters for the process investigated.

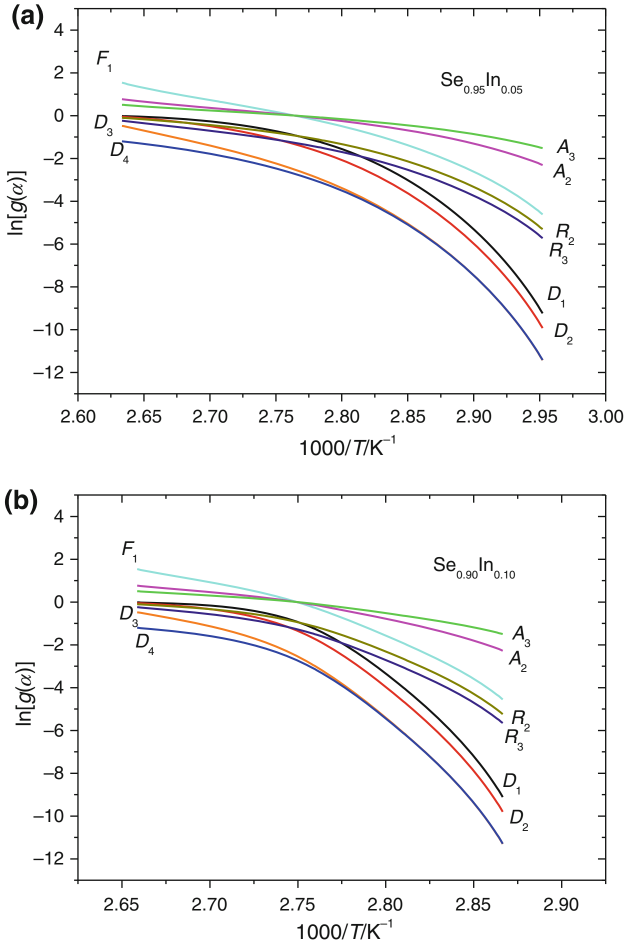

Fig. 2 Plots of $\ln[g(\alpha)]$ versus $1000/T$ for the investigated glasses for various kinetic equations with their labels according to the symbols given by Sharp et al. [15]

Evaluation of the kinetic parameters E_c and n

In non-isothermal crystallization, it is assumed that there is a constant heating rate; hence, the relation between the sample temperature and the heating rate can be written as

$$T = T_0 + \beta t \tag{11}$$

As the temperature constantly changes with time, K is no longer constant but varies with time in a more complicated form, and Eq. 1 becomes [16]

$$\alpha(t) = 1 - \exp\left[\left\{-K\left(\frac{T - T_0}{\beta}\right)^n\right\}\right] \tag{12}$$

After shuffling and taking double logarithms of Eq. 12 into account, one has

$$\ln[-\ln(1-\alpha)] = \ln x(T) - n\ln\beta \tag{13}$$

So, a plot of $\ln\beta$ versus $\ln[-\ln(1-\alpha)]$ should give a straight line with slope equals to n and the intercept of the ordinate is $x(T)$. The latter is constant at a particular temperature. Figure 3 shows just such a plot for both $Se_{0.95}In_{0.05}$ and $Se_{0.90}In_{0.10}$ glasses at different specific temperatures lie during the range of the exothermic crystallization peak. Here, it is worth highlighting that not all the considered heating rates (1, 5, 10, 15, and 20 °C/min) appear on each selected temperature in the figure. This arises as a result of the observed shift for the crystallization peak when changing β. Here, it is found that the calculated values of n varies in a non-monotonic approach and its average value is 0.86 ± 0.08 for $Se_{0.95}In_{0.05}$. That is, the transformation is considered to be one-dimensional growth. However, the average value of n is 1.65 ± 0.16 for $Se_{0.90}In_{0.10}$ indicating that the transformation is proceeded through two-dimensional growth. This means that the addition of 5 at% In to g-Se cannot greatly affect the main chain-ring structural frame-work of Se ($n \sim 1$). While, the addition of 10 at% In is accompanied with a change in the structure to be a layered one ($n \sim 2$) [17].

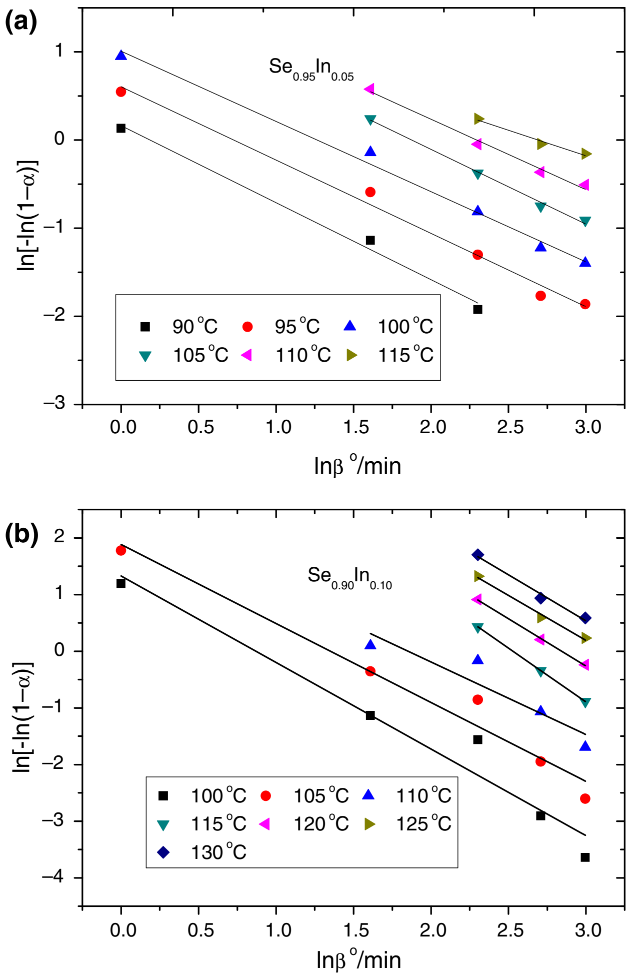

Fig. 3 Plots of $\ln[-\ln(1-\alpha)]$ versus $\ln\beta$ for the investigated glasses at different selected temperatures during the DTA exothermic peaks. The *solid lines* represent least-squares fitting

In order to determine the value of E_c using a continuous heating technique, it is necessary to consider, as previously mentioned, a reaction rate independent of the thermal history that expressed as the product of two separable functions: absolute temperature and fraction transformed (Eq. 4). Here, Eq. 7 can be rewritten in a simple form as follows:

$$g(\alpha) = \frac{K_0 E_c}{\beta R} p(x) \tag{14}$$

In fact, the temperature integral $p(x)$ for $x = E_c/RT$, does not have analytical solution, and several approximations have been introduced to solve it. In general, all of these approximations lead to direct isoconversion methods in the form [18]:

$$\ln\left(\frac{\beta}{T_\alpha^h}\right) = b - c\frac{E_c}{RT_\alpha} \tag{15}$$

For each degree of the conversion fraction (α), a corresponding temperature (T_α) and rate (β) are used to plot $\ln\left(\frac{\beta}{T_\alpha^h}\right)$ versus $1/T_\alpha$, where h, b, and c are constants depend on the used method of calculation. The apparent activation energy of crystallization, E_c, can be determined from the resulted regression slopes at the different stages of crystallization. In this respect, the evaluation of E_c for the two quenched $Se_{0.95}In_{0.05}$ and $Se_{0.90}In_{0.10}$ semiconductor chalcogenide glassy alloys has been done using the four most currently used models, namely Kissinger–Akahira–Sunose (KAS) [19, 20], Ozawa–Flynn–Wall (OFW) [21, 22], Tang [23] and Starink [24]. The difference in the accuracy between one method of calculation in these four models, as well as in others, depends on the method of solving the behavior of the exponential-integral function, $p(x)$.

Kissinger–Akahira–Sunose (KAS) method [19, 20]

Early in 1957, Kissinger derived a model for calculating the value of E_c at the maximum rate of crystallization that reached at T_c, as

$$\ln\left(\frac{\beta}{T_c^2}\right) = \text{Constant} - \frac{E_c}{RT_c} \tag{16}$$

Such a method of calculation has been improved by Akahira and Sunose and now is known as Kissinger–Akahira–Sunose (KAS) method. This method is based on the Coats–Redfern approximation [25] according to which $20 < x < 50$:

$$p(x) \cong \frac{\exp(-x)}{x^2}\left(1 - \frac{2}{x}\right) \tag{17}$$

From Eqs. 14 and 17, one gets

$$\ln\left(\frac{\beta}{T^2}\right) = C_{\mathrm{KAS}} - \frac{E_c}{RT} \tag{18}$$

where the pre-exponential factor $C_{\mathrm{KAS}} = \ln\frac{K_0 R}{E_c g(\alpha)}$. Here, a plot of $\ln\left(\frac{\beta}{T^2}\right)$ versus $1/T$ should give a straight line whose slope $-\left(\frac{E_c}{RT}\right)$ can be used to evaluate the value of E_c. Figure 4 shows just such a relation plotted at different values of the crystallized fraction ($\alpha = 0.1{:}0.9$) for both $\mathrm{Se}_{0.95}\mathrm{In}_{0.05}$ and $\mathrm{Se}_{0.90}\mathrm{In}_{0.10}$ glasses investigated; where the respective values of E_c at $\alpha = 0.5$ are found to be 117.97 and 113.8 kJ/mol. These values can be compared with those found when applying the first equation of Kissinger (Eq. 16; Fig. 5) that leads to 118.6 and 113.6 kJ/mol, respectively.

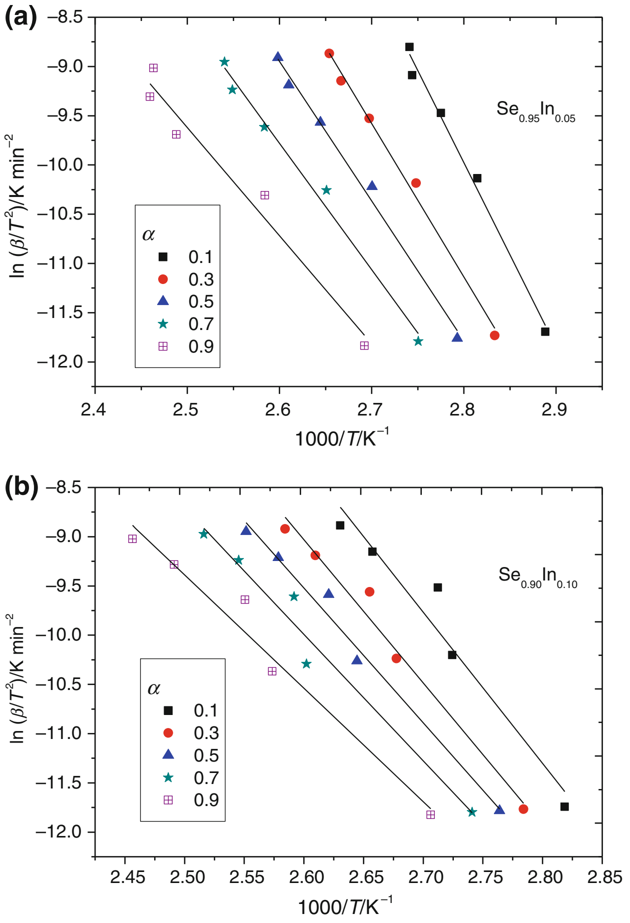

Fig. 4 Plots of $\ln\left(\frac{\beta}{T^2}\right)$ versus $1000/T$ for the investigated glasses at different crystallized fractions. The *solid lines* represent least-squares fitting

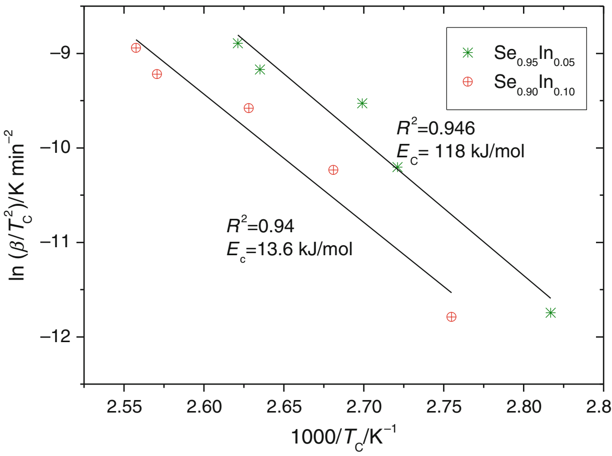

Fig. 5 Plots of $\ln\left(\frac{\beta}{T_c^2}\right)$ versus $1000/T$ for the investigated glasses. The *solid lines* represent least-squares fitting

Ozawa–Flynn–Wall (OFW) method [21, 22]

An isoconversional integral method that suggested independently by Ozawa [21] and by Flynn and wall [22] that using the Doyle's approximation for $p(x)$ [26] is

$$\log p(x) \cong \log p_0(x) = -2.315 + 0.4567x \tag{19}$$

Combing Eqs. 14 and 19 leads to

$$\ln\beta = C_{\mathrm{OFW}} - 1.052\frac{E_c}{RT} \tag{20}$$

where $C_{\mathrm{OFW}} = \ln\left(\frac{k_0 E_c}{Rg(\alpha)}\right)$. Thus, a plot of $\ln\beta$ versus $1/T$ for different selected values of α gives a group of straight lines whose slopes can be used to evaluate the values of E_c. The OFW plots are presented in Fig. 6 for both $\mathrm{Se}_{0.95}\mathrm{In}_{0.05}$ and $\mathrm{Se}_{0.90}\mathrm{In}_{0.10}$ glasses investigated, where the respective values of E_c at $\alpha = 0.5$ are found to be 118 and 114.06 kJ/mol.

Tang method [23]

This method depends on the values of $p(x)$ at different x that obtained directly from the numerical integration of the temperature integral in Eq. 14 without derivation from any approximating infinite series. Here, the equation for evaluation of the non-isothermal kinetic parameters has the following form:

$$\ln\left(\frac{\beta}{T^{1.894661}}\right) = C_{\mathrm{Tang}} - 1.052\frac{E_c}{RT} \tag{21}$$

where $C_{\mathrm{Tang}} = \left[\ln\left(\frac{K_0 E_c}{Rg(\alpha)}\right) + 3.635041 - 1.894661 \ln E_c\right]$. Accordingly, the Tang plot, i.e., the relation between

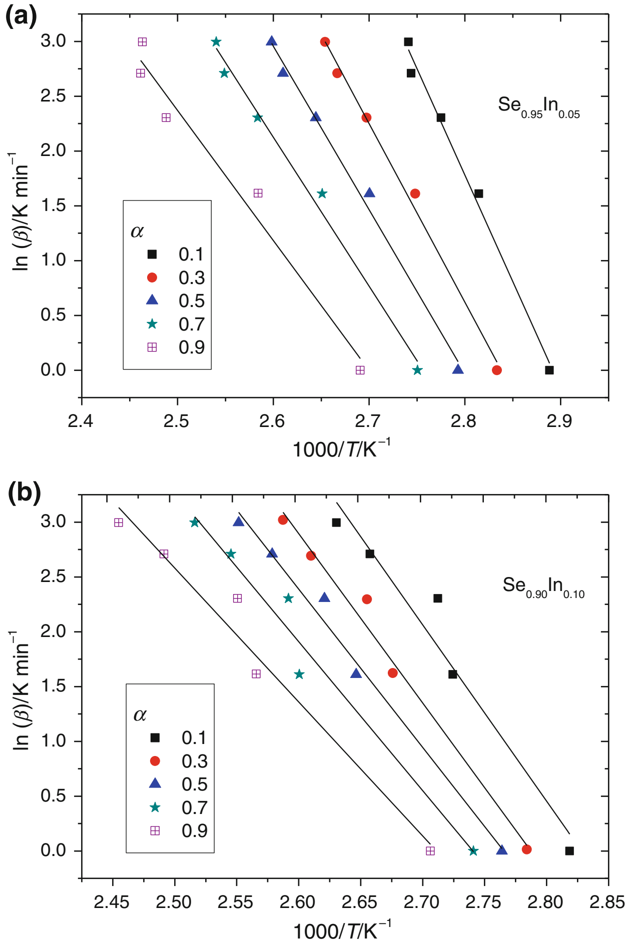

Fig. 6 Plots of lnβ versus 1000/T for the investigated glasses at different crystallized fractions. The *solid lines* represent least-squares fitting

$\left(\ln\frac{\beta}{T^{1.894661}}\right)$ versus 1/T, is shown in Fig. 7 at particular values of α. Here, the respective evaluated values of E_c at $\alpha = 0.5$ for both $Se_{0.95}In_{0.05}$ and $Se_{0.90}In_{0.10}$ are found to be 118.13 and 113.96 kJ/mol.

Starink method [24]

This method depends on a more general approximation (Doyle's approximation); i.e., $\left[p(x) \cong \frac{\exp(-x)}{x^2}\right]$ so that

$$p(x) \cong \frac{\exp(-\lambda x + \delta)}{x^l} \tag{22}$$

Such a class of approximations leads to a distinct group of methods; each value of the exponents l, λ, and δ can be optimized by minimizing the deviation between the approximation function and the exact integral. The one with $\lambda = 1$, that is most accurate for $20 < x < 60$, is obtained with $l = 1.95$, that leads to

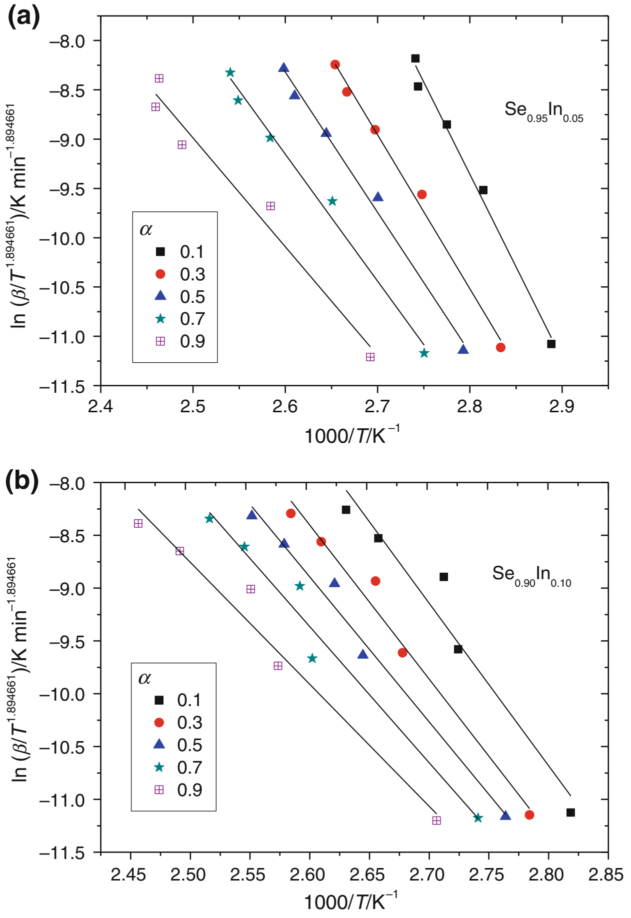

Fig. 7 Plots of ln($\beta/T^{1.894661}$) versus 1000/T for the investigated glasses at different crystallized fractions. The *solid lines* represent least-squares fitting

$$p(x) \cong \frac{\exp(-x - 0.253)}{x^{1.95}} \tag{23}$$

In addition, Starink made a further analysis for a highly accurate approximation assuming that λ is not required to be equal to 1. Hence, Eq. 23 becomes

$$p(x) \cong \frac{\exp(-1.0008x - 0.312)}{x^{1.92}} \tag{24}$$

Accordingly, combining Eqs. 24 and 14 leads to Starink formula [24]

$$\ln\left(\frac{\beta}{T^{1.92}}\right) = C_{\mathrm{Starink}} - 1.0008\frac{E_c}{RT} \tag{25}$$

where C_{Starink} is a constant. Figure 8 shows Starink plot; i.e., the relation between $\ln\left(\frac{\beta}{T^{1.92}}\right)$ and 1/T at specific values of α for both $Se_{0.95}In_{0.05}$ and $Se_{0.90}In_{0.10}$ glasses investigated. Here, the respective evaluated values for E_c at $\alpha = 0.5$ are found to be 118.13 and 113.95 kJ/mol. Comparing these latter two values for E_c with those obtained from the three previous models (KAS, OFW, and Tang), one can conclude

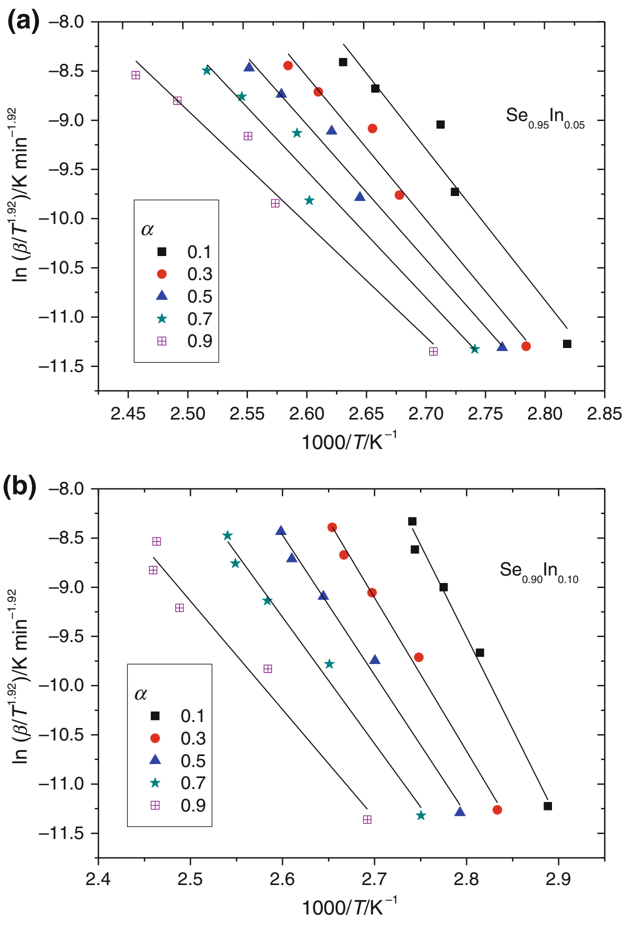

Fig. 8 Plots of $\ln(\beta/T^{1.92})$ versus $1000/T$ for the investigated glasses at different crystallized fractions. The *solid lines* represent least-squares fitting

an average value for E_c at $\alpha = 0.5$ to be 118.06 ± 0.16 kJ/mol for 5 at% In, and 113.94 ± 0.25 kJ/mol for 10 at% In. Moreover, the coincidence of the calculated values of E_c obtained by the used four calculation methods confirms that the crystallization activation energy of $Se_{0.95}In_{0.05}$ is greater than that of $Se_{0.90}In_{0.10}$. Comparing these values with that for pure g-Se (179 kJ/mol, [27]), indicates that the introduction of up to 10 at% In leads to decreasing its E_c value.

Figure 9 demonstrates the evaluated values of E_c at different fractional values α(0.1:0.9) for the two Se–In glassy compositions investigated. The figure declares a similar trend for the variation of the function $E_c = f(\alpha\%)$ for both compositions; i.e., decreasing the value of $E_c(\alpha)$. Also, the curve affirms a similar increase in the value of E_c with decreasing In-content in Se from 10 to 5 at%.

Here, it is significant noting that increasing the time (or temperature) during the process of crystallization (exothermic DTA curve) leading to the expected increase in the value of α. As a result, the calculated activation energies are apparent values, depending on the activation energy of the two elementary processes (nucleation and growth) involved in the crystallization process, remembering that the activation energy of nucleation is temperature-dependent. Such a behavior confirms the complex mechanisms of glass crystallization process, involving probably a self-accelerating effect. This behavior is similar to that found in other interesting glassy materials [28–30].

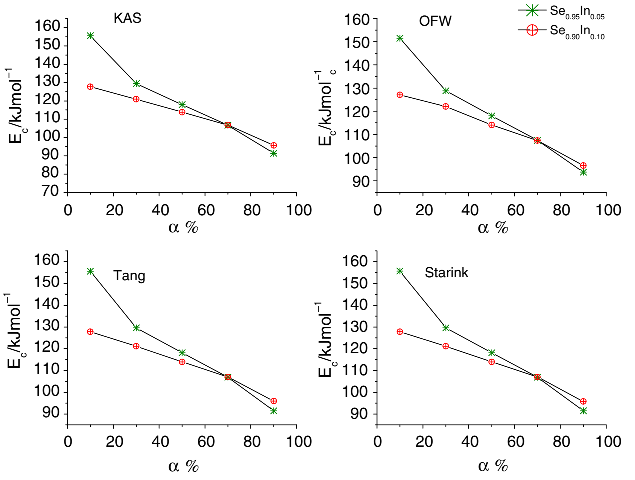

Fig. 9 Variation of E_c with fractional volume α as calculated from KAS, OFW, Tang, and Starink applied methods for the glasses investigated

Conclusions

Throughout the study introduced in this document, kinetics of the rate-controlling processes of the two interesting binary semiconductor chalcogenide Se–In alloys, namely $Se_{0.95}In_{0.05}$ and $Se_{0.90}In_{0.10}$, is analyzed applying the four most contemporary isoconversion methods (KAS, OFW, Tang, and Starink). This study leads to various interesting concluding remarks. Among these: the reaction mode n of the non-isothermal growth changed from one- to two-dimensional approaches with increasing the In-content in g-Se matrix. Values obtained for E_c upon using each of the four indicated methods are in reasonable agreement with one another. The value of E_c at $\alpha = 0.5$ showed a decrease from 179 kJ/mol for pure g-Se to 118.06 ± 0.16 kJ/mol for 5 at% In ($Se_{0.95}In_{0.05}$), to 113.94 ± 0.25 kJ/mol for 10 at% In ($Se_{0.90}In_{0.10}$). The observed decrease in the values of E_c while increasing the In-content confirms the previously obtained results of the different stability parameters for the same glassy compositions [7].

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