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Evaluation of the transformation kinetics of $Ga_{7.5}Se_{92.5}$ chalcogenide glass using the theoretical method developed and isoconversional analyses

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ABSTRACT

The transformation kinetics from glass to crystalline for $Ga_{7.5}Se_{92.5}$ chalcogenide glass were studied using the differential scanning calorimetry (DSC) technique. The kinetic parameters of present chalcogenide glass under non-isothermal conditions are analyzed by the theoretical method developed (TMD) and the isoconversional (model-free) method for a heating rate range of 5–90 K/min. The average values of the effective activation energy for crystallization ($E_{eff.}$) and the pre-exponential factor (A) are 73.61 ± 2.6 kJ/mol and 7.44×10^9 min^{-1}, respectively. The average value of the impingement exponent (γi) is 1.9636 ± 0.28 and the dependence of the maximum transformed fraction (α_P) on γi, indicates that the mode of impingement is due to "anisotropic growth". From the average values of the kinetic exponents (n and m), the transformation process of $Ga_{7.5}Se_{92.5}$ chalcogenide glass is volume nucleation with two- and one-dimensional growth, which are operating simultaneously during the glass–crystalline transformation. The average values of the separate activation energies for growth (E_G) and nucleation (E_N) are 78.02 ± 0.15 kJ/mol and 69.79 ± 0.74 kJ/mol, respectively. The results of the kinetic parameters of present chalcogenide glass using the isoconversional (model-free) method indicate that the effective activation energy of crystallization ($E_{eff.}(\alpha)$) is not constant but varies with the degree of transformation and hence with temperature. The reaction model that may describe transformation process is Avrami–Erofeev model ($g(\alpha) = [-\ln(1-\alpha)]^{1/n}$) with n equal to 3 and 2 for the heating rate ranges of 5–35 K/min and 40–90 K/min, respectively. Generally, the obtained results of all transformation kinetic parameters of $Ga_{7.5}Se_{92.5}$ chalcogenide glass using theoretical method developed analysis are in good agreement with that obtained according to the isoconversional method.

1. Introduction

Nano-crystalline metal selenide semiconductors have attracted considerable attention because of their size-dependent optical and electrical properties [1,2]. The applicability of gallium selenide in harmonic generation, parametric oscillation or frequency mixing in the near and middle infrared can be recognized in the literature [1,3]. Moreover, gallium selenide is suitable for fabrication of the optoelectronic devices in red and blue visible region [3,4].

Many techniques have been used to obtain bulk and thin film gallium selenide materials such as Bridgeman–Stockbarger method [1], ball milling [5], melt-quenching technique [6], chemical vapour deposition [7], chemical close-spaced vapour transport [8], vapour phase epitaxy [9], thermal evaporation [10] and molecular beam epitaxy [11]. GaSe chalcogenide is layered-type semiconductor that crystallized in a lattice with strong intralayer covalent bonds and weak interlayer van der Waals interactions [4]. GaSe is a diamagnetic semiconductor with each monolayer containing two gallium and two chalcogen closed-packed sublayers in the stacking sequence of Se–Ga–Ga–Se along *c*-axis. The photoconductivity, photovoltage and photoelectromagnetic effects have been studied at different excitation intensities between 80 K and 300 K for GaSe grown by the iodine transport method [12]. The experimental results give evidence that the conductivity of this material, which is n-type at room temperature, changes to p-type at low temperature [12]. Accordingly, great attentions have been devoted to study the structural [1,4,5], optical [13–15], electrical [16,17] and thermal [6,18] properties of GaSe and its compounds.

In the present work, the transformation kinetics of $Ga_{7.5}Se_{92.5}$ chalcogenide glass were studied using the differential scanning calorimetry, DSC, technique under non-isothermal conditions for a wide range of heating rates, β (5–90 K/min). From DSC data, the kinetic parameters such as effective activation energy, $E_{eff.}$, pre-exponential frequency, A, and growth (Avrami) exponent, n, are deduced using both the theoretical method developed (TMD) and isoconversional (model-free) analyses. In addition, the mode of impingement and the average values of the separate activation

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energies for growth, E_G, and nucleation, E_N, are evaluated. Finally, a verification of the corrected values of the kinetic parameters obtained, using both methods under non-isothermal conditions for a wide range of heating rates, have been achieved.

2. Theoretical background

2.1. Determination of kinetic parameters using the theoretical method developed (TMD)

2.1.1. Nucleation, growth and transformed fraction

The application of DSC to the characterization of the phase transformations has been previously examined by several workers [19–22]. Studies of the transformation kinetics of amorphous materials under non-isothermal conditions can be performed using several different ways and interpretations [23–31]. Generally, if the crystal growth is anisotropic and at time, t, the volume, $Y(t,\tau)$, of a particle nucleated at time τ is given as follows [24,25,32,33]:

$$Y(t,\tau) = g\prod_i \int_\tau^t \nu(t')dt' \tag{1-a}$$

In case of the crystal growth rate is isotropic, the above equation takes the following form:

$$Y(t,\tau) = g\left(\int_\tau^t \nu(t)dt\right)^{d/m} \tag{1-b}$$

where the expression $\prod_i \int_\tau^t \nu(t')dt'$ condenses the product of the integrals corresponding to the values of the above quoted subscript i, g is a geometric factor, which depends on the dimensionality and the shape of the crystal growth, m is the growth mode parameter ($m=1$ for interface-controlled growth, $m=2$ for volume diffusion-controlled growth) and d is the dimensionality of the growth ($d=1$–3). The growth velocity, $\nu(t)$, is given by [24,25,32,33]:

$$\nu(t) = \nu_o \ \exp\left(\frac{-E_G}{RT(t)}\right) \tag{2}$$

where E_G is the activation energy for growth. As mentioned by Starink and Zahra [23], the transformation is described using the so-called "extended volume" concept. In the "extended volume" individual particle (nuclei) grows without any limitation of space, where it is supposed that every nuclei grows in the absence of the other growing nucleus [23,32–34]. The extended transformed fraction, x_e, can be expressed in terms of Eq. (1) as [32–35]:

$$x_e = \int_0^t \dot{N}(T(\tau))Y(\tau,t)d\tau \tag{3}$$

where x_e (=V_e/V_o) is the extended transformed fraction, V_e is the extended volume and V_o is the sample volume. In case of continuous nucleation, the nucleation rate per unit volume, $\dot{N}(T(\tau))d\tau$, is expressed as follows [33–35]:

$$\dot{N}(T(t)) = N_o \ \exp(-E_N/RT(t)) \tag{4}$$

where N_o is temperature-independent nucleation rate, E_N temperature-independent activation energy for nucleation and R is gas constant. The relation between the change in the extended volume, V_e, and the actual (real) volume, V_a, is given by [32–34]:

$$dV_a = \left(\frac{V_o - V_a}{V_o}\right)dV_e \tag{5}$$

or

$$\frac{d\alpha}{dx_e} = 1-\alpha \tag{6}$$

where, α is the actual transformed fraction. The expression of the extended transformed fraction, x_e, in Eq. (3) takes the following form [24,25,32,33]:

$$x_e = (KRT^2E_{eff.}^{-1}\beta^{-1})^n \tag{7}$$

where n is the growth (Avrami) exponent, $E_{eff.}$ is the effective activation energy and K is the effective reaction rate constant, which is given as:

$$K = A \ \exp\left(\frac{-E_{eff.}}{RT}\right) \tag{8}$$

where A is pre-exponential frequency. The effective activation energy, $E_{eff.}$, which describes the overall transformation process has the following general relation with both the growth and nucleation activation energies [33,34]:

$$E_{eff.} = \frac{\{mE_G + (n-m)E_N\}}{n} \tag{9}$$

In the case of site saturation n equals to m and for continuous nucleation n equals to $(m+1)$. Using Eqs. (7)–(9), the extended transformed fraction, x_e, takes the following form [24,25,32,33]:

$$x_e = \left[ART^2E_{eff.}^{-1}\beta^{-1} \ \exp\left(\frac{-E_{eff.}}{RT}\right)\right]^n \tag{10}$$

2.1.2. Impingement mode and transformed fraction

As mentioned by Liu et al. [24,32], in case of anisotropic growing particles, the time interval that particles, after their randomly dispersed nucleation, can grow before blocking by other particles occurs, is generally smaller than for isotropic growth. So, this blocking effect due to the anisotropic growth leads to hard impingement. In other words, to obtain a general kinetic expression for the transformed fraction, the mutual interface of regions growing from separated nuclei must be considered [33]. Therefore, by taking in account that effect, the expression described by Eq. (6) could be rewritten as [24,32,33]:

$$\frac{d\alpha}{dx_e} = (1-\alpha)^{\gamma i} \tag{11}$$

where γi is impingement exponent or by using the definition of impingement factor [$\delta_i = 1/(\gamma i - 1)$]. The solution of Eq. (11) is given as [24,25,33]:

$$\alpha = 1 - [1 + {\delta_i}^{-1}x_e]^{-\delta_i} \tag{12}$$

or

$$\alpha = 1 - [1 + (\gamma i - 1)x_e]^{-1/(\gamma i - 1)}$$

Finally, a general expression of the actual transformed fraction for non-isothermal process, using both Eqs. (7) and (12) is given as [32,33]:

$$\alpha = 1 - \left\{1 + {\delta_i}^{-1}\left[KRT^2E_{eff.}^{-1}\beta^{-1})\right]^n\right\}^{-\delta_i} \tag{13}$$

2.2. Determination of kinetic parameters using isoconversional method

2.2.1. Isoconversion (model-free) analysis

Model-free methods are considered as one of the most reliable methods for calculation the effective activation energy of thermally activated reactions [36–44]. The assumption that the transformation rate of a solid-state reaction in isothermal conditions is the product of two functions, one dependent on the temperature, T, and the other dependent on the conversion fraction, α, can be generally described by [36–44]:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{14}$$

where $k(T)$ is the reaction rate constant and $f(\alpha)$ is the reaction model.

Under non-isothermal conditions with a constant heating rate of $\beta = dT/dt$, the kinetic equation combined with the Arrhenius approach to the temperature function of the reaction rate constant may be rewritten as:

$$\frac{d\alpha}{dT} = \frac{A}{\beta}\exp\left(-\frac{E}{RT}\right)f(\alpha) \tag{15}$$

where A is the pre-exponential (frequency) factor in (min^{-1}), E (kJ mol^{-1}) is the crystallization activation energy and R is the universal gas constant. This equation can be integrated by separation of variables [27,39,44]:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta}\int_{T_0}^{T}\exp\left(-\frac{E}{RT}\right)dT = \frac{AE}{\beta R}P(y) \equiv \frac{A}{\beta}I(E,T) \tag{16}$$

where

$$P(y) = \int_y^\alpha \frac{\exp(-y)}{y^2}dy \tag{17}$$

where T_0 is the initial temperature, $y = E/RT$ and T is the temperature at an equivalent (fixed) state of transformation. The integral on the right hand side is usually called the temperature integral, $P(y)$, and does not have analytical solution [45]. To solve the temperature integral in Eq. (17), several approximations were introduced. In general, all of these approximations lead to a direct isoconversional method. The most popular isoconversional methods used for calculation of the effective activation energy are Starink [39,44], Kissinger–Akahira–Sunose (KAS) [46–48], Tang [49], Flynn–Wall–Ozawa (FWO) [50,51] and Vyazovkin method [52,53]. Many authors [22,27,29,54,55] have been mentioned that there is a close agreement between KAS, Tang, Starink, FWO and Vyazovkin methods. So, in the present work the effective activation energy of crystallization will be concerned with Vyazovkin (as a non-linear method) and KAS method (as a linear one).

According to Vyazovkin method, a set of k experiments carried out at different heating rates, β, to obtain the effective activation energy, $E_{eff.}(\alpha)$, at any particular value of the degree of conversion, α, by fitting the value of $E_{eff.}(\alpha)$ which minimizes the objective function, Ω, according the following form:

$$\Omega = \sum_{i=1}^{k}\sum_{j\neq i}^{k}\frac{I[E_{eff.}(\alpha),T(\alpha_i)]\beta_j}{I[E_{eff.}(\alpha),T(\alpha_j)]\beta_i} \tag{18}$$

For KAS method, each degree of the conversion fraction, α, a corresponding $T(\alpha_i)$ and heating rate are used to plot $\ln[\beta_i/T^2(\alpha_i)]$ against $1000/T(\alpha_i)$ to obtain the effective activation energy, $E_{eff.}(\alpha)$. The value of $E_{eff.}(\alpha)$ is then determined from the regression slope according the following formula:

$$\ln\left(\frac{\beta_i}{T^2(\alpha_i)}\right) = C(\alpha) - \frac{E_{eff.}(\alpha)}{RT(\alpha_i)} \tag{19}$$

2.2.2. Model-fitting approach

For non-isothermal experiments, model-fitting involves fitting different models to $(\alpha - T)$ curves and simultaneously determining E and A [27–29]. One of these models proposed by Coats–Redfern method [56], which is represented through:

$$\ln\frac{g(\alpha)}{T^2} = \ln\left(\frac{AR}{\beta E}\left[1-\left(\frac{2RT^*}{E}\right)\right]\right) - \frac{E}{RT} \tag{20}$$

where T^* is the mean experimental temperature. Plotting $\ln[g(\alpha)/T^2]$ versus $1/T$ it gives a straight line. E and A will be obtained from the slope and the intercept, respectively, for different reaction models of $g(\alpha)$. The most common reaction models used to describe solid-state reactions are listed in a previous work [29].

3. Experimental procedure

Bulk material was prepared by the well-established melt-quench technique. The high purity (99.999%) Ga and Se in appropriate at.% proportion were weighed in a quartz glass ampoule (12 mm diameter). The contents of the ampoule were sealed under a vacuum of 0.01 Pa and heated at around 900 K for 24 h. During the melt process, the tube was frequently shaken to homogenize the resulting alloy. The melt was quenched in water at 273 K to obtain the glassy state.

The differential scanning calorimetry, DSC, was carried out on approximately 5 mg quantities of powder samples using a Shimadzu DSC-50 with sensitivity of ±10 μW. The accuracy of the heat flow is ±0.01 mW and the temperature precision as determined by the microprocessor of the thermal analyzer is ±0.1 K. The heating rates were varied from 5 K/min to 90 K/min under dry nitrogen supplied at the rate of 50 ml/min. To minimize the temperature gradient the samples were well granulated to form uniform fine powder and spread as thinly as possible on the bottom of the sample pan. Temperature and enthalpy calibration were checked with indium at heating rate of 10 K/min ($T_m = 156.6\,^\circ$C, $\Delta H_m = 28.55$ J/g) as a standard material supplied by Shimadzu. This calibration was also checked at different heating rates. In the present work, no specific heat treatment was given before the thermal analysis run to nucleate the samples.

4. Results

The DSC curves were recorded at different heating rates, β, from 5 K/min to 90 K/min for $Ga_{7.5}Se_{92.5}$ chalcogenide glass are shown in Fig. 1. The DSC curves are characterized by three temperatures effects. The glass transition temperature, T_g, as defined by the endothermic change in the DSC trace indicates a large change of viscosity, marking a transformation from amorphous solid phase to supercooled liquid state. Second, belongs to the extrapolation onset crystallization temperature, T_c. The last one is the exothermic peak temperature, T_P, which is used to identify the temperature at the maximum transformation rate. This behaviour is typical for a glass–crystalline transformation. Values of T_g, T_P and T_c as well as the full width at half maximum of the crystallization peak, ΔT, as a function of the heating rate, β, are listed in Table 1. As shown, all characteristic temperatures are shifted to higher temperature with increasing the heating rate.

On the other hand, the actual transformed fraction, α, was calculated using the partial area analysis. The fraction, α_i, crystallized

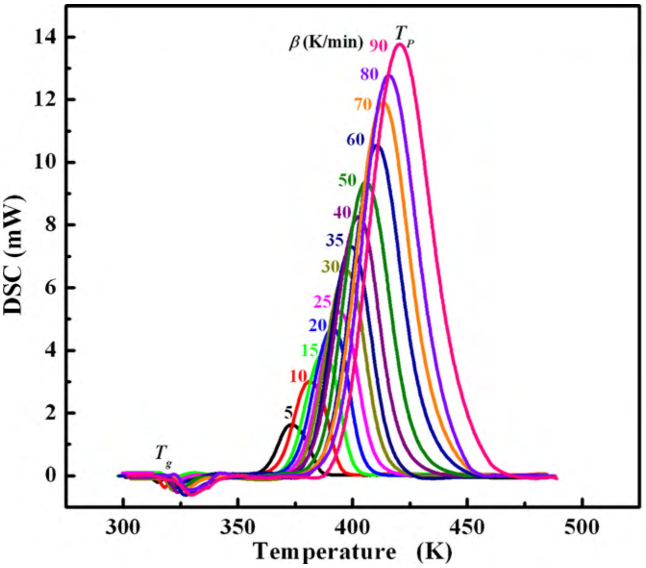

Fig. 1. Typical DSC curves of $Ga_{7.5}Se_{92.5}$ chalcogenide glass for β = 5–90 K/min.

Table 1
The values of the characteristic temperatures T_g, T_C, T_P, ΔT and the maximum transformation rate $(d\alpha/dt)_P$ for $Ga_{7.5}Se_{92.5}$ chalcogenide glass (for $\alpha = 0.05$–0.95).

β (K/min)	T_g (K)	T_C (K)	T_P (K)	ΔT (K)	$(d\alpha/dt)_P \times 10^{-3}$ (s^{-1})
5.0	316.44	363.48	373.72	12.26	4.96
10	318.17	365.40	381.27	13.57	9.21
15	319.14	369.58	387.06	13.92	13.84
20	320.21	372.09	391.32	14.74	16.54
25	321.01	374.69	394.5	15.99	19.18
30	321.97	376.68	397.5	16.96	21.16
35	322.70	379.40	399.10	17.40	25.10
40	323.95	380.13	402.69	18.54	25.30
50	325.58	384.31	405.96	19.76	28.78
60	327.07	386.94	410.70	21.62	32.17
70	328.18	389.82	413.35	22.98	34.45
80	329.40	391.40	415.81	23.55	38.44
90	330.34	393.25	420.72	26.53	38.85

at a given temperature (T_i) is given as a ratio between A_i and A_T, where A_T is the total area of the exothermic between the onset temperature (T_c) as crystallization just begins and the temperature, T_f, where the crystallization is completed and A_i is the area between T_c and T_i, i.e. $\alpha_i = (A_i/A_T)$. The derivative of this ratio with respect to time gives the transformation rate, $(d\alpha/dt)$. As shown in Table 1, the value of the maximum transformation rate, $(d\alpha/dt)_P$, increases with increasing the heating rate. This behaviour is widely observed in the literature [25,33].

5. Discussion

5.1. Evaluation of kinetic parameters of $Ga_{7.5}Se_{92.5}$ chalcogenide glass using the theoretical method developed (TMD)

In this section the values of kinetic parameters such as the effective activation energy, $E_{eff.}$, pre-exponential factor (frequency), A, and growth (Avrami) exponent, n_P, will be deduced using theoretical method developed (TMD) analysis, i.e. in terms of the maximum transformed fraction characteristics [T_P, α_P and $(d\alpha/dt)_P$]. The values of $E_{eff.}$ and A could be obtained according to the following equation [24,33]:

$$\ln\left(\frac{RT_P^2}{\beta}\right) = \frac{E_{eff.}}{RT_P} - \ln\left(\frac{A}{E_{eff.}}\right) \tag{21}$$

Plotting $\ln(RT_P^2/\beta)$ versus $1000/T_P$ for all heating rates used yields a straight line, Fig. 2. The slope of the above expression yields the value of $E_{eff.}$ and from the intercept one can determine the value of A. The obtained values of $E_{eff.}$ and A are 73.61 ± 2.6 kJ/mol and 7.44×10^9 min^{-1}, respectively.

The value of the Avrami exponent, n_P, as a function of the heating rate depends on the value of the impingement factor, δ_i. To obtain the values of δ_i as a function of heating rate, β, the actual transformed fraction described by Eq. (13) will be differentiated with respect to the time, t, which yields the following expression [25,33]:

$$\frac{d\alpha}{dt} = \left(\frac{R}{E_{eff.}}\right)^n n\beta^{-1}(KT^2\beta^{-1})^{n-1}(1-\alpha)^{\gamma i}\left(T^2\frac{dK}{dt} + 2T\beta K\right) \tag{22}$$

At the maximum transformation rate the first derivative of Eq. (22) yields $d\alpha^2/dt^2 = 0$ and using the approximation $(E_{eff.}/RT) \gg 1$, Eq. (22) leads to [25,33]:

$$(\delta_i + 1)\delta_i^{-1}(1-\alpha_P)^{1/\delta_i}(RK_PT_P^2/E_{eff.}\beta)^n = 1 \tag{23}$$

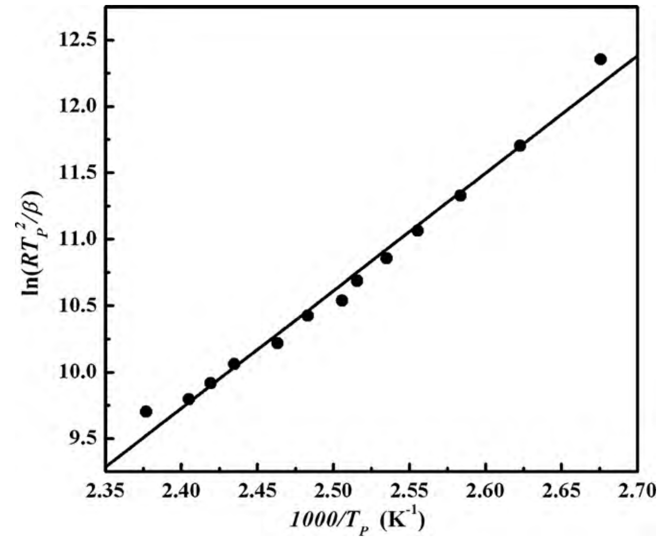

Fig. 2. A plot of $\ln(RT_P^2/\beta)$ versus $1000/T_P$ of $Ga_{7.5}Se_{92.5}$ chalcogenide glass for $\beta = 5$–90 K/min.

By using the expression of Eq. (13) at the maximum transformed fraction position, α_P, with Eq. (23), yields:

$$(1-\alpha_P) = \left(\frac{\delta_i}{\delta_i + 1}\right)^{\delta_i} \tag{24}$$

The value of the impingement factor, δ_i, could be obtained using an iteration method for Eq. (24) with the help of experimental value of α_P. The values of the impingement factor, δ_i, for each heating rate are given in Table 2, as well as its average value. As mentioned by Vazquez et al. [33], the calorimetric analysis is an indirect method which only makes it possible to obtain average values for the parameters that control the mechanism of a reaction. Accordingly, the average value calculated for δ_i is 1.1263 ± 0.34. It is well known that when $\gamma i \geq 1$ ($\gamma i = \delta_i^{-1} + 1$), the mode of impingement is due to "anisotropic growth" [24,25,32,33]. Moreover, As stated by Liu et al. [24], when the maximum transformed fraction, α_P, decreases with increasing impingement exponent, γi, the impingement mode is an anisotropic growth. This conclusion is in good agree with the result given in Fig. 3, which the value of γi increases (from 1.5240 to 2.4191) with decreasing α_P with an average of γi equals to 1.9636 ± 0.28.

Table 2
The values of the experimental (actual) transformed fraction, α_P, impingement factor, δ_i, the verification of Eq. (23) and its difference percentage from unit for $Ga_{7.5}Se_{92.5}$ chalcogenide glass.

β (K/min)	α_P	δ_i	The verification of Eq. (23)	Difference % from unit value
5.0	0.5199	1.24324	1.0027	0.27
10	0.5126	1.14446	0.9974	0.26
15	0.5251	1.32193	0.9932	0.68
20	0.5525	1.90837	1.0179	1.79
25	0.5324	1.44641	1.0250	2.50
30	0.5332	1.46118	1.0392	3.92
35	0.4844	0.85582	0.9913	0.87
40	0.5138	1.15985	1.0247	2.47
50	0.4841	0.85335	0.9371	6.29
60	0.4861	0.87001	1.0099	0.99
70	0.4928	0.92936	1.0086	0.86
80	0.4693	0.74310	1.0356	3.56
90	0.4634	0.70467	1.05500	5.50
Average	0.5054 ± 0.03	1.1263 ± 0.34	1.0105 ± 0.03	–

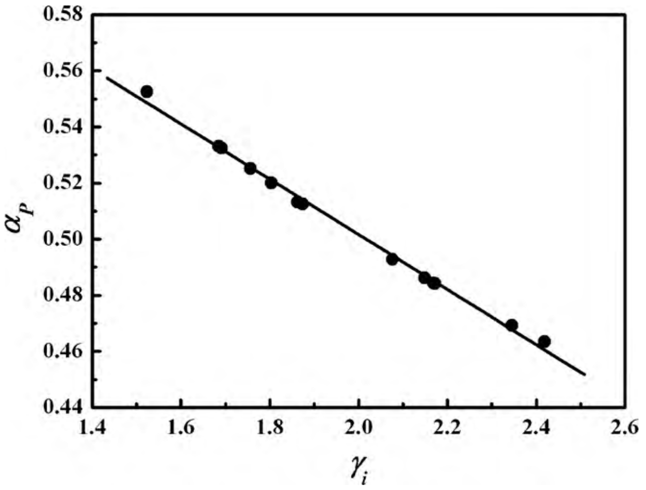

Fig. 3. The dependence of the maximum transformed fraction, α_P, on the impingement exponent, γi, for $Ga_{7.5}Se_{92.5}$ chalcogenide glass.

To determine the Avarmi exponent at the maximum transformed fraction, n_P, the term $[KRT^2E_{eff.}^{-1}\beta^{-1})]^n$ of Eq. (13) and the value of $(d\alpha/dt)_P$ obtained from Eq. (22) along with the value of $(1-\alpha_P)$ in Eq. (24) will yield an expression of n_P as follows [32,33]:

$$n_P = RT_P^2\left(\frac{d\alpha}{dt}\right)_P[(1-\alpha_P)^{\gamma i}\beta E_{eff.}]^{-1} \tag{25}$$

According to Eq. (25), the value of n_P could be calculated using the experimental values of the maximum transformation rate $(d\alpha/dt)_P$ and the corresponding temperature, T_P, transformed fraction, α_P, for each heating rate, along with the calculated values of the effective activation energy, $E_{eff.}$, and the impingement exponent, γi. The calculated values of n_P as function of heating rate using Eq. (25) are shown in Fig. 4. It is clear from the dependence of n_P on β that the value of n_P decreases from 3.25 to 2.03 with increasing β with an average value of 2.59 ± 0.42. The Avrami exponent was further evaluated using another common method [57] for non-isothermal analysis developed by Augis and Bennett [58]:

$$n_P = \frac{2.5RT_P^2}{\Delta TE_{eff.}} \tag{26}$$

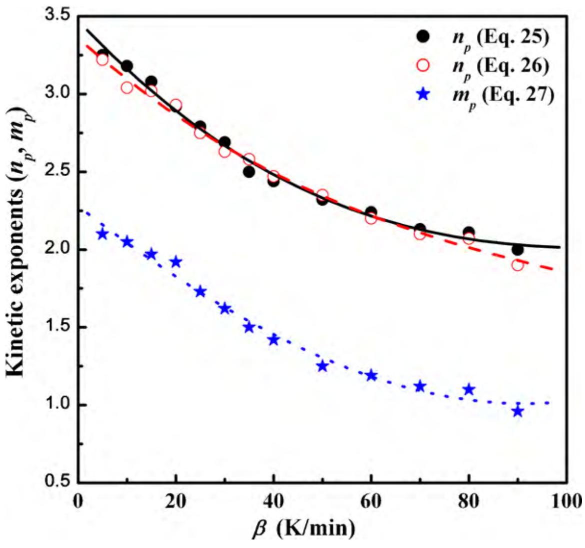

Fig. 4. The dependence of the kinetic exponents n_P and m_P on the heating rate, β, for $Ga_{7.5}Se_{92.5}$ chalcogenide glass.

A plot of Avrami exponent versus heating rate, using Eq. (26), is shown also in Fig. 4. As shown, the value of n_P decreases from 3.22 to 1.90 with increasing β with an average value of 2.56 ± 0.42. It is obviously that there is a good agreement between the Avrami exponent deduced using Eq. (25) and that deduced from Eq. (26). The maximum difference percentage between both average values is less than 1.2%.

As mentioned in the experimental part, no specific heat treatment was given before the thermal analysis run to nucleate the samples. Therefore, n can be taken to be equal to $(m+1)$, where m and n are integer or half-integer numbers have values between 1 and 4 depending on the growth mechanism and the dimensionality of the crystal growth [59]. Mahadevan et al. [59] have shown that n may be 4, 3, 2, or 1, which are related to different glass-crystal transformation mechanisms: $n = 4$, volume nucleation, three-dimensional growth; $n = 3$, volume nucleation, two-dimensional growth, $n = 2$, volume nucleation, one-dimensional growth; $n = 1$, surface nucleation, one-dimensional growth from surface to the inside. For studying the transformation kinetics for glasses when the nuclei formed during the heating at constant rate, β, are dominant, the kinetic exponent, n, is equal to $(m+1)$. The value of the kinetic exponent, m_P, for each heating rate could be obtained using the following parameters: the maximum transformation rate, $[d\alpha/dt]_P$, the maximum transformed fraction, α_P, the effective activation energy of crystallization, $E_{eff.}$, and the temperature corresponding to the maximum transformed fraction, T_P, according to the following expression [60]:

$$m_P = \frac{R[d\alpha/dt]_P T_P^2}{E_{eff.}(1-\alpha_P)\beta} \tag{27}$$

Fig. 4 shows the dependence of kinetic exponent, m_P, on the heating rate, β, as the value of m_P decreases from 2.1 to 0.96 with increasing β with an average value of 1.53 ± 0.40. The differences between the average values of n_P evaluated using Eqs. (25) and (26) and the average value of m_P using Eq. (27) are 1.06 and 1.03, respectively. These results indicated that the nuclei formed during the heating at constant rate, β, are dominant. According to the average values of both n_P and m_P, the transformation process of $Ga_{7.5}Se_{92.5}$ chalcogenide glass is volume nucleation with two- and one-dimensional growth, which are operating simultaneously during the glass–crystalline transformation, this conclusion will be confirmed later in Section 5.2.

On the other hand, once the values of n, m and the average value of $E_{eff.}$ are known the average values of both the activation energies for nucleation, E_N, and growth, E_G, could be calculated using Eq. (9). After rearrangement Eq. (9), the relation between the kinetic exponents n and m could take the following form:

$$n = m\left(\frac{E_G}{E_{eff.}}\right) + \left(\frac{E_N}{E_{eff.}}\right) \tag{28}$$

Comparing the above with the expression $n = m + 1$ for continuous nucleation, one can conclude that the average values of $E_G/E_{eff.}$ and $E_N/E_{eff.}$ are equal to 1. Plotting of n_P values, deduced from Eqs. (25) and (26) versus m_P deduced from Eq. (27) are shown in Fig. 5. This figure shows linear relationships between n_P and m_P with correlation coefficients of 0.98705 and 0.99368 using Eqs. (25) and (26), respectively. The average value of the slopes of these linear relationships (=$E_G/E_{eff.}$) equals to 1.05995 ± 0.002. Accordingly, the average value of the activation energy for growth is 78.02 ± 0.15 kJ/mol (using $E_{eff.}$ = 73.61 ± 2.6 kJ/mol). In addition, the average value of the intercepts (=$E_N/E_{eff.}$) equals to 0.94808 ± 0.01. Then, the average activation energy for nucleation is 69.79 ± 0.74 kJ/mol.

A correctness of the deduced values of kinetic parameters, using the TMD analysis, could be achieved by the verification of the left

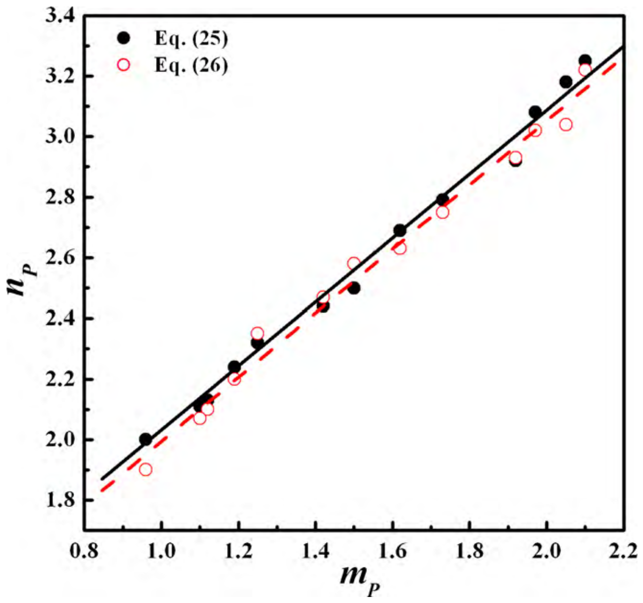

Fig. 5. The dependence of Avrami exponent, n_P, on the kinetic exponent, m_P, for $Ga_{7.5}Se_{92.5}$ chalcogenide glass using Eq. (28).

hand side value of Eq. (23) for each heating rate. The values of left hand side of Eq. (23), which are listed in Table 2 along with its difference percentage from the unit value, were calculated using the deduced parameters of $E_{eff.}$, A, n_P and δ_i with the experimental values of both T_P and α_P. It is clear from Table 2 that the maximum deviation from the unit value, according to the right hand side of Eq. (23), is about 6.29% which means that the obtained values of the kinetic parameters and impingement exponent are reasonable. Moreover, another confirmation about correctness of all kinetic parameters obtained ($E_{eff.}$, A, n_P) along with δ_i using TMD analysis is shown in Fig. 6. This figure shows the experimental transformation rate, ($d\alpha/\beta dt = d\alpha/dT$), as symbols, along with the calculated values (as lines) using Eq. (22) as a function of temperature, T. It is obviously that there is a reasonable agreement between the experimental and calculated ($d\alpha/dT$) curves, using all kinetic parameters obtained by the TMD analysis.

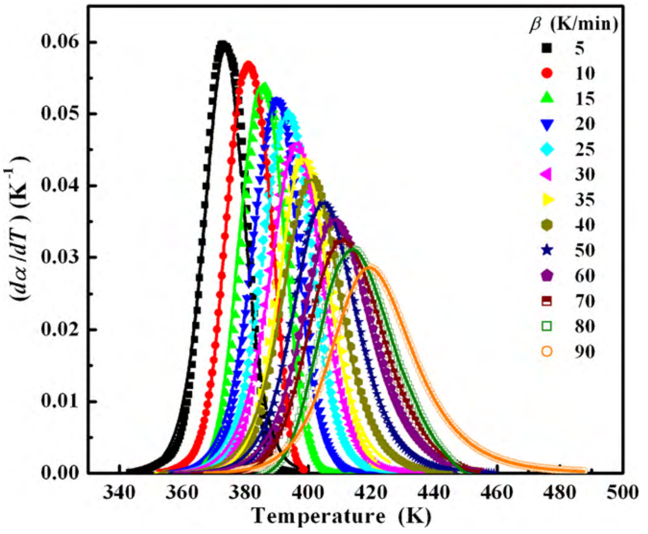

Fig. 6. A plot of the experimental and the calculated curves of ($d\alpha/dT$) versus temperature, T, for $Ga_{7.5}Se_{92.5}$ chalcogenide glass.

5.2. *Evaluation of kinetic parameters of $Ga_{7.5}Se_{92.5}$ chalcogenide glass using the isoconversional (model-free) method*

To get the information about the kinetic parameters, the effective activation energy, $E_{eff.}(\alpha)$, pre-exponential factor, $A(\alpha)$, and reaction model, $g(\alpha)$, the differential scanning calorimetry, DSC, data will be analyzed using the isoconversional (model-free) with the help of the model-fitting method. The dependence of transformation (crystallization) kinetic parameters ($E_{eff.}(\alpha)$, $A(\alpha)$, and $g(\alpha)$) with the extent of conversion, α, for $Ga_{7.5}Se_{92.5}$ chalcogenide glass will discuss in the next sections.

5.2.1. *Evaluation of the effective activation energy of crystallization $E_{eff.}(\alpha)$*

Isoconversional methods (Vyazovkin and KAS methods) were used to investigate the variation of the effective activation energy with extent of transformation, α, and with temperature, T. Fig. 7 shows the variation of the effective activation energy of crystallization, $E_{eff.}(\alpha)$, as a function of both α, Fig. 7a, and T, Fig. 7b, according to Vyazovkin and KAS methods. As shown in Fig. 7, the values of $E_{eff.}(\alpha)$ obtained using the Vyazovkin (non-linear) method, as a function of α, are in agree well with those obtained by the KAS (non-linear) method. The maximum percentage difference of the effective activation energy obtained using Vyazovkin and KAS methods is less than 1%. This close agreement between Vyazovkin and KAS isoconversional methods was also reported by many authors [22,27,29,54,55]. Accordingly, this variation of the effective activation energy can be attributed to the variation of $E_{eff.}$ (α) with temperature, see Fig. 7b. As stated by Vyazovkin [26], this behaviour demonstrated that the rate constant of the crystallization is in fact determined by the rates of two processes, nucleation and diffusion, which resulting in varying the effective activation energy of the transformation with temperature [26].

It is evident from the observed temperature dependence of the effective activation energy in the present glass that the

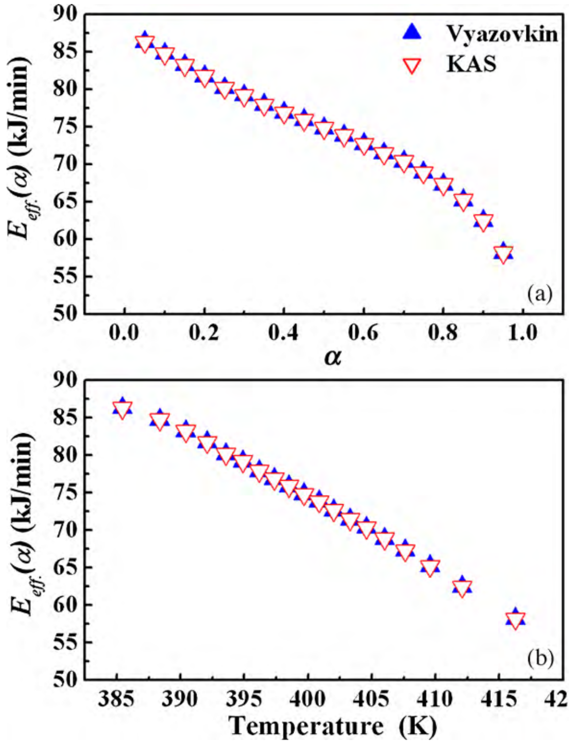

Fig. 7. The dependence of the effective activation energy of crystallization, $E_{eff.}(\alpha)$ on: (a) the transformed fraction, α. (b) The temperature, T, using all heating rates (β = 5–90 K/min) for $Ga_{7.5}Se_{92.5}$ chalcogenide glass.

glass–crystalline transformation cannot be generally described by a single-step mechanism. Therefore, the transformation demonstrates complex multi-step involving several processes of growth with different activation energies and mechanisms for the present glass [22,29]. On the other hand, the value of $E_{eff.}(\alpha)$ at $\alpha = 0.5$ is about 74.81 kJ/mol, which is closed to the value of 73.61 kJ/mol, obtained using Eq. (21) in Section 5.1, with a maximum percentage difference of 1.63%.

5.2.2. Evaluation of the pre-exponential factor $A(\alpha)$

The values of $\ln A_L$ and E_L of different reaction models are related linearly according to the compensation form ($\ln A_L = a + bE_L$) [27,29,42], where a is an artificial isokinetic rate constant ($a = \ln K_{iso}$) and constant b is given by ($b = 1/RT_{iso}$) where K_{iso} is an artificial isokinetic rate constant and T_{iso} is an artificial isokinetic temperature. The subscript L refers to one of possible reaction models $g(\alpha)$ or $f(\alpha)$ that listed in Ref. [29]. By using all reaction models, the isokinetic relationship ($\ln A_L$ versus E_L) of $Ga_{7.5}Se_{92.5}$ chalcogenide glass using Coats–Redfern method for $\beta = 5$–90 K/min, for the whole range of α(0.05–0.95) is shown in Fig. 8. The value of a, b, K_{iso}, T_{iso}, T_r and R_C, where T_r is the experimental temperature range of each β and R_C is correlation coefficient of the linear relationships for $Ga_{7.5}Se_{92.5}$ chalcogenide glass for all heating rates are listed in Table 3. From Table 3, both K_{iso} and T_{iso} increase with increasing β, as well as the value of T_{iso} lies within the experimental temperature range, T_r, for each β, which indicates that the reaction models $g(\alpha)$, which assumed to describe the transformation process, were properly chosen. If the value of T_{iso} will lie outside the experimental temperature range of a particular rate, then the reaction models chosen were not the suitable models [22,29].

After the correlation parameters have been obtained, see Fig. 8 and Table 3, the values of $E_{eff.}(\alpha)$ are substituted for E_L in the above mentioned compensation form to obtain the corresponding $\ln A(\alpha)$. This procedure could be applied for multi-step reactions that involving several processes, as it is originally applied to a single-step process [22,29,61,62]. Fig. 9 shows the dependence of $\ln A(\alpha)$ on α for $Ga_{7.5}Se_{92.5}$ chalcogenide glass for each heating rates used. It is clear from this figure that this dependence ($\ln A(\alpha)$ versus α) is typically as the dependence of $E_{eff.}(\alpha)$ on α. Furthermore, the value of A at $\alpha = 0.5$, for $\beta = 5$ K/min, equal to 7.62×10^9 min^{-1} (i.e. $\ln A(0.5) = 22.75$) is good agree with the value of $A = 7.44 \times 10^9$ min^{-1} obtained using TMD analysis, see Section 5.1. Now, after the experimental values of $E_{eff.}(\alpha)$ and $\ln A(\alpha)$ are known then the reaction model, $g(\alpha)$, could reconstruct numerically [22,29,42].

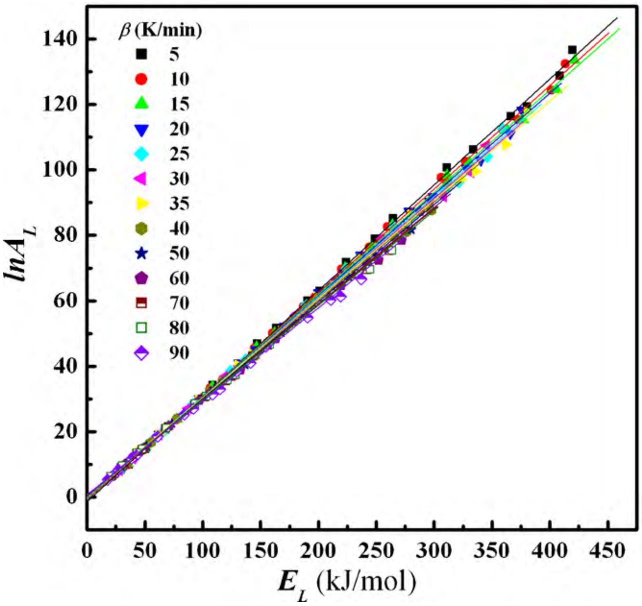

Fig. 8. The isokinetic relationships using Coats–Redfern method, for $Ga_{7.5}Se_{92.5}$ chalcogenide glass.

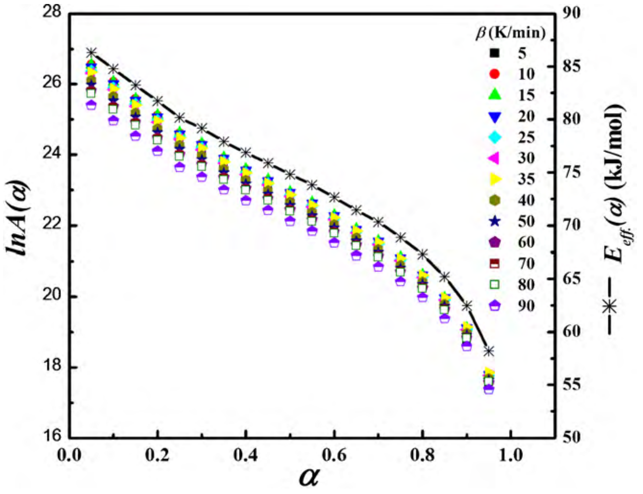

Fig. 9. The dependence of the experimental value of $\ln A(\alpha)$ on the transformed fraction, α, for $Ga_{7.5}Se_{92.5}$ chalcogenide glass.

5.2.3. Evaluation of the reaction model $g(\alpha)$

The suitable reaction model $g(\alpha)$ will be chosen to describe the transformation process of $Ga_{7.5}Se_{92.5}$ chalcogenide glass [22,29,42], by comparing the obtained experimental values of $E_{eff.}(\alpha)$ and $\ln A(\alpha)$ with those obtained from each model, as well as the best value of R_C. Fig. 10 shows the $g(\alpha)/g(0.5)$ reconstructed from the experimental data (as symbols) and the corresponding reaction model chosen (model An), Avrami–Erofeev model

Table 3

The values of a, b, K_{iso}, T_{iso}, T_r and R_C, Coats–Redfern method, using all reaction models for $Ga_{7.5}Se_{92.5}$ chalcogenide glass (for $\alpha = 0.05$–0.95).

β (K/min)	a (min^{-1})	b (mol/kJ)	K_{iso} (min^{-1})	T_{iso} (K)	T_r (K)	R_C
5.0	−1.3868	0.3227	0.2499	372.73	361–382	0.99970
10	−0.7541	0.3164	0.4704	380.15	368–390	0.99967
15	−0.3760	0.3119	0.6866	385.63	374–396	0.99967
20	−0.1890	0.3090	0.8277	389.25	376–401	0.99959
25	−0.0529	0.3063	0.9485	392.68	379–406	0.99954
30	0.0767	0.3039	1.0797	395.78	381–410	0.99949
35	0.2820	0.3019	1.3257	398.41	386–411	0.99956
40	0.2315	0.2998	1.2605	401.20	385–418	0.99935
50	0.3677	0.2968	1.4444	405.25	388–425	0.99926
60	0.5001	0.2933	1.6489	410.09	393–430	0.99920
70	0.6115	0.2917	1.8432	412.34	394–433	0.99913
80	0.7331	0.2894	2.0815	415.62	397–436	0.99913
90	0.7448	0.2858	2.1060	420.85	401–445	0.99890

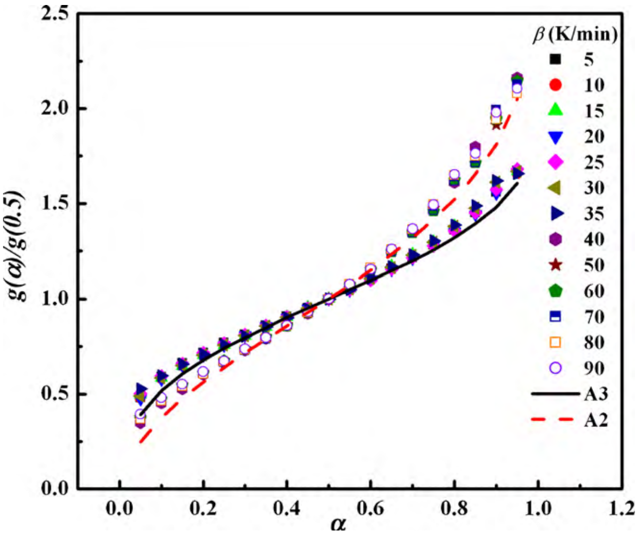

Fig. 10. The dependence of the experimental value of $g(\alpha)/g(0.5)$ on the transformed fraction, α. The solid lines represent the theoretical models of $g(\alpha)/g(0.5)$, for $Ga_{7.5}Se_{92.5}$ chalcogenide glass.

($g(\alpha)=[-\ln(1-\alpha)]^{1/n}$), (as lines) for the whole range of α using all heating rates 5–90 K/min, where g(0.5) refers to $g(\alpha)$ at $\alpha=0.5$. The models that fit the experimental results are model A3 ($n=3$) for the heating rates range of 5–35 K/min, and model A2 ($n=2$) for the heating rates range of 40–90 K/min. To confirm that, the kinetic exponent, n, can also calculate from the logarithmic form of the above mentioned reaction model and after rearrangement of this form yields:

$$\frac{1}{n}=\frac{\partial\{\ln[g(\alpha)]\}}{\partial\{\ln[-\ln(1-\alpha)]\}} \tag{29}$$

The dependence of the logarithmic form of the experimental reaction model $\ln[g(\alpha)]$ on the theoretical model $\ln[-\ln(1-\alpha)]$ for all heating rates used for $Ga_{7.5}Se_{92.5}$ chalcogenide glass is shown in Fig. 11. The average value of the kinetic exponent, n, will be obtained from the slope of each straight line. On the other hand, Table 4 shows the values of the average kinetic exponent, n, and the correlation coefficient, R_C, for each heating rate using Eq. (29). As shown in Table 4, the n values lie between 3.09 and 3.22 for $\beta=5$–35 K/min with an average value of 3.15 ± 0.04. The values of n for $\beta=40$–90 K/min are ranged from 2.07 to 2.12 with an average value of 2.10 ± 0.02 for $Ga_{7.5}Se_{92.5}$ chalcogenide glass. It is obviously that, the obtained values of n that listed in Table 4 are agree well with the results illustrated in Fig. 10.

Table 4
The values of the average kinetic exponent, n, and correlation coefficient, R_C, for $Ga_{7.5}Se_{92.5}$ chalcogenide glass.

β (K/min)	n Eq. (29)	R_C	Avrami–Erofeev model $g(\alpha)=[-\ln(1-\alpha)]^{1/n}$
5.0	3.19 ± 0.01	0.99458	$n=3$
10	3.13 ± 0.01	0.99506	
15	3.13 ± 0.01	0.99869	
20	3.14 ± 0.01	0.99851	
25	3.22 ± 0.01	0.99654	
30	3.18 ± 0.01	0.99626	
35	3.09 ± 0.01	0.99789	
Average	3.15 ± 0.04	–	
40	2.07 ± 0.01	0.99978	$n=2$
50	2.10 ± 0.01	0.99965	
60	2.11 ± 0.01	0.99968	
70	2.10 ± 0.01	0.99845	
80	2.08 ± 0.01	0.99633	
90	2.12 ± 0.01	0.99400	
Average	2.10 ± 0.02	–	

Furthermore, Lu et al. [63] deduced an equation in order to calculate local Avrami exponent for non-isothermal experiments as a function of α, which is expressed as follows:

$$n(\alpha)=\frac{-R\,\partial\ln[-\ln(1-\alpha)]}{E_{eff.}(\alpha)\,\partial(1/T)} \tag{30}$$

For the non-isothermal conditions, Avrami exponent can be obtained from the slope of the linear relationship between $\ln[-\ln(1-\alpha)]$ and $1000/T$ for different heating rates as shown in Fig. 12 and the values of $E_{eff.}(\alpha)$ calculated from the isoconversional method, see Fig. 7a. Fig. 13 shows the local Avrami exponent, $n(\alpha)$, as a function of transformed fraction, α, for $Ga_{7.5}Se_{92.5}$ chalcogenide glass. According to the results obtained from Fig. 13, the value of $n(\alpha)$ is increased with increasing α for each heating rate, in addition, for each α the value n decreases with increasing β. Moreover, for each α the dependence of $n(\alpha)$ on β indicates that two heating rate regions can be identified. The first one for a heating rate from

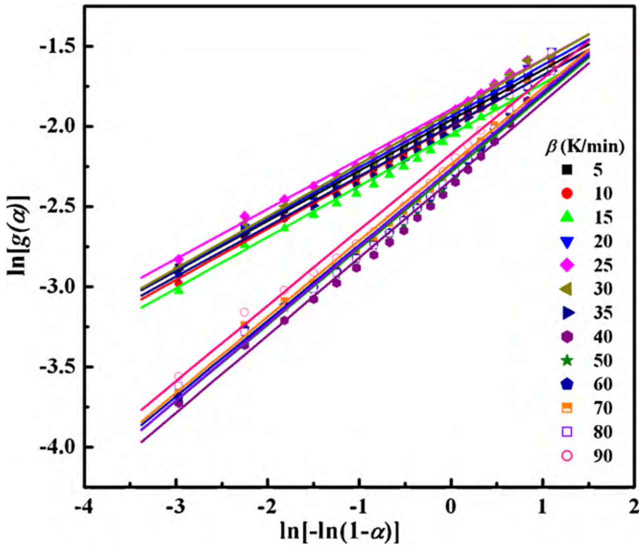

Fig. 11. The dependence of the experimental reaction model $\ln[g(\alpha)]$ on the theoretical model $\ln[-\ln(1-\alpha)]$ for $Ga_{7.5}Se_{92.5}$ chalcogenide glass.

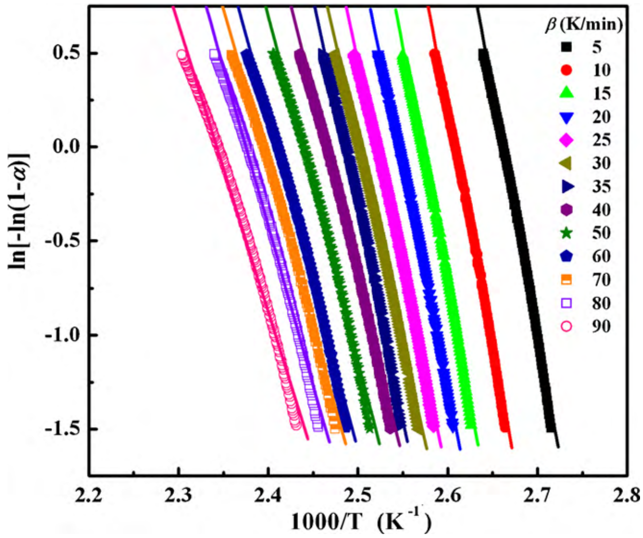

Fig. 12. The variation of $\ln[-\ln(1-\alpha)]$ with $1000/T$ $Ga_{7.5}Se_{92.5}$ chalcogenide glass.

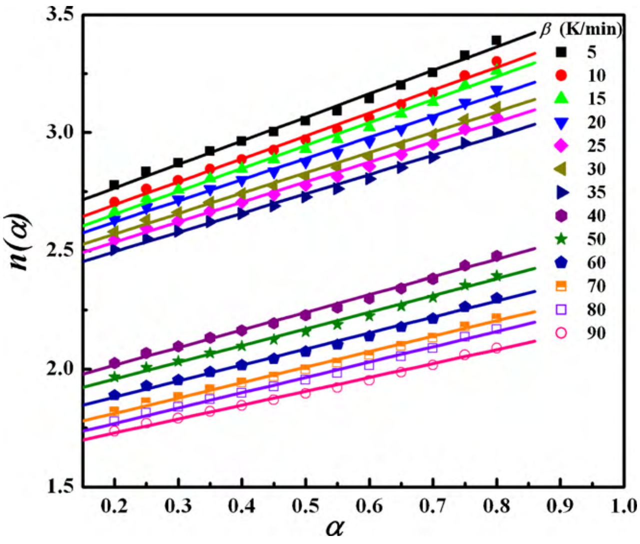

Fig. 13. The variation of local Avrami exponent, $n(\alpha)$, with the transformed fraction, α, for $Ga_{7.5}Se_{92.5}$ chalcogenide glass.

5 K/min to 35 K/min, the second one is for a higher heating rate (40–90 K/min), for all values of α.

It is clear from Fig. 13 that the n values ranged from 2.50 to 3.40 for $\beta = 5$–35 K/min. These results are agree with those obtained according to TMD analysis (2.50–3.25 and 2.58–3.22), see Fig. 4, for $\beta = 5$–35 K/min. Moreover, the average values of n_P (2.92 ± 0.27 and 2.88 ± 0.24) obtained according to TMD analysis are also agree with the reaction model A3 ($n = 3$), see Fig. 10, and with the average value given in Table 4 (3.15 ± 0.04) for $\beta = 5$–35 K/min. On the other hand, for $\beta = 40$–90 K/min, the n values ranged from 1.74 to 2.49, see Fig. 13. These results are agree with those obtained according to TMD analysis (2.03–2.44 and 1.90–2.47) for $\beta = 40$–90 K/min, Fig. 4. In addition, the average values of n_P (2.21 ± 0.16 and 2.18 ± 0.21) obtained according to TMD analysis are agree with the reaction model A2 ($n = 2$), Fig. 10, and with the average value shown in Table 4 (2.01 ± 0.02) for $\beta = 40$–90 K/min. It obviously that, the n values obtained using the isoconversional method (Figs. 10, 13 and Table 4) are in good agree with those obtained according to TMD analysis (see Figs. 4 and 5) for $\beta = 5$–90 K/min.

Accordingly, the values of Avrami exponent, n, using isoconversional and TMD analyses along with the result of kinetic exponent, m, Figs. 4 and 5, indicated that two mechanisms (volume nucleation with two- and one-dimensional growth) are responsible for the transformation process, which operating simultaneously during the glass–crystalline transformation of the $Ga_{7.5}Se_{92.5}$ chalcogenide glass for the range of heating rates of 5–90 K/min.

By using all evaluated transformation kinetic parameters ($E_{eff.}(\alpha)$, $A(\alpha)$ and $g(\alpha)$) according to the isoconversional method for $Ga_{7.5}Se_{92.5}$ chalcogenide glass, a reasonable agreement between both the experimental (as symbols) and calculated ($\alpha - T$) curves (as lines) for $\beta = 5$–90 K/min, has been achieved, see Fig. 14. This agreement between the experimental and calculated ($\alpha - T$) means that the obtained kinetic parameters are the suitable values that may describe the transformation kinetic process of the present glass using the isoconversional analysis. According to the results obtained using the isoconversional method, the transformation from glass to crystalline for $Ga_{7.5}Se_{92.5}$ chalcogenide glass cannot be generally described by a single-step mechanism. The transformation demonstrates complex multi-step involving several processes of growth with different activation energies and mechanisms.

Finally, the obtained results of all transformation kinetic parameters using theoretical method developed analysis are in good agreement with that obtained according to the isoconversional one under non-isothermal regime. This conclusion indicates that the feasibility of the two methods for evaluating the transformation kinetic parameters to describe the glass–crystalline transformation process of $Ga_{7.5}Se_{92.5}$ chalcogenide glass.

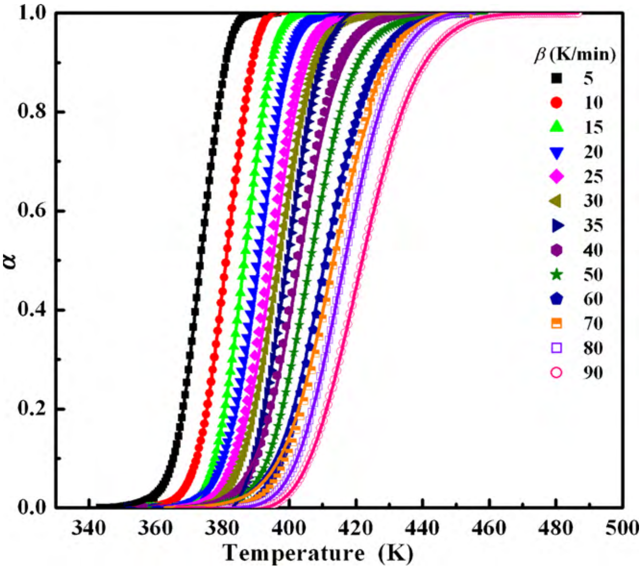

Fig. 14. The experimental and the calculated transformed fraction, α, against temperature T, for $Ga_{7.5}Se_{92.5}$ chalcogenide glass.

6. Conclusion

The transformation kinetics from glass to crystalline for $Ga_{7.5}Se_{92.5}$ chalcogenide glass were studied using DSC technique. The kinetic parameters of present chalcogenide glass under non-isothermal conditions are analyzed by the theoretical method developed and the isoconversional (model-free) methods for the heating rates range of 5–90 K/min.

The results of the kinetic parameters of $Ga_{7.5}Se_{92.5}$ chalcogenide glass using the theoretical method developed are summarized as:

- The average values of the effective activation energy, $E_{eff.}$, and the pre-exponential factor, A, are 73.61 ± 2.6 kJ/mol and 7.44×10^9 min^{-1}, respectively.
- The average values of the impingement factor, δ_i, and the impingement exponent, γi are (1.1263 ± 0.34) and (1.9636 ± 0.28), respectively. From the average value of γi and the dependence of the maximum transformed fraction, α_P, on γi, the mode of impingement is due to “anisotropic growth”.
- The average values of Avrami exponent, n_P, calculated using TMD method are 2.92 ± 0.27 and 2.88 ± 0.24 for the heating rates range of 5–35 K/min using Eqs. (25) and (26), respectively. While, for the heating rates range of 40–90 K/min, the average values of n_P are 2.21 ± 0.16 and 2.18 ± 0.21.
- The average values of the kinetic exponent, m_P, are 1.84 ± 0.23 and 1.17 ± 0.16 for the heating rates ranges of 5–35 and 40–90 K/min, respectively.
- According to the average values of the kinetic exponents n_P and m_P, the transformation process of $Ga_{7.5}Se_{92.5}$ chalcogenide glass is volume nucleation with two- and one-dimensional growth, which are operating simultaneously during the glass–crystalline transformation.
- The average values of the separate activation energies for growth, E_G, and nucleation, E_N, are 78.02 ± 0.15 kJ/mol and 69.79 ± 0.74 kJ/mol, respectively.

The results of the kinetic parameters of $Ga_{7.5}Se_{92.5}$ chalcogenide glass using the isoconversional (model-free) method are summarized as:

- The effective activation energy of crystallization, $E_{eff.}(\alpha)$, is not constant but varies with the degree of transformation (crystallization) and hence with temperature.
- The reaction model that may describe crystallization process of $Ga_{7.5}Se_{92.5}$ chalcogenide glass is Avrami–Erofeev model ($g(\alpha)=[-\ln(1-\alpha)]^{1/n}$) with n equal to 3 and 2 for the heating rates ranges of 5–35 K/min and 40–90 K/min, respectively.
- The transformation mechanisms examined using the local Avrami exponent indicate that two mechanisms (two- and one-dimensional growth) are responsible for the crystallization process of $Ga_{7.5}Se_{92.5}$ chalcogenide glass.

Finally, the obtained results of all transformation kinetic parameters using theoretical method developed analysis are in good agreement with that obtained according to the isoconversional one under non-isothermal regime. This conclusion indicates that the feasibility of the two methods for evaluating the transformation kinetic parameters to describe the glass–crystalline transformation process of $Ga_{7.5}Se_{92.5}$ chalcogenide glass.

References

[1] T.P. Gujar, V.R. Shinde, J.-W. Parka, H.K. Lee, K.-D. Jung, O.-S. Joo, Electrochim. Acta 54 (2008) 829.
[2] Z.A. Peng, X. Peng, J. Am. Chem. Soc 123 (2001) 183.
[3] A. Segura, J. Bouvier, M.V. Andres, F.J. Manjon, V. Munoz, Phys. Rev. B 56 (1997) 4075.
[4] C.H. Ho, C.C. Wu, Z.H. Cheng, J. Cryst. Growth 279 (2005) 321.
[5] C.E.M. Campos, J.C. de Lima, T.A. Grandi, K.D. Machado, P.S. Pizani, Solid State Commun. 126 (2003) 611.
[6] M.A. El-Oyoun, G.M. Shurit, A. Gaber, N. Afify, J. Phys. Chem. Solids 64 (2003) 821.
[7] J.H. Park, M. Afzaal, M. Helliwell, M.A. Malik, P. O'Brien, J. Raftery, Chem. Mater. 15 (2003) 4205.
[8] M. Rusu, S. Wiesner, S. Lindner, E. Strub, J. Rohrich, R. Wurz, W. Fritsch, W. Bohne, T. Schedel-Niedrig, M.C. Lux-Steiner, C. Giesen, M. Heuken, J. Phys. Condens. Matter 15 (2003) 8185.
[9] A.C. Wright, J.O. Williams, A. Krost, W. Richter, D.R.T. Zahn, J. Cryst. Growth 121 (1992) 111.
[10] M.A. Afifi, A.E. Bekheet, H.T. El-Shair, I.T. Zedan, Physica B 325 (2003) 308.
[11] K. Ueno, S. Tokuchi, K. Saiki, A. Koma, J. Cryst. Growth 237–239 (2002) 1610.
[12] F. Adduci, A. Cingolani, M. Ferrara, A. Minafra, I.M. Catalano, Solid State Commun. 19 (1976) 1111.
[13] K.R. Allakhverdiev, T. Baykara, S. Joosten, E. Gunay, A.A. Kaya, A. Kulibekov (Gulubayov), A. Seilmeier, E.Yu. Salaev, Opt. Commun. 261 (2006) 60.
[14] K. Jamshidi-Ghaleh, M. Karimi, Opt. Commun. 281 (2008) 5561.
[15] A.O. Kodolbas, G.M. Mamedov, Mater. Sci. Eng. B 110 (2004) 52.
[16] V.G. Voevodin, O.V. Voevodina, S.A. Bereznaya, Z.V. Korotchenko, A.N. Morozov, S.Yu. Sarkisov, N.C. Fernelius, J.T. Goldstein, Opt. Mater. 26 (2004) 495.
[17] S.I. Drapak, S.V. Gavrylyuk, Z.D. Kovalyuk, O.S. Lytvyn, Appl. Surf. Sci. 254 (2008) 2067.
[18] O.A. Balitskii, V.P. Savchyn, P.J. Stakhira, N.N. Berchenko, Vacuum 67 (2002) 69.
[19] J.X. Lin, C.Y. Wang, Y.Y. Zheng, Comput. Chem. Eng. 32 (2008) 3023.
[20] M. Abu El-Oyoun, J. Phys. D: Appl. Phys. 33 (2000) 2211.
[21] H.C. Yang, H.C. Eun, Y.Z. Cho, H.S. Lee, I.T. Kim, Thermochim. Acta 484 (2009) 77.
[22] M. Abu El-Oyoun, J. Alloys Compd. 486 (2009) 1.
[23] M.J. Starink, A.M. Zahra, Thermochim. Acta 292 (1997) 159.
[24] F. Liu, S.J. Song, F. Sommer, E.J. Mittemeijer, Acta Mater. 57 (2009) 6176.
[25] J.L. Cardenas-Leal, J. Vazquez, D. Garcia, G. Barreda, P.L. Lopez-Alemany, P. Villares, R. Jimenez-Garay, Thermochim. Acta 484 (2009) 70.
[26] S. Vyazovkin, I. Dranca, Macromol. Chem. Phys. 207 (2006) 20.
[27] B. Jankovic, B. Adnadevic, J. Jovanovic, Thermochim. Acta 452 (2007) 106.
[28] G. Chen, C. Lee, Y.-L. Kuo, Y.-W. Yen, Thermochim. Acta 456 (2007) 89.
[29] M. Abu El-Oyoun, Thermochim. Acta 494 (2009) 129.
[30] M.S. Rasheedy, A.S. Soltan, A.A.I. Abd-Elmageed, J. Alloys Compd. 472 (2009) 581.
[31] N. Afify, Phys. Chem. Solids 69 (2008) 1691.
[32] F. Liu, F. Sommer, C. Bos, E.J. Mittemeijer, Int. Mater. Rev. 52 (2007) 193.
[33] J. Vazquez, D. Garcıa, G. Barreda, P.L. Lopez-Alemany, P. Villares, R. Jimenez-Garay, Mater. Chem. Phys. 96 (2006) 107.
[34] F. Liu, G.C. Yang, J.N. Liu, Thermochim. Acta 438 (2005) 83.
[35] D. Wang, Y. Liu, Z. Gao, Y. Zhang, J. Non-Cryst. Solids 354 (2008) 3990.
[36] S. Vyazovkin, Thermochim. Acta 355 (2000) 155.
[37] S. Vyazovkin, N. Sbirrazzuoli, Macromol. Rapid Commun. 23 (2002) 766.
[38] S. Vyazovkin, N. Sbirrazzuoli, J. Therm. Anal. Calorim. 72 (2003) 681.
[39] M.J. Starink, Thermochim. Acta 404 (2003) 163.
[40] S. Vyazovkin, N. Sbirrazzuoli, Macromol. Rapid Commun. 25 (2004) 733.
[41] A. Khawam, D.R. Flanagan, Thermochim. Acta 436 (2005) 101.
[42] S. Vyazovkin, J. Therm. Anal. Calorim. 83 (2006) 45.
[43] S. Vyazovkin, N. Sbirrazzuoli, Macromol. Rapid Commun. 27 (2006) 1515.
[44] M.J. Starink, J. Mater. Sci. 42 (2007) 483.
[45] A.A. Joraid, A.A. Abu-Sehly, M. Abu El-Oyoun, S.N. Alamri, Thermochim. Acta 470 (2008) 98.
[46] H.E. Kissinger, J. Res. Nat. Bur. Stand. 57 (1956) 217.
[47] H.E. Kissinger, Anal. Chem. 29 (1957) 1702.
[48] T. Akahira, T. Sunose, Res. Rep. Chiba Inst. Technol. 16 (1971) 22.
[49] W. Tang, Y. Liu, H. Zhang, C. Wang, Thermochim. Acta 408 (2003) 39.
[50] J.H. Flynn, L.A. Wall, J. Res. Natl. Bur. Stand. Sect. A 70 (1966) 487.
[51] T. Ozawa, Bull. Chem. Soc. Jpn. 38 (1965) 1881.
[52] S. Vyazovkin, J. Comput. Chem. 18 (1997) 393.
[53] S. Vyazovkin, J. Comput. Chem. 22 (2001) 178.
[54] B. Jankovic, J. Chem. Eng. 139 (2008) 128.
[55] P. Budrugeac, D. Homentcovschi, E. Segal, Therm. Anal. Calorim. 66 (2001) 557.
[56] A.W. Coats, J.P. Redfern, J. Polym. Sci. Part B: Polym. Lett. 3 (1965) 917.
[57] C.S. Ray, D.E. Day, J. Am. Ceram. Soc. 73 (1990) 439.
[58] J.A. Augis, J.E. Bennett, J. Therm. Anal. 13 (1978) 283.
[59] S. Mahadevan, A. Giridhar, A.K. Singh, J. Non-Cryst. Solids 88 (1986) 11.
[60] A.M. Abd Elnaeim, K.A. Aly, N. Afify, A.M. Abousehlly, J. Alloys Compd. 491 (2010) 85.
[61] S. Vyazovkin, W. Linert, Chem. Phys. 193 (1995) 109.
[62] S. Vyazovkin, A.I. Lesnikovich, Thermochim. Acta 128 (1988) 297.
[63] W. Lu, B. Yan, W. Huang, J. Non-Cryst. Solids 351 (2005) 3320.