Non-isothermal crystallization kinetics of $Cd_{10}Se_{90}$ chalcogenide glass

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Abstract

The structure and kinetics of the crystallization reaction of amorphous $Cd_{10}Se_{90}$ were studied at different heating rates (5–30 K/min) under non-isothermal conditionsby X-ray powder diffraction, scanning electron microscopy (SEM) and differential thermal analysis (DTA) techniques. The Johnson–Mehl–Avrami(JMA) and isoconversional models were used to describe the DTA crystallization data.A strong heating rate dependence of the activation energy was observed when the data were analyzed using Matusita method. This variation of the activation energy was confirmed by the application of the isoconversional methods of Kissinger–Akahira–Sunose (KAS), Flynn–Wall–Ozawa (FWO), Tang, Starink, and Friedman. These methods showed that the activation energy of crystallization is not constant but varies with the degree of conversion and hence with temperature. This variation indicates that the transformation from amorphous to crystalline phase is a complex process involving different mechanisms of nucleation and growth.

Keywords: Crystallization kinetics, Chalcogenide glass; Activation energy, isoconversional methods.

Introduction

Recently, there is a growing interest in amorphous semiconductors, especially those known as chalcogenide glasses. This is due to the fact that some amorphous materials show certain unusual switching properties that could be important in modern technological applications such as switching, electrophotography, and memory devices [29,13]. Cadmium Selenide system is an example of the wide-band gap II-VI systems that is considered as a promising semiconductor material for optoelectronics and photovoltaic devices [34,33,14].

The stoichiometry of chalcogenide glasses is expected also to have a significant influence on their transport mechanisms, thermal stability and practical applications. However; no enough studies are reported on the growth, characterization and properties of non-stoichiometric Cadmium Selenide [20]. Previously we have studied the optical and electrical properties of selenium-rich Cadmium Selenide, SR-CdSe, thin films deposited by thermal evaporation [27,28].

The main objective of the kinetic analysis of crystallization process is to determine the kinetic parameters such as activation energy, pre-exponential factor and reaction model [9]. Information about this kinetic triplet (E, A, $f(\alpha)$ or $g(\alpha)$, α being the extent of conversion) can be used to identify the crystallization process mechanism(s). Once the values of these parameters are known, an extrapolation of the kinetic behavior of the system in different conditions can be made. The methods commonly used for analyzing non-isothermal kinetic data are generally grouped into two categories: model-fitting and isoconversional (model-free) methods. Model-fitting methods were widely used because of their ability to directly determine the kinetic triplet. These methods involve fitting different reaction models to experimental data leading to a simultaneous determination of the kinetic parameters. In model-fitting methods the kinetic parameters are assumed constant. On the other hand, isoconversional (model free) methods are becoming more popular because of their ability to determine the activation energy at progressive extent of conversion (α) without assuming any reaction model.

The variation of the activation energy with the degree of crystallization is an important issue in the kinetics of amorphous to crystalline transformation. It can provide useful information about the different mechanisms involved in the transformation process as indicated by Vyazovkin [45] . Liu et al. [25] have considered a generalization of the Johnson–Mehl–Avrami (JMA) model to account for the variation of the activation energy. In contrast to the original formalism of the JMA theory,

where only nucleation site saturation or continuous nucleation was assumed, Liu et al. model predicts that the activation energy is not constant throughout the crystallization process when mixed nucleation (a combination of pre-existing nuclei and continuous nucleation modes, with site saturation and continuous nucleation as two extremes) is considered. In order to reveal this variation of the activation energy of crystallization, two approaches are normally used [17]. The first approach is to use Matusita et al. [30] method to determine the kinetic parameters such as the activation energy E and the Avrami exponent n of the crystallization process. The variation of the activation energy can be further analyzed using isoconversional methods which were widely used by different authors to investigate different kinetic processes associated with this transformation [24,18,37,39,40,46,41,15,35].

In the present work, the kinetics of crystallization of amorphous Cd$_{10}$Se$_{90}$ alloy is studied using the differential thermal analysis(DTA) technique at different constant heating rates. The DTA data are analyzed using of the Matusita and the isoconversional methods to investigate the growth processes involved in the transformation. The heating rate dependence of the activation energy of crystallization (E) is discussed.

Theoretical Background

The kinetics of isothermal crystallization involving nucleation and growth is usually analyzed using JMA model [16,6,7,8]. According to this model, the volume fraction of crystallites (α) is given by

$$\alpha = 1 - \exp(-kt^n) \qquad (1)$$

where n is the Avrami exponent that is associated with the nucleation and growth mechanisms and k is the reaction rate constant. In this thermally activated process, the rate constant is related to temperature T via the Arrhenius equation

$$k = A\exp\left(\frac{-E}{RT}\right) \qquad (2)$$

where E is the activation energy of crystallization, A the preexponential factor and R the gas constant. In the framework of the JMA model, the kinetic parameters n, A and E are constant during the crystallization process. However, as pointed out by Vyazovkin [45], the crystallization process is generally determined by nucleation and growth, which are likely to have different activation energies. It is also possible that different growth mechanisms are operating at different degree of crystallization leading to temperature-dependent activation energy.

Kissinger method

This method [22] is most commonly used in analyzing crystallization data in DTA. According to this method, the activation energy can be evaluated using the following equation:

$$\ln\left(\frac{\beta}{T^2}\right) = C_K(\alpha) - \frac{E}{RT} \qquad (3)$$

where T_p is the crystallization peak temperature and β is the heating rate.

Matusita method

The activation energy for crystallization as well as the Avrami exponent can be obtained using a method suggested specifically for non-isothermal experiments by Matusita et al. [30]. The volume fraction of crystallites (α) precipitated in a glass heated at constant heating rate (β) is related to the effective activation energy for crystallization (E) through the following expression:

$$\ln\left[-\ln(1-\alpha)\right] = -n\ln(\beta) - 1.052\frac{mE_c}{RT} + const. \qquad (4)$$

where m is an integer which depends on the dimensionality of the crystal, and n is a numerical factor (the Avrami exponent) which also depends on the nucleation process. When the nuclei

formed during the heating at a constant rate dominate, $n = m + 1$ and when nuclei formed during any previous heat treatment prior to thermal analysis are dominant, $n = m$ [26].

Isoconversional methods

Model-free isoconversion methods are the most reliable methods for the calculation of the activation energy of thermally activated reactions [43,42,44,21,36]. A large number of isoconversion methods have been conducted for polymer materials, but only a few for studies on chalcogenide glasses. 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:

$$\frac{d\alpha}{dt} = k(T) f(\alpha) , (5)$$

where $k(T)$ is the reaction rate constant, $f(\alpha)$ is the reaction model, and α is the conversion fraction that represents the volume of the crystallized fraction. The reaction rate constant, $k(T)$, usually has an Arrhenian temperature dependence:

$$k - A \exp(-E/RT) , (6)$$

where A (s^{-1}) is the pre-exponential (frequency) factor, E (kJ mol^{-1}) is the activation energy, and R is the universal gas constant. Thus, the kinetic equation combined with the Arrhenius approach can be described as:

$$\frac{d\alpha}{dt} = A \exp(-E/RT) f(\alpha) \qquad (7)$$

There is a wide range of theoretical models and mathematical treatments to estimate the activation energy of a reaction. These models can be categorized into the two most popular (linear) and (non-linear) methods, as described below.

Under non-isothermal conditions with a constant heating rate of $\beta = dT/dt$, Eq. (7) may be rewritten as:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) f(\alpha) \qquad (8)$$

This equation can be integrated by separation of variables [37, 15, 36]:

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^T \exp\left(-\frac{E}{RT}\right) dT \approx \frac{AE}{\beta R} \int_0^T \frac{\exp(-y)}{y^2} dy \quad (9)$$

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.

$$p(y) = \int_{y_f}^\infty \frac{\exp(-y)}{y^2} dy \ (10)$$

To solve the temperature integral, several approximations were introduced. In general, all of these approximations lead to a direct isoconversion (linear) method in the form of:

$$\ln\left(\frac{\beta_i}{T_{\alpha i}^k}\right) = C - \frac{E_\alpha}{RT_{\alpha i}} (10)$$

The subscript i denotes different heating rates. For each degree of the conversion fraction, α, a corresponding $T_{\alpha i}$ and heating rate β are used to plot $\ln\left(\beta_i/T_{\alpha i}^k\right)$ against $1/T_{\alpha i}$. The plot should be a straight line whose slope can be used to calculate the activation energy E_α. However, the most popular models used for calculation of activation energy are:

1- The Kissinger-Akahira-Sunose (KAS) method [23,5], which takes the form:

$$\ln\left(\frac{\beta_i}{T_{\alpha i}^2}\right) = C_K(\alpha) - \frac{E_\alpha}{RT_{\alpha i}} \qquad (11)$$

2- The Flynn-Wall-Ozawa (FWO) method, suggested independently by Flynn and Wall [11] and Ozawa [32]. This method is given by:

$$\ln(\beta_i) = C_W(\alpha) - 1.0518\frac{E_\alpha}{RT_{\alpha i}} \quad (12)$$

3- The Tang method. A more precise formula for the temperature integral has been suggested by Tang *et al* [38], which can be put in the form:

$$\ln\left(\frac{\beta_i}{T_{\alpha i}^{1.894661}}\right) = C_T(\alpha) - 1.00145033\frac{E_\alpha}{RT_{\alpha i}} \quad (13)$$

4- The Starink method [36, 37], another new method, which is given by:

$$\ln\left(\frac{\beta_i}{T_{\alpha i}^{1.92}}\right) = C_S(\alpha) - 1.0008\frac{E_\alpha}{RT_{\alpha i}} \qquad (14)$$

5- For various heating rates β, the Friedman method[12] can be obtained directly from Eq. (7) at specific crystallization fraction α, as:

$$\ln\left(\frac{d\alpha}{dt}\right)_{\alpha i} = C_F(\alpha) - \frac{E_\alpha}{RT_{\alpha i}} \qquad (15)$$

Experimental techniques

The bulk Cd₁₀Se₉₀ were prepared from a mixture of Cd and Se elements with purity 99.999% (Aldrich Chem Co,USA). The constituent elements were weighed according to their atomic percentage and were sealed in a quartz ampoule (inner diameter ~ 8 mm) under vacuum of 10⁻³Torr. The sealed ampoules were kept inside a furnace and heated gradually up to 1173 K and kept at that temperature for 16hrs. Continuous stirring of the melt was carried out to ensure good homogeneity. The melt was then rapidly quenched in ice-water mixture to obtain the glassy state. After quenching, the solid ingots were removed from the ampoules and kept in dry atmosphere.

The structure and phases of the films were confirmed by using X-ray diffractometer (Philips type PW 1710 with Cu as a target and Ni as a filter, λ=1.5418 Å). The surface morphology of the films was examined using scanning electron microscopy (SEM) technique, Jeol (JSM)-T200 type. The chemical composition of the films was studied by using the standard Energy Dispersive analysis of X-ray (EDX) technique. An EDX unit attached to the scanning electron microscope was employed for these measurements.

The thermal behavior under non-isothermal conditions was investigated using a differential thermal analyzer (Shimadzu DTA-60 H) on approximately 10mgm quantities of fine powder samples. The heating rates β, were varied from 5 to 30 K/min in the temperature range from 310 to 600 K. The melting temperature and melting enthalpy of Cd, and Se were used to calibrate the temperature and energy of the instrument.The measurements were carried out under nitrogen atmosphere to prevent the oxidation of the samples. The accuracy of the heat flow was ±0.01 mW. The glass transition temperature T_g, the crystallization onset temperature T_c and the crystallization peak temperature T_p were determined with accuracy ±1 K using the microprocessor of the thermal analyzer. The crystallized fraction α was calculated using the partial area analysis.

Results and discussion

The EDX peaks of the studied composition shown in Fig. 1(a) confirm the presence of the elements Cd, and Se. In addition, analyzing the EDX data showed that the relative proportions of

Cd and Se in the studied alloy are 9.44and 90.56respectively, which is very near to our targeted Cd:Se ratio (10:90). The X-ray diffraction examination indicates the amorphous structure of the as-prepared Cd$_{10}$Se$_{90}$ bulk as shown in Fig. 1(b). Fig. 1(c) shows the SEM of a fractured as-prepared bulk specimen. A conchoidal contour of the fractured specimen indicates the glass structure.
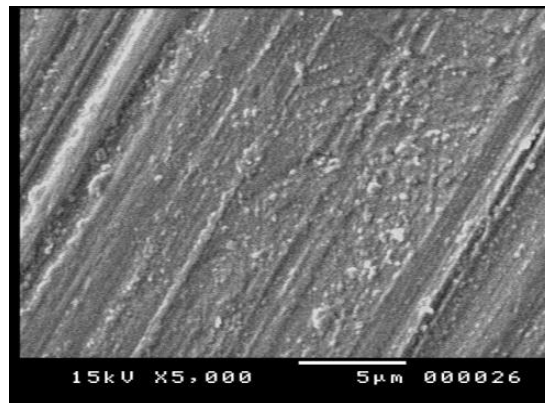
(a)
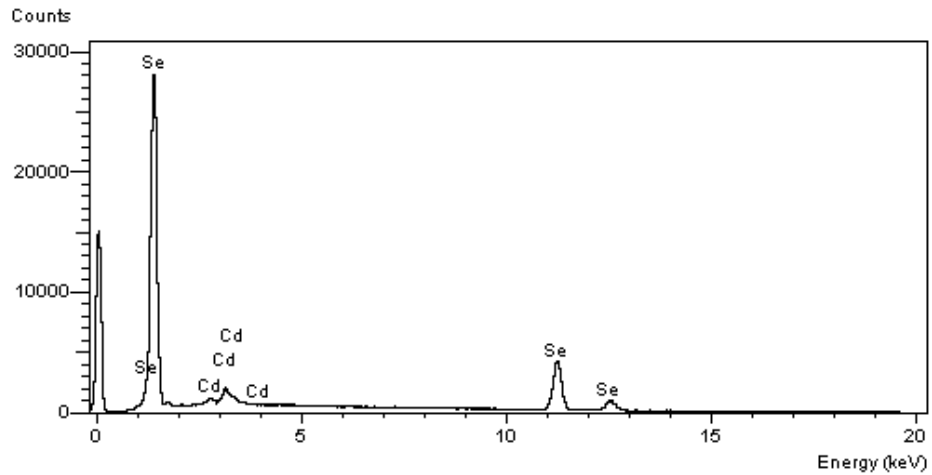
(b)
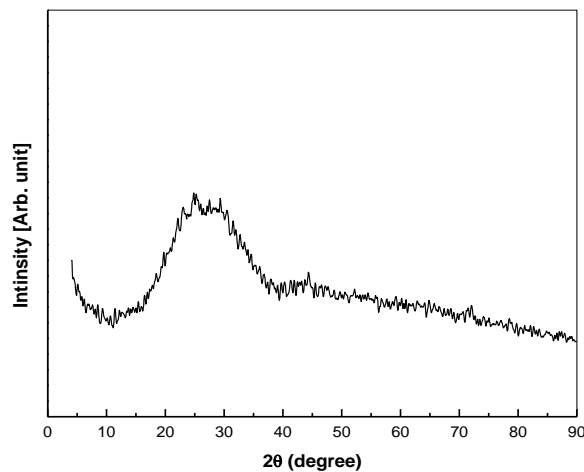
(c)

Fig. 1. (a) EDX spectrum (b) X-ray diffractometer (c) SEM micrograph of the as-prepared Cd$_{10}$Se$_{90}$ bulk specimen

DTA curves of the crystallization process of the Cd$_{10}$Se$_{90}$chalcogenide glass obtained at different heating rates are shown in Fig.2. The DTA thermo grams are characterized by two temperatures. The glass temperature T_g as defined by the endothermic change in the DTA trace, indicates a large change of viscosity, marking a transformation from amorphous solid phase to super cooled liquid state. The exothermic peak temperature T_p is used to identify the crystallization process. It is evident from this figure that both T_p and T_g shift to higher temperatures with increasing heating rate. The variation of the T_p at various heating rates is shown in Fig. 3. The shift of T_p arises from the dependence of the induction time, t_{in} associated with nucleation process. Crystallization is controlled by nucleation and there exist an induction time for nucleation. As the heating rate increases, the temperature at which t_{in} becomes zero increases leading to the observed shift of crystallization to higher temperatures.
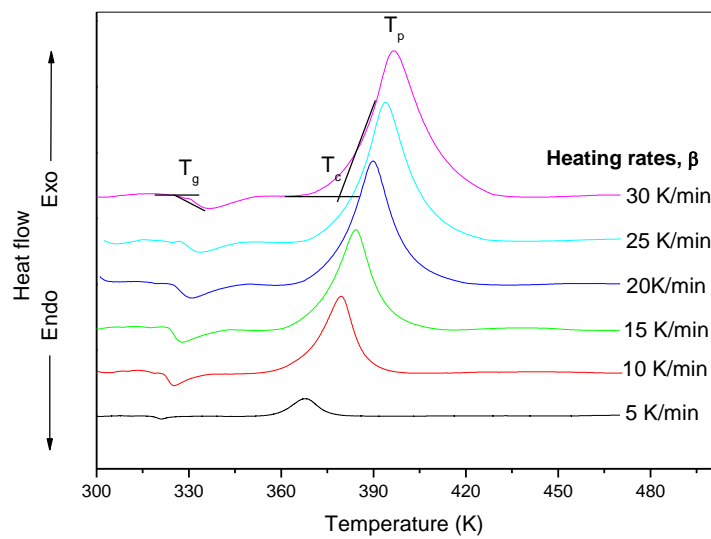

Fig. 2 DTA curves of the Cd$_{10}$Se$_{90}$chalcogenide glass at different heating rates.
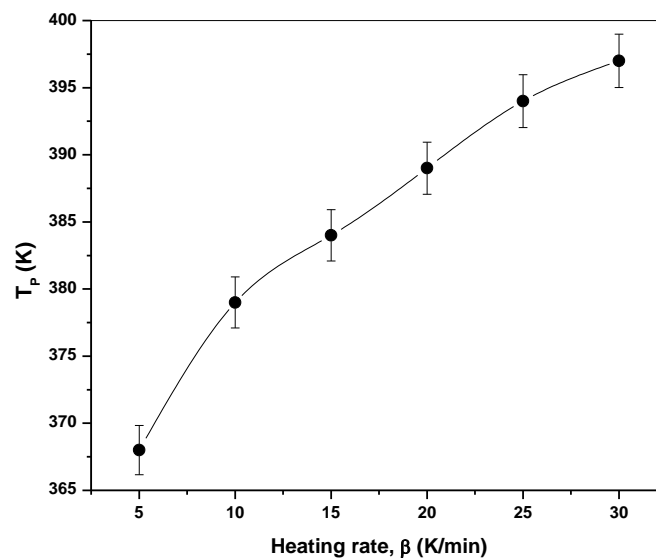

Fig. 3 Variation of the T_p at various heating rates.

The activation energy of the crystallization process is obtained using Kissinger equation (Eq. (3)).Astraight line is obtained by plotting $\ln(\beta/T^2)$ versus $1/T_p$, as shown in Fig. 4. From the slope of the straight line, it is possible to derive the value of the activation energy of crystallization, yielding $E = 69.14 \pm 0.27$ kJ/mol. Because of the fact that the variation in $\ln(1/T^2)$ is much slower than $\ln(\beta)$, Kissinger equation was approximated by Mahadevan et al. [26] as

$$\ln(\beta) = C_M(\alpha) - \frac{E}{RT} \qquad (16)$$

From the linear $\ln(\beta)$ versus $(1/T_p)$ plot, shown also in Fig. 4, the calculated value of E is equal to 75.49 ± 0.2 kJ/mol.
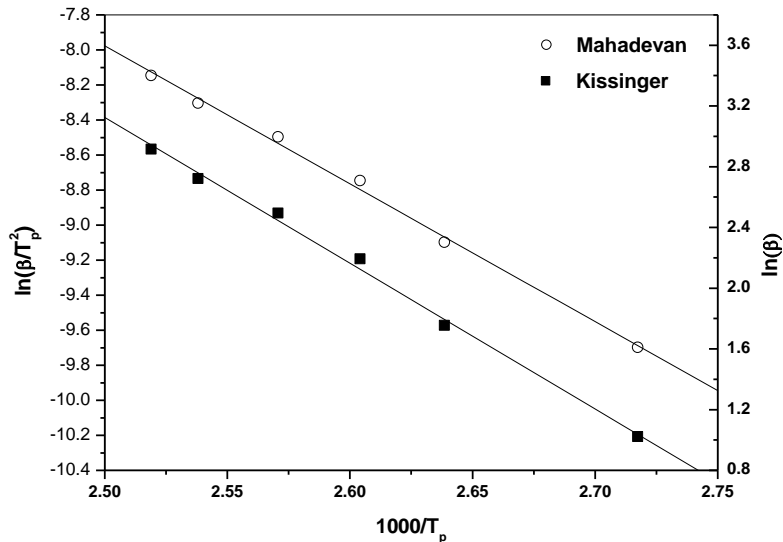

Fig. 4   A plot of $\ln(\beta/T^2)$ and $\ln(\beta)$ versus 1000/T. The straight lines are fit to Kissinger and Mahadevan equations.

The volume of crystallization fraction, α, was calculated using the partial area method as shown in Fig.5. The fraction (α) crystallized at a given temperature (T) is given as α= (A_T/A), where A is the total area of the exothermic between the onset temperature (T_i) where crystallization just begins and the temperature, T_f, where the crystallization is completed, $A_T$is the area between $T_i$and T. From this figure we notice a systematic shift in α to higher temperature with an increase in heating rate β.
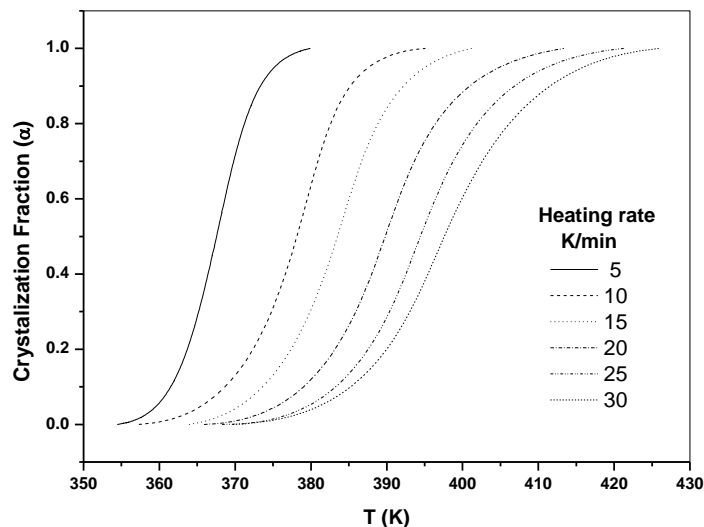

Fig. 5   Extent of crystallization, α, as a function of temperature at different heating rates

In order to investigate the heating rate dependence of the kinetic parameters, n and E, we analyzed the data using Matusita model (Eq. (4)). Using the data of Fig. 5, plots of ln[-ln(1-α)] against $1/T$ at different heating rates are obtained, as shown in Fig. 6. The straight lines in this graph are linear fittings according to Eq. (4). From the slope of each straight line, shown in Fig. 6, *mE* value was calculated. It is evident from this figure that different values of *mE* are obtained for different heating rates. If the crystallization fraction, α, is determined at a fixed temperature, at different heating rates, then the Avrami exponent *n* can be obtained from the slope of the following equation [30]:

$$\frac{d\left\{\ln\left[-\ln(1-\alpha)\right]\right\}}{d(\ln \beta)}\Bigg|_{T} = -n \qquad (17)$$

The value of n can be obtained by plottingln[-ln(1-α)] versus lnβ at different temperatures. Fig. 7 shows these plots for the studied composition. It is clear from the figure that *n* is temperature dependent, as shown in Fig. 8. The average value of *n*is 3.04 ±0.25. The calculated *n* values were not integers. This means that the crystallization occurs by more than one mechanism [1]. Furthermore, this could indicate the possibility of a combination of two and three dimensional crystal growths with heterogeneous nucleation [31].Once the value of *n* is obtained, the effective activation energy *E* can be evaluated at different heating rates. As the sample is preannealed for a period of time before each experimental run at temperature below the glass transition temperature (T$_g$), the condition of site saturation could be fulfilled and hence we can assume n=m.

Fig. 9 shows the variation of the effective activation energy with the heating rate showing a dramatic decrease in *E* as the heating rate increases. A similar behavior was observed in chalcogenide glass by [3,19,4]. The observed dependence of the effective activation energy on the heating rate can be attributed to the possible variation of *E* with temperature.
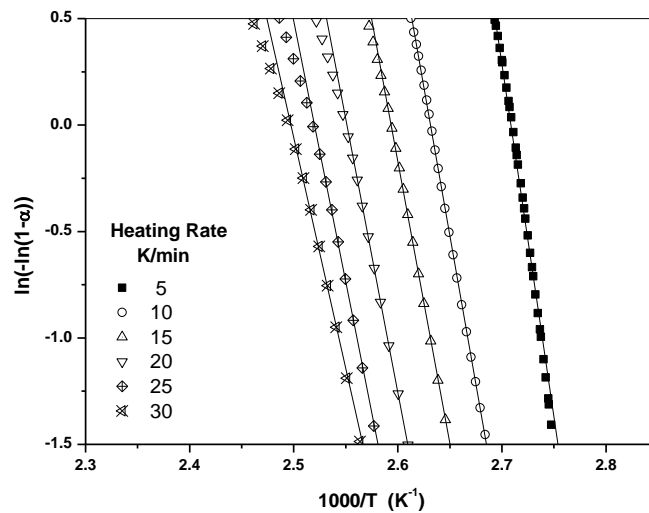

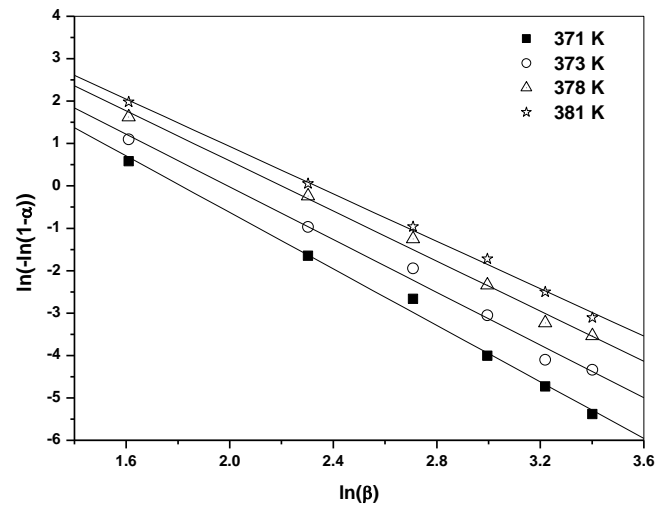Fig. 6ln[-ln(1-α)] versus 1000/*T* plots at different heating rates for the Cd$_{10}$Se$_{90}$chalcogenide glass.

Fig. 7 ln[-ln(1-α)] versus ln(β) plots at different temperatures for the Cd$_{10}$Se$_{90}$chalcogenide glass.
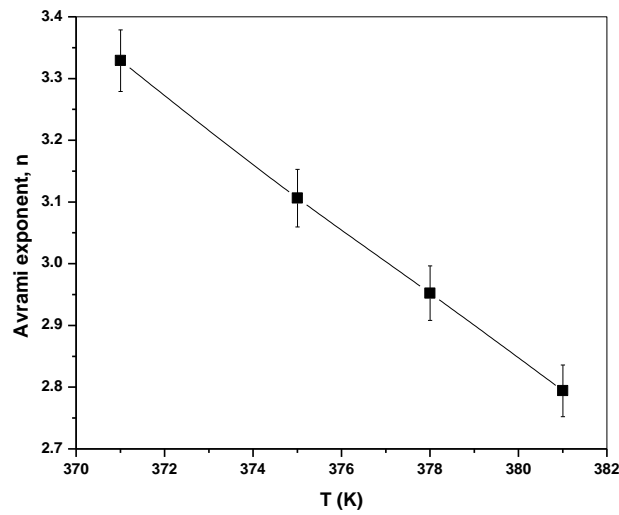

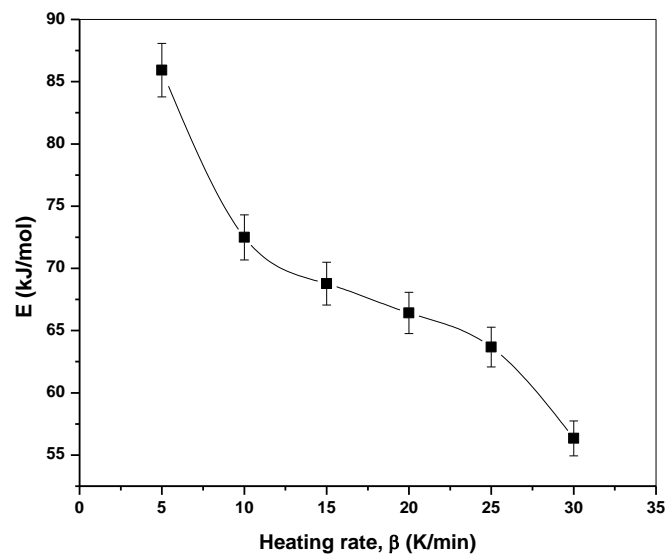Fig. 8   Variation of the Avrami exponent *n* with temperature.

Fig. 9   Effective activation energy (*E*) as a function of heating rate for the Cd$_{10}$Se$_{90}$chalcogenide glass.

In order to confirm this possibility, KAS, FWO, Tang, Starink, and Friedman isoconversional methods were used to investigate the variation of the effective activation energy with extent of crystallizationand hence with temperature.Using the experimental data shown in Fig.5, the five isoconversional methods are used to evaluate the activation energies at different values of α. According to the KAS, FWO, Tang, Starinkand Friedman methods, the effective activation energy of crystallization can be obtained by plotting $\ln(\beta/T^2)$, $\ln(\beta)$, $\ln(\beta/T^{1.894661})$, $\ln(\beta/T^{1.92})$ and dα/dtversus $1000/T$ respectively for all heating rates. Fig.10 represents an example of such a plot$\ln(\beta/T^2)$ versus $1000/T$. The slopes of the straight lines shown in the figure are used to calculate the activation energy for that particular α value. This procedure is repeated for other values of α. As shown in Fig. 11, a pronounced variation of the effective activation energy, E, as a function of the degree of conversion α is observed in the five isoconversional methods. It can be seen that the five methods yield a decrease of the activation energy with increasing α. The KAS, Tang, and Starink, give similar values of E_α. The FWO method gives values of E_α of only 4 % higher than the values obtained by the other methods.
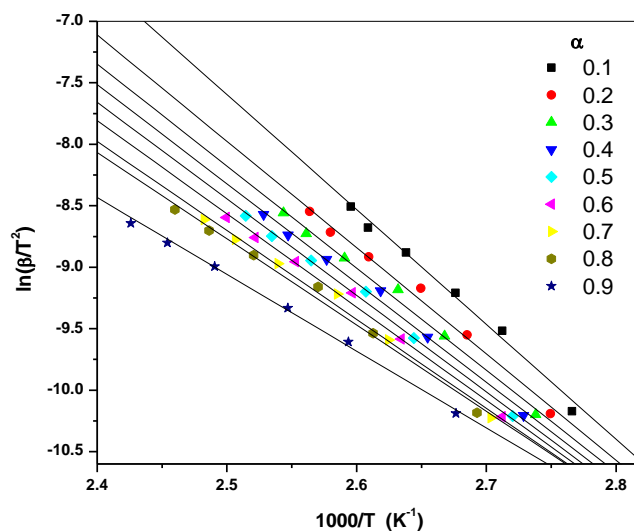

Fig. 10   A plot of $\ln(\beta/T^2)$ versus 1000/T (for α value). The straight lines are fit to Kissinger-Akahira-Sunose (KAS) equation.
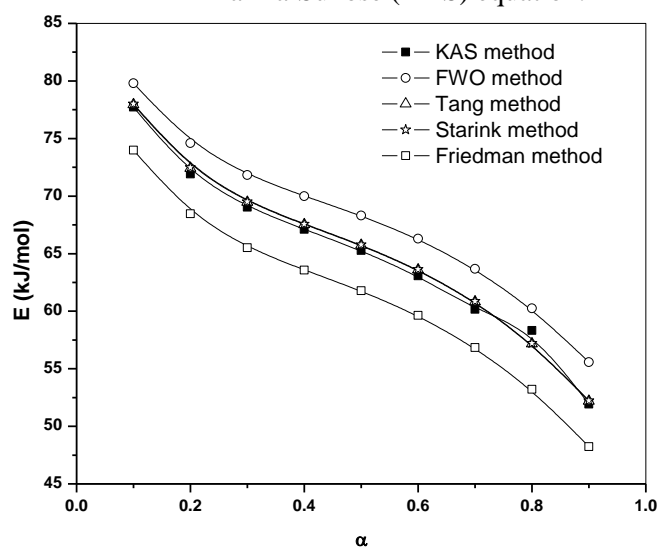

Fig. 11The effective activation energy$E$ as a function of α as determined using different isoconversional methods

The temperature dependence of E_α can be obtained [2] by replacing α with a corresponding average temperature calculated from Fig. 5. This temperature dependence is shown in Fig. 12.It is evident from the observed temperature dependence of the activation energy in the present system that the amorphous to crystalline transformation cannot be described by a single-step mechanism. The transformation demonstrates complex multi-step reactions involving several processes of growth with different activation energies and mechanisms. The observed decrease of the activation energy with temperature demonstrates that the rate constant of crystallization is in fact determined by the rates of two processes; nucleation and diffusion. Because these two mechanisms are likely to have different activation energies, the effective activation energy of the transformation will vary with temperature. This interpretation is based on the nucleation theory proposed by Turnbull and Fisher [10]. According to this theory, the temperature dependence of the crystallization rate r is given by:

$$r = r_\circ \exp\left(\frac{-E_D}{k_B T}\right)\exp\left(\frac{-\Delta F}{k_B T}\right) \qquad (17)$$

where $r_\circ$ is the pre-exponential factor, k_B is the Boltzmann constant, E_D is the activation energy for diffusion and ΔF is the maximum free energy necessary for nucleus formation. The simplified kinetic analysis in which the activation energy is assumed constant is not appropriate to describe the present data. The present findings also indicate that, since the effective energy is not constant during the transformation, Matusita et al model cannot be used to extract accurate values of the kinetic parameters E and n for the transformation.
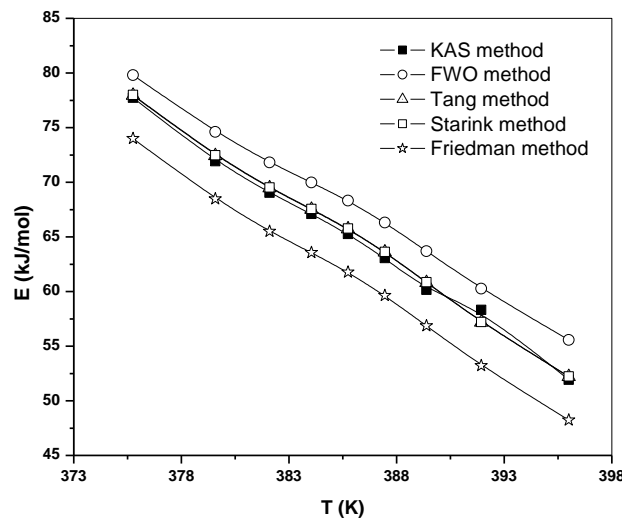

Fig. 12 Temperature dependence of the effective activation energy for the Cd$_{10}$Se$_{90}$chalcogenide glass.

Conclusions

The kinetics of transformation from amorphous to crystalline phase in Cd$_{10}$Se$_{90}$chalcogenide glass is studied using DTA technique. The heating rate dependence of the effective activation energy of crystallization was determined from Matusita method. It is suggested that the observed strong dependence of the effective activation energy with β may be attributed to the variation of E with α and T. This was confirmed when the five different isoconversional methods were used to investigate the variation of the effective activation energy with extent of crystallization and hence with temperature. The activation energy was found to vary with extent of conversion (and with temperature) which explains the observed strong heating rate dependence of the activation energy. The present work shows that the transformation from amorphous to crystalline phase in Cd$_{10}$Se$_{90}$ is a complex process involving different mechanisms of nucleation and growth.

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ميكانيكية التحول البلوري لسبائك الكادميوم– سيلينيد Cd$_{10}$Se$_{90}$ الأمورفية والغنية بالسيلينيوم

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الملخص

تكتسب أشباه الموصلات الأمورفية أهمية خاصة نظراً لما تمتاز به هذه المواد من رخص تكاليف تصنيعها و تغير خواصها مع تغير التركيب لها و من ثَم استخداماتها المتعددة في مجال الالكترونيات التي تتطور يوماً بعد يوم. ولهذا الغرض تم تحضير مركبات الـ Cd$_{10}$Se$_{90}$ الأمورفية والغنية بالسيلينيوم وفقا للأوزان الذرية لهذه العناصر من مواد عالية النقاء 99.999% بتقنية الصهر- التبريد المفاجئ، وتم التأكد من خصائصها الأمورفية و نسبها الوزنية بواسطة حيود الأشعة السينية XRD ، تحليل الأشعة السينية متبددة الطاقة EDX و المجهر الالكتروني الماسح SEM على التوالي.

تم عمل تحليل تفاضلي حراري DTA لبودرة تم تحضيرها من السبائك الصلبة تحت ظروف غير متساوية حرارياًNon-isothermal بمعدلات تسخين حراري مختلفة من 5 إلى 30 درجة/دقيقة. أثبتت نتائج التحليل الحراري لمركب الـ Cd$_{10}$Se$_{90}$ وجود مرحلة واحدة من التحول الزجاجي و مرحلة واحدة من التحول البلوري، بالإضافة إلى أنَّ درجة حرارة التحول الزجاجي T$_g$ و درجة حرارة قمة التبلور T$_p$ تزداد بزيادة معدل التسخين.

على النحو الآخر, تم حساب ميكانيكية التحول البلوري بواسطة النموذج النظرى لجونسون – ميهل – آفرامىJMA و نموذج التحول المتماثل Isoconversional، ووجد انَّ طاقة التنشيط للتحول البلوري E ليست ثابتة وتتغير بتغير معدل التسخين. هذا التغير تم تأكيده بمعادلات التحول المتماثل المختلفة بالإضافة إلى أنَّ طاقة التنشيط للتحول البلوري تتغير أيضا تبعا لتغير درجة التبلور ودرجة الحرارة، و تبين من قيم أس آفرامى Avrami Exponent (n) المحسوبة أنَّ الإنماء البلوري يحدث في خليط من ثلاثة أبعاد و بعدين. هذه النتائج تثبت أنَّ ميكانيكية التحول البلوري عملية معقدة وتحتوي على آليات مختلفة لعمليتي التنوي nucleation الإنماء growth.

الكلمات المفتاحية: أشباه الموصلات الأمورفية، ميكانيكية التبلور، طاقة التنشيط، التحليل التفاضلي الحراري، المجهر الالكتروني الماسح.