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# Estimating the activation energy for the non-isothermal crystallization of an amorphous $Sb_{9.1}Te_{20.1}Se_{70.8}$ alloy

A.A. Joraid*

*Department of Physics, Taibah University, Madinah, Saudi Arabia*

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**Abstract**

In this work, the activation energies of crystallization of amorphous $Sb_{9.1}Te_{20.1}Se_{70.8}$ have been studied under non-isothermal conditions using a differential scanning calorimetric (DSC) technique. The analysis focuses on the effect of temperature ($413 \leq T \leq 437$ K) on the DSC results. The three isoconversional methods of Friedman, Kissinger–Akahira–Sunose (KAS) and Vyazovkin were used to determine the variation of the activation energy for crystallization with temperature, $E_\alpha(T)$. The KAS and Vyazovkin methods gave identical values, and the range of $E_\alpha(T)$ was found to vary from 128.7 down to 77.8 kJ mol$^{-1}$, while the Friedman method gave lower values with $E_\alpha(T)$ from 84.1 to 31.2 kJ mol$^{-1}$. The effects of annealing were revealed by studying the morphology of the samples using scanning electron microscopy.

*Keywords:* Crystallization kinetics; DSC; Thermal analysis; Annealing effect

## 1. Introduction

The study of amorphous solids is one of the most active fields of research in the field of the physics of materials science today. One reason for this increase in interest lies in the fact that some amorphous substances show certain unusual switching properties, which could be important in modern technological applications such as switching, electrophotography, and memory devices. The study of crystallization kinetics in amorphous materials by differential scanning calorimetry (DSC) methods has been extensively discussed in the literature [1–3].

The transformation rate equation of a solid-state reaction in isothermal conditions can be generally described by [4–11]:

$$\frac{d\alpha}{dt} = k\, f(\alpha), \tag{1}$$

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

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

where $A$ (s$^{-1}$) is the pre-exponential (frequency) factor; $E$ (kJ mol$^{-1}$) the activation energy; $R$ is the universal gas constant.

The isothermal transformation rate $d\alpha(t)/dt$ can be given from Eq. (1) as

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right) f(\alpha). \tag{3}$$

Under non-isothermal conditions with a constant heating rate of $\beta = dT/dt$, Eq. (3) may be rewritten as

$$\frac{d\alpha}{dT} = \frac{d\alpha}{dt}\left(\frac{1}{\beta}\right) = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) f(\alpha). \tag{4}$$

Since there is a large variety of theoretical models and mathematical treatments to explain the estimation of crystallization kinetics, the three most popular methods have been used to analyze the crystallization kinetics of the $Sb_{9.1}Te_{20.1}Se_{70.8}$ alloy. An outline of these methods is described as follows.

For various heating rates, $\beta_i$, the Friedman method [12] can be used directly from Eq. (3) at a specific crystallization fraction, $\alpha$, as

$$\ln\left(\frac{d\alpha}{dt}\right)_{\alpha_i} = \ln(A_\alpha f(\alpha)) - \frac{E_\alpha}{RT_{\alpha_i}}. \tag{5}$$

The subscript $i$ denotes different heating rates. By introducing the parameter $C_F(\alpha) = \ln(A_\alpha f(\alpha))$, one can rewrite the above

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* Tel.: +966 48226462; fax: +966 48233727.
*E-mail addresses:* aaljoraid@taibahu.edu.sa, aaljoraid@kau.edu.sa.

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equation as

$$\ln\left(\frac{d\alpha}{dt}\right)_{\alpha_i} = C_F(\alpha) - \frac{E_\alpha}{RT_{\alpha_i}}, \tag{6}$$

For a specific $\alpha$ value and several heating rates $\beta_i$, pairs of $(d\alpha/dt)_{\alpha_i}$ and $T_{\alpha_i}$ are determined experimentally from the DSC thermograph. The parameters $E_\alpha$ and $C_F(\alpha)$, at this specific value of $\alpha$, are then estimated from a plot of $\ln(d\alpha/dt)_{\alpha_i}$ versus $1/T_{\alpha_i}$ (Eq. (6)) across at least three different heating rates. The procedure is repeated for many values of $\alpha$, yielding continuous functions of $\alpha$ for $E_\alpha$ and $C_F(\alpha)$. The Friedman method is useful because Eq. (6) does not introduce any approximations and the method is not restricted to the constant heating rate mode [13].

The Kissinger–Akahira–Sunose method [14–16] (or the generalized Kissinger method as it is sometimes called) may be obtained through derivation of Eq. (4). Subsequent logarithm application and rearrangement yield:

$$\ln\left(\frac{\beta_i}{T^2_{\alpha_i}}\right) = \ln\left[\left|\frac{df(\alpha)}{d\alpha}\right|\frac{AR}{E_\alpha}\right] - \frac{E_\alpha}{RT_{\alpha_i}}. \tag{7}$$

Again this equation can be rewritten by introducing a new parameter $C_K(\alpha) = \ln[|df(\alpha)/d\alpha|AR/E_\alpha]$:

$$\ln\left(\frac{\beta_i}{T^2_{\alpha_i}}\right) = C_K(\alpha) - \frac{E_\alpha}{RT_{\alpha_i}}. \tag{8}$$

The experimental determination of $E_\alpha$ and $C_K(\alpha)$ is similar to that of the Friedman method. For each degree of the conversion fraction, $\alpha$, a corresponding $T_{\alpha_i}$ and heating rate are used to plot $\ln(\beta_i/T^2_{\alpha_i})$ against $1/T_{\alpha_i}$. The two parameters $E_\alpha$ and $C_K(\alpha)$ are then determined from the regression slope and intercept, respectively.

The third way of extracting the same information is by using the advanced isoconversional method developed by Vyazovkin [17,18]. For a set of $n$ experiments carried out at different heating rates, the activation energy can be determined at any particular value of $\alpha$ by finding the value of $E_\alpha$ which minimizes the objective function $\Omega$, where

$$\Omega = \sum_{i=1}^{n}\sum_{j\neq i}^{n}\frac{I(E_\alpha, T_{\alpha_i})\beta_j}{I(E_\alpha, T_{\alpha_j})\beta_i}, \tag{9}$$

and

$$I(E_\alpha, T_{\alpha_i}) = \int_0^{T_{\alpha_i}} \exp\left(\frac{-E_\alpha}{RT}\right) dT. \tag{10}$$

The temperature integral, $I$, was evaluated using an approximation suggested by Gorbachev [19]:

$$\int_0^{T} \exp\left(\frac{-E}{RT}\right) dT = \frac{RT^2}{E}\left(\frac{1}{1+(2RT/E)}\right)\exp\left(\frac{-E}{RT}\right). \tag{11}$$

This study is concerned with examining the crystallization kinetics and the effect of temperature on the activation energy of $Sb_{9.1}Te_{20.1}Se_{70.8}$ chalcogenide glass by means of non-isothermal techniques. The three above-mentioned methods of analysis have been used to analyze the crystallization kinetics of the $Sb_{9.1}Te_{20.1}Se_{70.8}$ alloy. The effect of annealing on the structure was investigated by scanning electron microscopy (SEM).

## 2. Experimental

Bulk material was prepared by the well-established melt-quench technique. High purity (99.999%) Sb, Te and Se in appropriate atomic wt% proportions were weighed and sealed in a quartz glass ampoule (12 mm diameter) under a vacuum of $10^{-4}$ Torr. The contents were heated at around 950 K for 24 h. During the melt process, the tube was frequently shaken to homogenize the resulting alloy. The melt was quenched in ice water to obtain the material in a glassy state.

The DSC experiments presented in this paper were performed by using a Shimadzu DSC-60 instrument with an accuracy of ±0.1 K, under dry nitrogen supplied at the rate of 35 ml min$^{-1}$. The samples were encapsulated in standard aluminum sample pans. To minimize temperature gradients, the samples were well granulated to form a uniform fine powder and spread as thinly as possible across the bottom of the sample pan. The weight of sample was kept very low (between 2.4 and 3 mg). Non-isothermal DSC curves were obtained at selected heating rates between 2 and 70 K min$^{-1}$. The temperature and enthalpy calibrations were checked with indium ($T_m = 156.6\,^\circ C$, $\Delta H_m = 28.55\ J\ g^{-1}$) as a standard material supplied by Shimadzu.

The surface microstructure was revealed by the scanning electron microscope (SEM) (model Shimadzu Superscan SSX-550), and the contents of the alloy were checked by EDX.

## 3. Results and discussion

### 3.1. Structural studies

Qualitative and quantitative calculations were performed using the EDX technique accomplished with SEM from the displayed characteristic X-ray. The results obtained are shown in Fig. 1. The atomic percentage ratios of Sb, Te and Se were found to be 9.1, 20.1 and 70.8, respectively.

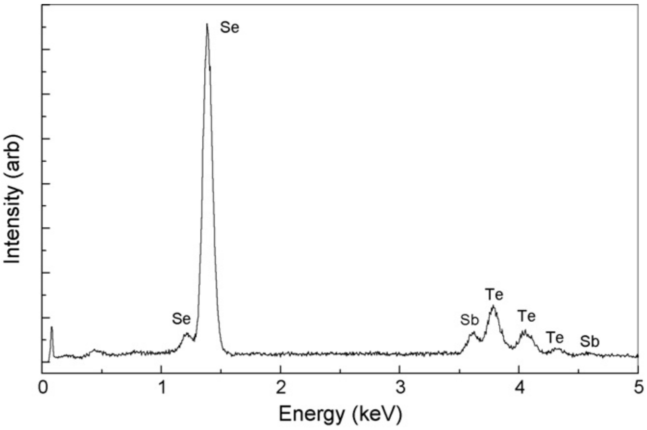

Fig. 1. EDX results of the chalcogenide $Sb_{9.1}Te_{20.1}Se_{70.8}$.

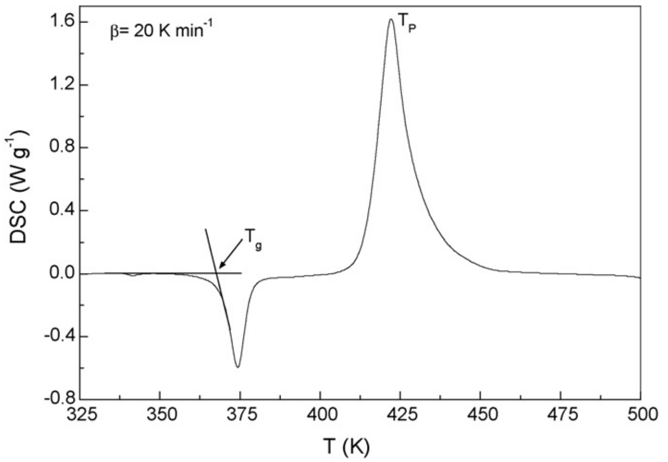

Fig. 2. Typical DSC trace of the chalcogenide $Sb_{9.1}Te_{20.1}Se_{70.8}$ heated at a constant rate of 20 K $min^{-1}$.

A typical (DSC) curve obtained at a constant rate of 20 K $min^{-1}$ is shown in Fig. 2. The exothermic peak traces at different heating rates $\beta$ are shown in Fig. 3. As evident from this figure, the peak temperature, $T_p$, increases with increasing $\beta$. This phenomenon has been reported throughout the literature [20].

The transformation from the amorphous to the crystalline state was investigated by studying the morphology of the samples. The change in the morphological nature under isothermal annealing has been recorded by SEM. Fig. 4a shows an SEM image of a fractured, as prepared, bulk specimen of $Sb_{9.1}Te_{20.1}Se_{70.8}$. The micrograph shows the conchoidal contours, which are a good indication for glass structure.

On the other hand, Fig. 4b–e shows the effect of annealing temperature on the morphology in nitrogen flow. Fig. 4b shows an SEM micrograph of a $Sb_{9.1}Te_{20.1}Se_{70.8}$ glass specimen annealed at 393 K for 30 min, showing surface crystallization. The crystallization morphology is not distinct. This is probably due to the fact that the crystallization is only in its initial stages. By increasing the annealing temperature to 408 K for 30 min, the crystalline morphology covered the specimen surface and extended into the bulk material as shown in Fig. 4c. This indicates that the amount of transformed crystalline phase is increased by increasing the annealing temperature. Both Fig. 4d and e shows SEM micrographs of a $Sb_{9.1}Te_{20.1}Se_{70.8}$ glass specimen annealed at 413 K for 30 min. As evidenced from both figures, the crystalline morphology is homogenous and covers the specimen surface completely. In addition, the fractured regions show a laminar crystalline (two-dimensional) morphology.

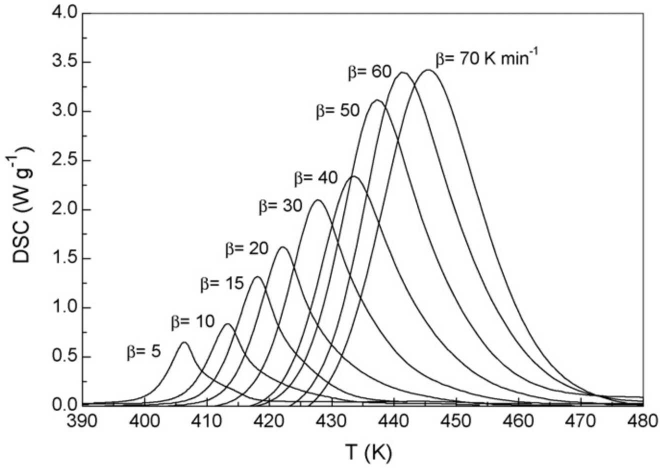

Fig. 3. The exothermic peak traces at different heating rates.

### 3.2. *The activation energy of crystallization*

The activation energy of crystallization is normally obtained using different theoretical models. The most widely used model is the JMA model for non-isothermal kinetics. This model implies that the Avrami exponent, $n$, and the activation energy, $E$, should be constant during the transformation process. Recent papers in this field have shown that $n$ and $E$ are not necessarily constants, but show variation in different stages of the transformation [21–24]. The system Se–Te–Sb is thought to be promising media, so it has drawn great attention. Abdel-Rahim [25] found the activation energy of crystallization for the alloy $Sb_{9.1}Te_{15}Se_{76}$ to be in the range of 92–100 kJ $mol^{-1}$ by using Augis and Bennet, and Gao et al. models, respectively. By using the Kissinger model, Moharram et al. [26] obtained a value of 89.6 kJ $mol^{-1}$ for $E$ for the composition $Sb_9Te_{20}Se_{71}$. Via the results of Moharram et al. [26], Sahay and Krishnan [21] have suggested that the activation energy for crystallization, $E$, should vary for different heating rates. Joraid [22] has shown that the validity of the JMA model in non-isothermal conditions is reasonably satisfied for $Sb_{9.1}Te_{20.1}Se_{70.8}$, but only at high heating rates (60 K $min^{-1}$). More recently, Abu-Sehly and Elabbar [23] from our group have studied the alloy $Sb_{5.7}Te_{21.1}Se_{73.2}$, and they showed a remarkable heating rate dependence of the activation energy of crystallization. They have recognized that the data obtained can be fit to a Kissinger model in two regions, leading to two different values for the activation energy, $E = 82$ and 103 kJ $mol^{-1}$.

With the aim of calculating the activation energy for the crystallization of the chalcogenide $Sb_{9.1}Te_{20.1}Se_{70.8}$ glass, $E$, the Friedman and Kissinger equations (Eqs. (6) and (8)) were used on a conversion range of $\alpha = 0.5$ at different heating rates, $\beta_i$. The plots of $\ln(\beta_i/T^2_{\alpha_i})$ and $\ln(d\alpha/dT_{\alpha_i})$ against $10^3/T_{\alpha_i}$ are shown in Fig. 5. It is evident that the data in this figure can be fitted for both equations in two regions leading to two different values of the activation energy for crystallization, 129 ± 3 and 76 ± 3 kJ $mol^{-1}$ from the Kissinger method and 86 ± 5 and 46 ± 5 kJ $mol^{-1}$ from the Friedman method.

The first step in the evaluation of the activation energy for crystallization, $E_\alpha(T)$, is the application of the isoconversional methods mentioned in Eqs. (6), (8) and (9) to the overall crystallization data to obtain the dependence of $E_\alpha(T)$ on $\alpha$ for all heating rates applied. By replacing $\alpha$ with the respective temperature interval, the dependencies of $E_\alpha$ on temperature can be obtained [8,27,28].

Fig. 6 shows the dependence of $E_\alpha$ on the volume fraction crystallized, $\alpha$, obtained by applying the three isoconversional methods of Friedman, KAS and Vyazovkin mentioned in Eqs.

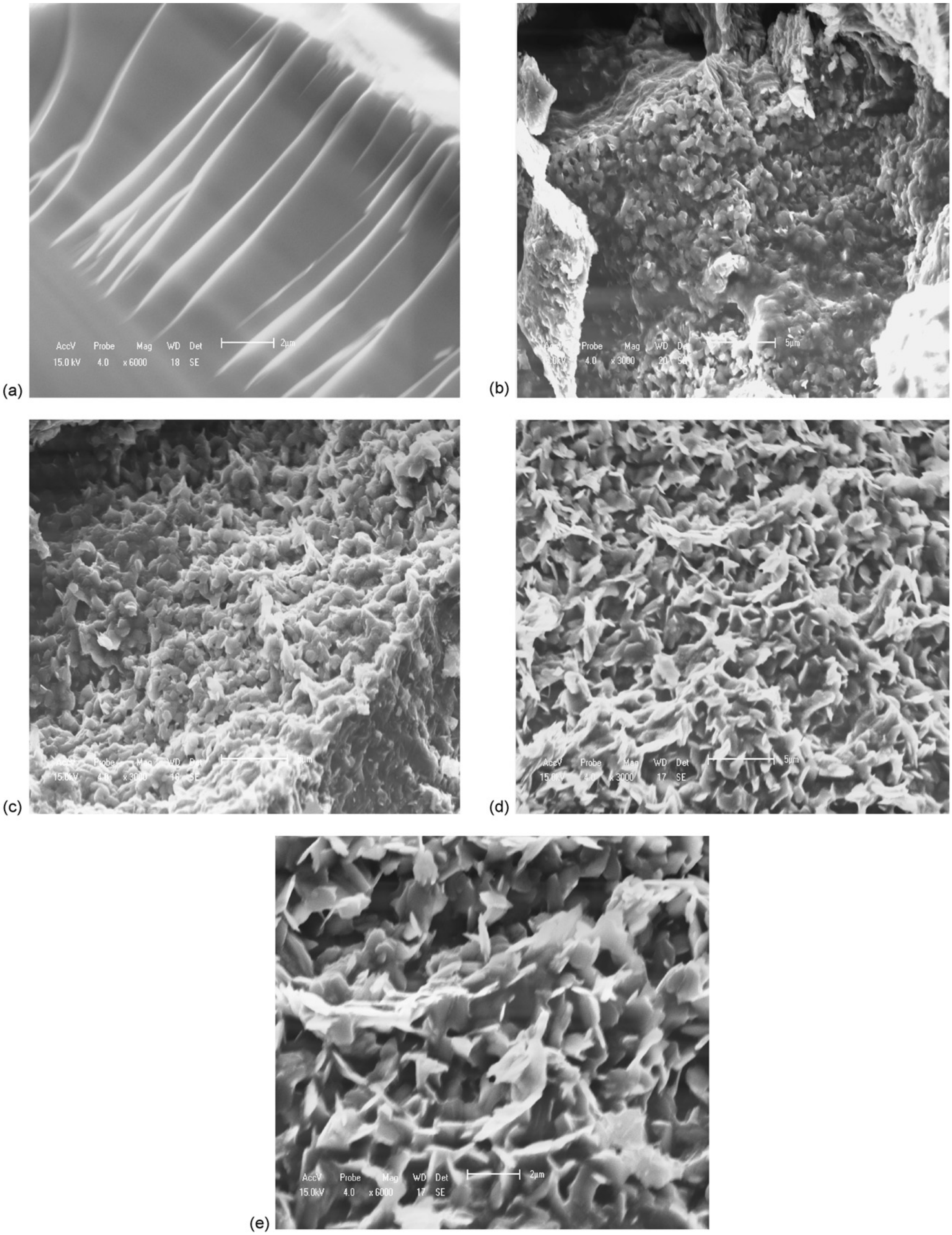

Fig. 4. Electron microscope patterns of $Sb_{9.1}Te_{20.1}Se_{70.8}$ annealed for 30 min at different temperatures: (a) as prepared in bulk specimen; (b) annealed at 393 K; (c) annealed at 408 K; (d) annealed at 413 K, 3000×; (e) annealed at 413 K, 6000×.

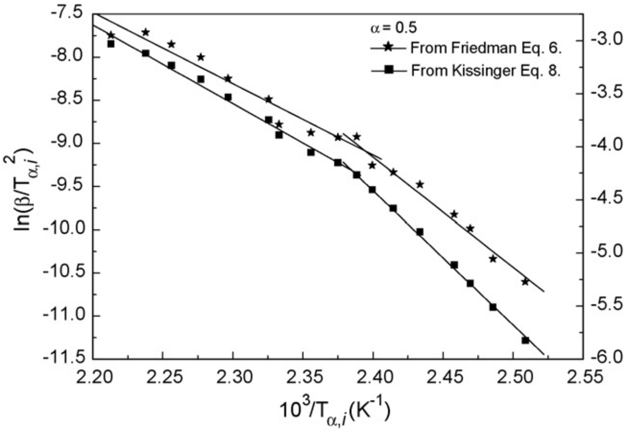

Fig. 5. Experimental plot of $\ln(\beta/T_p^2)$ vs. $10^3/T_p$, $\ln(d\alpha/dT)$ vs. $10^3/T_p$ and a straight regression lines, for $\beta = 2$–$70\,\mathrm{K\,min^{-1}}$.

(6), (8) and (9), respectively. The resulting $T$ versus $\alpha$ dependence is shown in Fig. 6 also. The results obtained by the Friedman method show that the activation energy, $E_\alpha$, is particularly independent of the value of $\alpha$ in the $0.2 < \alpha < 0.7$ range. All methods show somewhat lower values in the terminal stage of the crystallization.

Fig. 7 displays the resulting $E_\alpha(T)$ dependence as obtained from Eqs. (6), (8) and (9). The results obtained by the KAS and Vyazovkin methods are well matched and give identical values. While the Friedman method avoids the mathematical approximations used in the KAS and Vyazovkin methods, it introduces some new measurement uncertainties as the measurement of the rate conversion, d$\alpha$/d$t$, is sensitive to the determination of the baseline and the calibration of the thermal analysis equipment [7]. These uncertainties in baseline calibration may cause a shift in the values of $E_\alpha$ obtained by the Friedman method to lower values. But, the DSC curves as shown in Fig. 2 present a good baseline, so this cannot be a serious problem. Vyazovkin and Sbirrazzuoli [11] mention that $E_\alpha$ should be constant in $I(E,T)$ through the whole interval of integration, i.e., 0–$\alpha$. This assumption introduces a systematic error in the value of $E_\alpha$ if the actual value varies with $\alpha$. In the case of strong variations, the error can reach 20–30%. This error can be eliminated by assuming a small interval of conversions, $\Delta\alpha$. In this work identical values of $E_\alpha(T)$ were obtained by using two intervals of conversion, $\Delta\alpha = 0.05$ and 0.01.

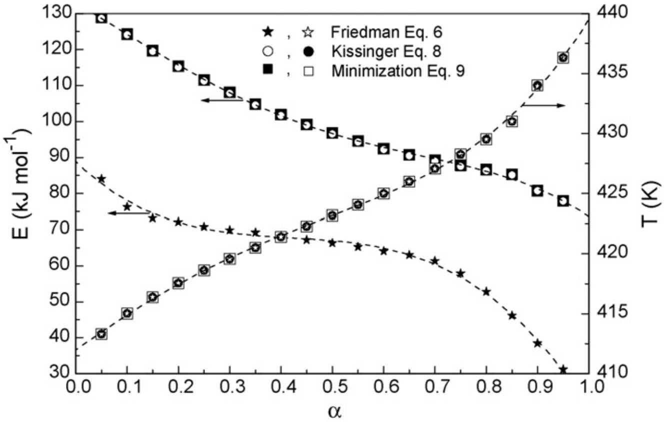

Fig. 6. Dependence of the activation energy for crystallization, $E_\alpha$, and the corresponding temperature on the volume of the crystallized fraction, $\alpha$.

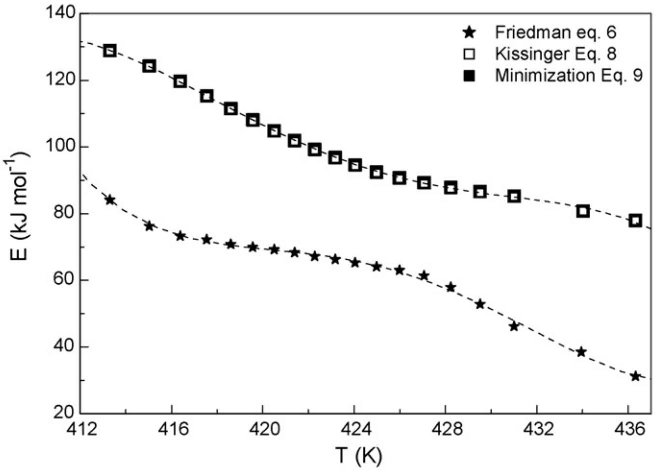

Fig. 7. Dependence of the activation energy for crystallization, $E_\alpha$, on the temperature.

The values of $E_\alpha$ are positive and decrease with temperature for the three methods used, which simply indicates that the crystallization rate increases with increasing temperature. This behavior 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 [28]. This interpretation is based on the nucleation theory proposed by Fisher and Turnbull [29]. According to this theory, the temperature dependence of the crystallization rate, $r$, is given by

$$r = r_0 \exp\left(\frac{-E_D}{k_B T}\right) \exp\left(\frac{-\Delta F}{k_B T}\right), \qquad (12)$$

where $r_0$ is the pre-exponential factor; $k_B$ the Boltzmann constant; $E_D$ the activation energy for diffusion; $\Delta F$ is the maximum free energy necessary for nucleus formation.

## 4. Conclusion

By applying three isoconversional methods, the activation energies of crystallization, $E_\alpha(T)$, of $Sb_{9.1}Te_{20.1}Se_{70.8}$ were found to be strongly temperature-dependent. The results show a decrease in the activation energy for crystallization with increasing temperature. The morphology of a specimen annealed at 413 K for 30 min showed a laminar crystalline structure. The temperature dependence of $E_\alpha(T)$ was explained in light of the nucleation theory of Turnbull and Fisher.

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