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An integral method to analyze the glass-crystal transformation kinetics by differential scanning calorimetry under non-isothermal regime. Application to the crystallization of the $Ge_{0.08}Sb_{0.15}Se_{0.77}$ chalcogenide glass

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Abstract In this article, a theoretical procedure has been developed for the kinetic study of the glass-crystal transformations under continuous heating regime in materials involving formation and growth of nuclei, obtaining the corresponding parameters: kinetic exponent, activation energy, and pre-exponential frequency. It is an integral procedure, which is based on a transformation rate independent of the thermal history of the material and assumes that the quoted rate depends only on the transformed fraction, *x*, across the *f*(*x*) function, and temperature, considering that these variables are independent ones. Therefore, the transformation rate is expressed as the product of two separable functions of absolute temperature and the transformed fraction. The quoted *f*(*x*) function corresponds to a theoretical method that we have developed and recently published, whose details are given in the Sect. "Basic theory" of this study. The above-mentioned integral procedure considers the same pair of temperatures for the different heating rates and obtains a constant value for temperature integral and, therefore, a plot of a function of the transformed fraction versus the reciprocal of the heating rate leads to a straight line with an intercept of zero, if the value of kinetic exponent is correctly chosen. The process may be repeated for other pairs of temperatures and, consequently, other straight lines will be obtained. By using different values of kinetic exponent for each of the quoted lines, it is taken the best correlation coefficient to choose the quoted exponent more suitable. On the other hand, by using the first mean value theorem to approach the temperature integral, one obtains a relationship between a function of the temperature and other function of the transformed fraction. The logarithmic form of the quoted relationship leads to a straight line, whose slope and intercept allow the obtaining of the activation energy and of the pre-exponential frequency. In addition, this study applies the quoted procedure to the analysis of the crystallization kinetics of the $Ge_{0.08}Sb_{0.15}Se_{0.77}$ glassy alloy resulting in ranges of variation both of the kinetic exponent, *n*, with the temperature and of the activation energy, *E*, with the crystallized fraction, which contain the values of *n* and *E*, obtained according to the already quoted theoretical method, that we have developed and recently published. This fact shows the reliability of the theoretical procedure described in this article to analyze the glass-crystal transformation kinetics of glassy alloy.

Introduction

During the past decades, solid state physics has meant crystal physics. Solidity and crystallinity were considered as synonymous in the texts on condensed matter. Nevertheless, one of the most active fields of solid state research in recent years is the study of solids that are not crystals, solids in which the arrangement of the atoms lacks the slightest vestige of long-range order. The advances that have been made in the physics and chemistry of these materials, which are known as non-crystalline solids are widely appreciated within the research community.

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Solid-state phase transformations play an important role in the production of many materials. Therefore, the glass-crystal transformation has been studied intensively by the researchers of the last six decades, especially since Duwez et al. [1] published their introduction to the preparation of glassy alloys by quenching technique. In this sense, a great impulse has been given at the study of a general description of the kinetics of phase transformations [2], and moreover, these materials have received great attention in the past 50 years due to their unique isotropic, structural, and chemical properties [3, 4]. An understanding of the kinetic of crystallization in glasses is important for the manufacturing of glass–ceramics and in preventing devitrification. Bearing these facts in mind , it is understandable that the last 50 years have seen a theoretical and practical interest in the application of calorimetric analysis techniques to the study of the already quoted transformations [5–7]. Thus, the classical theory of nucleation and crystal growth has been developed over the last 60 years. A full development of the theory is given by Christian [8] and a noticeable review published by Kelton [9].

The calorimetric analysis techniques are very quick and need very small quantities of glass samples to obtain the kinetic parameters of a transformation. There are two thermal analysis regimes: one is the isothermal regime [7–10], in which glass samples are quickly heated up and held at a temperature above glass transition temperature, and the other is so-called non-isothermal regime [11–15], in which glass samples are heated up at a fixed heating rate. In general, an isothermal experiment takes longer times than a non-isothermal experiment, but isothermal experimental data can be interpreted by the well-established Johnson–Mehl–Avrami (JMA) kinetic equation [16–19]. On the contrary, non-isothermal experiments have as an advantage, the rapidity that makes this type of experiments more attractive. The use of non-isothermal techniques to study solid-state transformations and to determine the kinetic parameters of the rate controlling processes has been increasingly widespread. Therefore, the use of the non-isothermal regime has produced a large number of mathematical treatments to analyze thermal process data.

The quantitative study of the glass-crystal transformation in different glassy systems by means of differential scanning calorimetry (DSC) methods has been widely discussed in the literature [9–22] during the last half century. There is a large variety of theoretical models and theoretical functions proposed to explain the glass-crystal transformation kinetics. The application of each of them depends on the type of non-crystalline material studied and how it has been made. Thus, it is well known that the theoretical basis for interpreting DSC results is provided by the formal theory of transformation kinetics as developed by JMA [16–19]. In the case of isothermal crystallization with nucleation frequency and crystal growth rate independent of time, the JMA expression can be easily integrated, giving a straightforward equation. It should be noted, however, that the quoted equation strictly applies only to isothermal experiments [23]. Nevertheless, many authors have used the above-mentioned equation to derive expressions describing non-isothermal transformations [24, 25]. This fact shows an incomplete understanding of the formal theory of transformation kinetics, as Henderson has suggested in a notable study [26].

In this article, an integral method is developed to analyze the glass-crystal transformation kinetics and to calculate the corresponding parameters: kinetic exponent, activation energy, and pre-exponential frequency of glassy alloys. The quoted method assumes that the reaction rate depends only on the transformed fraction, x, across the $f(x)$ function, and temperature, and that these variables are independent ones [27, 28]. The quoted $f(x)$ function corresponds to the theoretical method developed (TMD), which we have published recently in Ref. [29]. The integral method developed on this study considers a pair of temperatures for the different heating rates and obtains a constant value for the temperature integral and, therefore, a plot of a function of the transformed fraction versus the reciprocal of the heating rate leads to a straight line with an intercept of zero. The procedure may be repeated for other pairs of temperatures and, consequently, other straight lines will be obtained. By using different values of kinetic exponent for each of the quoted lines, it is taken the best correlation coefficient to choose the quoted exponent more suitable. On the other hand, by using the first mean value theorem to approach the temperature integral, one obtains a relationship between a function of the temperature and other function of the transformed fraction. The logarithmic form of the quoted relationship leads to a straight line, whose slope and intercept allow obtaining the activation energy and the pre-exponential frequency.

In addition, this article applies the quoted method to the analysis of the crystallization kinetics of the $Ge_{0.08}Sb_{0.15}Se_{0.77}$ chalcogenide glass resulting in ranges of variation both of the kinetic exponent, n, with the temperature and of the activation energy, E, with the crystallized fraction, which contain the values of n and E, obtained according to the TMD recently published in Ref. [29].

Basic theory

It is well known that the main finality of the kinetic analysis of a glass-crystal transformation under non-isothermal conditions is the determination of the corresponding parameters: activation energy, E, kinetic exponent, n, and pre-exponential frequency, A_0. The methods used to evaluate the quoted parameters are usually classified as differential and integral methods [27]. Both types of method may be classified further as being based on data acquired for one or more heating rates. It is considered that an integral method based on data recorded for various heating rates could give results which are more reliable and less affected by errors, since the quoted method evaluates the whole experimental data set and it is based on the primary experimentally acquired data x and T. The integral method proposed in this study assumes, as in most solid-state transformations, that the reaction rate, dx/dt, for thermal treatments under non-isothermal conditions can be expressed as a product of two separable functions of absolute temperature, T, and the transformed fraction, x [28].

$$\frac{\mathrm{d}x}{\mathrm{d}t} = K(T)f(x) \tag{1}$$

where $K(T)$ is the reaction rate constant and $f(x)$ a function of x and reflects the mechanism of transformation.

Some authors [30] introduce the following requirement: that $f(x)$ is independent of the heating rate, β.

In this study, we introduce the $f(x)$ function corresponding to the transformation mechanism deduced from the TMD, that we have recently published in Ref. [29]. From this point view the crystallization rate, dx/dt, is obtained, taking the derivative of the actual transformed fraction (Eq. 24 of the quoted reference) with respect to time, resulting in

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \left(1 + x_\mathrm{e}\delta_\mathrm{i}^{-1}\right)^{-(\delta_\mathrm{i}+1)}\frac{\mathrm{d}x_\mathrm{e}}{\mathrm{d}t} = (1-x)^{(\delta_\mathrm{i}+1)/\delta_\mathrm{i}}\frac{\mathrm{d}x_\mathrm{e}}{\mathrm{d}t} \tag{2}$$

x_e being the extended crystallized fraction and δ_i is the impingement factor [31, 32].

Taking the derivative with respect to time of the extended crystallized fraction, given in Eq. 21 of Ref. [29], one obtains

$$\frac{\mathrm{d}x_\mathrm{e}}{\mathrm{d}t} = n x_\mathrm{e}^{\frac{n-1}{n}}\left[D^{1/n}T\exp\left(-\frac{E}{RT}\right)\right]\left(2+\frac{E}{RT}\right) = n x_\mathrm{e}^{\frac{n-1}{n}}A(T) \tag{3}$$

where n is the kinetic exponent, D can be considered as a constant, with a dimension equation $[\theta T]^{-n}$ ($[\theta]$ and $[T]$ are the temperature and the time, respectively), see Ref. [29], and bearing in mind that in most transformation reactions $E/RT \gg 1$ (usually $E/RT \geq 25$) [23], the factor $2 + E/RT \approx E/RT$.

Substituting Eq. 3 into Eq. 2, the actual transformed fraction can be written as

$$\begin{aligned}\frac{\mathrm{d}x}{\mathrm{d}t} &= n(1-x)^{(\delta_\mathrm{i}+1)/\delta_\mathrm{i}}\left\{\delta_\mathrm{i}\left[(1-x)^{-1/\delta_\mathrm{i}}-1\right]\right\}^{\frac{n-1}{n}}A(T)\\ &= f(x)A(T)\end{aligned} \tag{4}$$

where the x_e expression is obtained from Eq. 24 of Ref. [29].

It should be noted that Eq. 4 represents a product of two separable functions of absolute temperature and the transformed fraction as Eq. 1. Accordingly, following the literature [27] the above-mentioned Eq. 4 can be integrated with the usual change of the variable time into temperature, giving

$$F_\mathrm{rs} = \int_{x_\mathrm{r}}^{x_\mathrm{s}} \frac{\mathrm{d}x}{f(x)} = \frac{1}{\beta}\int_{T_\mathrm{r}}^{T_\mathrm{s}} A(T)\mathrm{d}T = \frac{1}{\beta}I_\mathrm{rs} \tag{5}$$

where x_r, x_s are two different degrees of conversion, T_r, T_s are their corresponding temperatures, and it is considered a heating rate $\beta = \mathrm{d}T/\mathrm{d}t$.

By using the substitution $y = \delta_\mathrm{i}\left[(1-x)^{-1/\delta_\mathrm{i}}-1\right]$ the integral of the left-hand side of Eq. 5 becomes

$$\begin{aligned}F_\mathrm{rs} &= \frac{1}{n}\int_{y_\mathrm{r}}^{y_\mathrm{s}} y^{\frac{1-n}{n}}\mathrm{d}y = \left[y^{\frac{1}{n}}\right]_{y_\mathrm{r}}^{y_\mathrm{s}}\\ &= \left\{\left[\delta_\mathrm{i}\left((1-x)^{-1/\delta_\mathrm{i}}-1\right)\right]^{1/n}\right\}_{x_\mathrm{r}}^{x_\mathrm{s}}\end{aligned} \tag{6}$$

It should be noted that if the impingement factor $\delta_\mathrm{i} \to \infty$ the $F(x)$ function can be written as

$$\begin{aligned}F(x) &= \lim_{\delta_\mathrm{i}\to\infty}\left[\frac{(1-x)^{-1/\delta_\mathrm{i}}-1}{1/\delta_\mathrm{i}}\right]^{1/n} = \lim_{\delta_\mathrm{i}\to\infty}\left[\frac{\frac{-1}{\delta_\mathrm{i}}\ln(1-x)}{1/\delta_\mathrm{i}}\right]^{1/n}\\ &= [-\ln(1-x)]^{1/n}\end{aligned} \tag{7}$$

where the limit has been evaluated using the equivalence $\ln\alpha \sim (\alpha - 1)$, when $\alpha \to 1$, being $\alpha = (1-x)^{-1/\delta_\mathrm{i}}$ for $\delta_\mathrm{i} \to \infty$.

Equally, when $\delta_\mathrm{i} \to \infty$ the $f(x)$ function of Eq. 4 is written as

$$\begin{aligned}f(x) &= n\lim_{\delta_\mathrm{i}\to\infty}\left\{(1-x)^{(\delta_\mathrm{i}+1)/\delta_\mathrm{i}}\left[\delta_i\left((1-x)^{-1/\delta_\mathrm{i}}-1\right)\right]^{(n-1)/n}\right\}\\ &= n(1-x)[-\ln(1-x)]^{(n-1)/n}\end{aligned} \tag{8}$$

It is well known that the impingement factor $\delta_\mathrm{i} \to \infty$ correspond to the JMA model. Moreover, according to Eqs. 7 and 8 the functions $F(x)$ and $f(x)$ of the TMD become the corresponding functions of the JMA model. These facts display the large advantage of the TMD, its generality, since, as Eqs. 7 and 8 show, the JMA model is a particular case of the method recently published in Ref. [29].

Besides, it seems interesting to develop a simple procedure that allows to show the reliability of the above-mentioned TMD for the analysis of the glass-crystal transformation kinetics of glassy alloys, confirming again the already quoted large advantage of the same, its generality. In this sense, we define the functions $y(x)$ and $z(x)$ that can be easily obtained by a simple transformation of experimental data. The quoted functions are proportional to the $f(x)$ and $f(x)F(x) = f(x)\int_0^x \frac{dx'}{f(x')}$ functions, respectively.

When the continuous heating regime is used, it is necessary to define $y(x) = (\Delta H_c)(dx/dt)\exp(E/RT)$, with ΔH_c the total enthalpy change associated with the transformation, and considering Eqs. 3 and 4, one obtains

$$y(x) = A_1 f(x) \tag{9}$$

where $A_1 = (\Delta H_c)\, D^{1/n} E/R$ is a constant.

In the case of $z(x)$ function, by using the substitution $u' = E/RT'$, the temperature integral $\int_{T_0}^{T} A(T')dT'$, Eq. 5, is transformed in an exponential integral of order two, which can be expressed, in accordance with the literature [33], by an alternating series, and Eq. 5 in the interval of transformed fraction ($0 \le x' \le x$) becomes

$$F(x) = \frac{D^{1/n}E^2}{\beta R^2}\left[\frac{e^{-u'}}{u'^2}\sum_{k=0}^{\infty}\frac{(-1)^k(k+1)!}{u'^k}\right]_{u_0}^{u} \tag{10}$$

Given that $T > T_0$ (T_0 is the starting temperature) and, therefore, $u_0 = qu$ with $q > 1$, Eq. 10 can be expressed as

$$F(x) = \frac{D^{1/n}E^2}{\beta R^2}\frac{e^{-u}}{u^2}\left[\sum_{k=0}^{\infty}\frac{(-1)^k(k+1)!}{u^k}\right](1-Q) \tag{11}$$

with $Q = \frac{1}{q^2}e^{-(q-1)u}\frac{\sum_{k=0}^{\infty}\frac{(-1)^k(k+1)!}{q^k u^k}}{\sum_{k=0}^{\infty}\frac{(-1)^k(k+1)!}{u^k}}$

Bearing in mind that in most glass-crystal transformation $u = E/RT \gg 1$, usually $E/RT \ge 25$ [23] the exponential function $e^{-(q-1)u} \ll 1$. Moreover, it should be noted that, in practice, the quoted temperatures T and T_0 do not differ by more than 5–10%, in accordance with the literature [25] and it be verified that, in the worse case (difference of 10%), the quotient of the series in the Q function is approximately 1. Accordingly, the quoted Q function is negligible in comparison with the unit, and Eq. 11 becomes

$$\begin{aligned} F(x) &= \frac{D^{1/n}E^2}{\beta R^2}\frac{e^{-u}}{u^2}\sum_{k=0}^{\infty}\frac{(-1)^k(k+1)!}{u^k} \\ &= \frac{D^{1/n}ET}{\beta R}\left[\exp\left(-\frac{E}{RT}\right)\right]S\left(\frac{E}{RT}\right) \end{aligned} \tag{12}$$

where the function $S(E/RT)$ is defined as $S(u) = S(E/RT) = \frac{1}{u}\sum\limits_{k=0}^{\infty}\frac{(-1)^k(k+1)!}{u^k}$.

Next, we define the $z(x) = (\Delta H_c)T^2 dx/dt$ function and bearing in mind Eqs. 4 and 12, one obtains

$$z(x) = A_2 f(x)F(x) \tag{13}$$

and considering again the assumption $E/RT \ge 25$ [23], it is possible to use only the first term of the series of Eq. 12, and the approximation $S(E/RT) \approx RT/E$ is sufficiently accurate. It should be noted that $A_2 = (\Delta H_c)\beta E/R$ is a constant.

From Eqs. 9 and 13 invariant with respect to the experimental variables it can be shown the quoted reliability of the TMD to analyze the crystallization of glassy alloys. Thus, considering for the quoted method the corresponding $f(x)$ function, given in Eq. 4, taking the derivative of Eq. 9 with respect x and equalling to zero the resulting expression leads to

$$\begin{aligned} \left.\frac{df(x)}{dx}\right|_{x_q} &= (\delta_i+1)(1-x_q)^{1/\delta_i}\left[(1-x_q)^{-1/\delta_i}-1\right]-\frac{n-1}{n} \\ &= 0 \end{aligned} \tag{14}$$

This equation allows obtaining an expression of x_q, which depends on the kinetic exponent and the impingement factor

$$x_q = 1-\left(1-\frac{n-1}{n}\frac{1}{\delta_i+1}\right)^{\delta_i} \tag{15}$$

giving a maximum value for the $y(x)$ function.

In the case of the $z(x)$ function, taking the derivative of Eq. 13 with respect to x and setting the resulting expression equal to zero yields

$$\left.\frac{df(x)}{dx}\right|_{x_p} F(x_p)+1 = 0 \tag{16}$$

the condition that must be fulfilled by x_p at the maximum of the $z(x)$ function.

Introducing into Eq. 16 the functions $f(x)$ and $F(x) = \int_0^x \frac{dx'}{f(x')}$, given in Eqs. 4 and 6 one obtains the expression

$$(\delta_i+1)\left[(1-x_p)^{1/\delta_i}-1\right]+1 = 0 \tag{17}$$

which gives the value of the transformed fraction

$$x_p = 1-\left(\frac{\delta_i}{\delta_i+1}\right)^{\delta_i} \tag{18}$$

corresponding to the maximum value of the $z(x)$ function.

As an illustrative example of the previous affirmations, we have normalized the $y(x)$ and $z(x)$ functions within the (0, 1) range, as it is shown in Fig. 1 for the TMD, recently published in Ref. [29], with values of the kinetic exponent $n = 1.95$ and of the impingement factor $\delta_i = 1.59$, which are included in the obtained intervals for these quantities of the $Ge_{0.08}Sb_{0.15}Se_{0.77}$ glassy alloy studied in this study (see Table 3).

Once by means of the previous facts described, the reliability of the $f(x)$ function corresponding to the TMD to analyze the glass-crystal transformation kinetics of a glassy

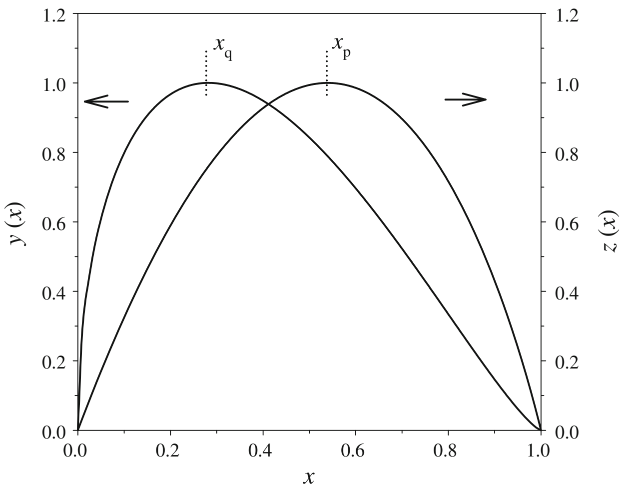

Fig. 1 Normalized $y(x)$ and $z(x)$ functions obtained from the theoretical method developed (TMD) with the values of the kinetic exponent, $n = 1.95$, and of the impingement factor, $\delta_i = 1.59$. The *broken lines* show the theoretical x_q and x_p values corresponding to the quoted model

alloy has been confirmed, we return to Eq. 5 with the aim to obtaining values of the kinetic exponent for different temperatures. In this sense, according to quoted Eq. 5 for a selected temperature pair T_r and T_s, one can determine pairs of values of x, i.e.,(x_{r1}, x_{s1}), (x_{r2}, x_{s2}),…for the experimental data at different heating rates β_i. From these pairs, the values of F_{rs1}, F_{rs2},…can be evaluated according to Eq. 6, taking for δ_i the arithmetical mean of the values of this quantity obtained for the different heating rates, according to Eq. 32 of Ref. [29]. As the temperatures T_r and T_s are the same for all the experiments, considering again Eq. 5, it follows that I_{rs} integral is constant, and therefore the plots of the values of F_{rs} versus $1/\beta$ have to lead to a straight line with an intercept of zero. The procedure may be repeated for other pairs of temperatures and, consequently, other straight lines will be obtained, by using the best correlation coefficient to choose the more suitable value for the kinetic exponent

Once by means of Eq. 5 it is possible to find the most probable kinetic exponent for each temperature of the glass-crystal transformation studied, it is necessary to calculate the values of the other kinetic parameters: activation energy, E, and the pre-exponential frequency, $A_0 = D^{1/n}E/R$, [27]. Assuming an Arrhenian temperature dependence for $A(T)$ in Eq. 3, the simplest approach of I_{rs} integral in Eq. 5 is to use the first mean value theorem for definite integrals, obtaining

$$\int_{T_r}^{T_s} \left[\exp\left(-\frac{E}{RT}\right)\right] \mathrm{d}T = (T_s - T_r)\exp\left(\frac{-E}{R\bar{T}}\right) \tag{19}$$

where $\bar{T}$ belongs to the (T_r, T_s) range, and accordingly, the logarithmic form of Eq. 5 can be written as

$$\ln\frac{\beta}{T_s - T_r} = \ln\frac{D^{1/n}E}{RF_{rs}} - \frac{E}{R\bar{T}} = \ln\frac{A_0}{F_{rs}} - \frac{E}{R\bar{T}} \tag{20}$$

For two selected transformed fractions x_r and x_s, one can determine pairs of values of T, i.e., (T_{ri}, T_{si}) corresponding to each β_i value. The plot of $\ln[\beta/(T_s - T_r)]$ versus $1/\bar{T}$ leads to a straight line whose slope, $-E/R$, and intercept, $\ln(D^{1/n}E/RF_{rs})$, allow the calculation of E and $D^{1/n}$, respectively. The method may be repeated for other pairs of transformed fraction, and, accordingly, other straight lines are obtained.

Experimental part

The $Ge_{0.08}Sb_{0.15}Se_{0.77}$ glassy semiconductor was prepared in bulk form by the standard melt quenching procedure. High purity (99.999%) germanium, antimony, and selenium in appropriate atomic percentage proportions were weighed, pulverized to less than 64 μm, and introduced into a quartz glass ampoule (6 mm diameter). The content of the ampoule (7 g total) was sealed at a pressure of 10^{-2} Pa, heated in a rotating furnace at around 1225 K for 72 h and submitted to a longitudinal rotation of 1/3 rpm to ensure the homogeneity of the molten material. Next, the quoted ampoule was immersed in a receptacle containing water with ice to solidify the material quickly, avoiding the crystallization of the alloy. Finally, the above-mentioned ampoule was put into a mixture of hydrofluoric acid and hydrogen peroxide to corrode the quartz and make it easier to extract the material.

The amorphous state of the compound was checked through a diffractometric X-ray scan, in a Bruker AXS, D8 Advance model diffractometer. Figure 2 presents the diffractogram corresponding to the glassy semiconductor studied in this study. The quoted diffractogram shows the broad humps, which are a characteristic of the amorphous state. The homogeneity and composition of the sample were verified through scanning electron microscopy (SEM) in a JEOL, scanning microscope JSM 820. The thermal behavior was investigated using a Perkin-Elmer DSC7 differential scanning calorimeter with an accuracy of ±0.1 K. Temperature and energy calibrations of the instrument were performed, for each heating rate, using the well-known melting temperatures and melting enthalpies of high purity zinc and indium supplied with the instrument [34].

The powdered samples weighing about 10 mg (particle size around 40 μm) were crimped in aluminum pans and scanned from room temperature through their glass transition temperature, T_g, at different heating rates of 4, 8, 16, 32, and 64 K min^{-1}. An empty aluminum pan was used as

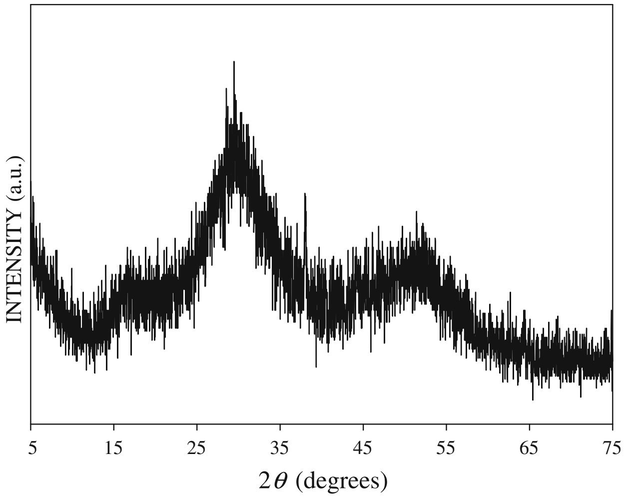

Fig. 2 Diffractogram of the $Ge_{0.08}Sb_{0.15}Se_{0.77}$ semiconductor glass

reference, and in all cases a constant 60 mL min^{-1} flow of nitrogen was maintained to provide a constant thermal blanket within DSC cell, thus eliminating thermal gradients and ensuring the validity of the applied calibration standard from sample to sample. The glass transition temperature, T_g, was considered as a temperature corresponding to the inflection of the lambda-like trace on the DSC scan, as shown in Fig. 3.

The transformed fraction, x, at any temperature, T, is given by $x = A_T/A$, where A is the total area limited by exotherm between the temperature, T_i, where the transformation just begins and the temperature, T_f, where the transformation is completed and A_T is the area between the initial temperature and a generic temperature T, see Fig. 3.

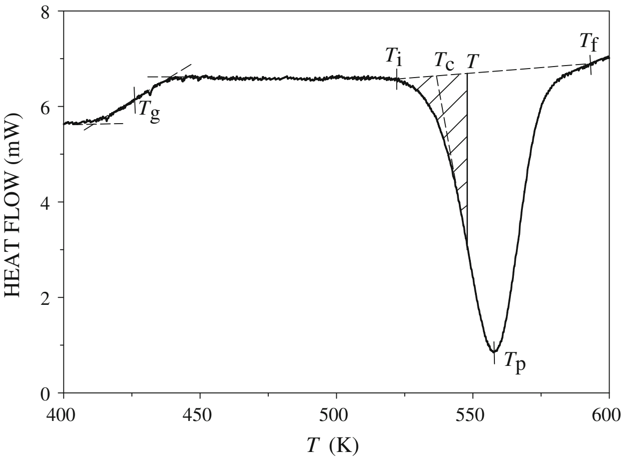

Fig. 3 Typical DSC trace of $Ge_{0.08}Sb_{0.15}Se_{0.77}$ semiconductor alloy at a heating rate of 16 K min^{-1}. The hatched area shows A_T, the area between T_i and T

Results

The typical DSC trace of $Ge_{0.08}Sb_{0.15}Se_{0.77}$ glassy alloy obtained at a heating rate of 16 K min^{-1} and plotted in Fig. 3 shows three characteristic phenomena, which are resolved in the temperature region studied. The first one ($T = 425.6$ K) corresponds to the glass transition temperature, T_g, the second ($T = 538.6$ K) to the extrapolated onset crystallization temperature, T_c, and the third ($T = 557.6$ K) to the peak temperature of crystallization, T_p, of the above-mentioned glassy alloy. The quoted DSC trace shows the typical behavior of a glass-crystal transformation. The data of the thermograms for the different heating rates, β, quoted in "Experimental part" section, show values of the quantities T_g, T_c, and T_p, which increase with increasing β, a property which has been reported in the literature [35, 36].

Kinetic analysis of the glass-crystal transformation

It is well known that the kinetic analysis of the crystallization reactions is related to the knowledge of the reaction rate constant as a function of the temperature. Thus, a great number of analytical methods, proposed in the literature to describe the quoted reactions, assume that the above-mentioned constant can be represented by means of an Arrhenius type temperature dependence [23, 37], as it occurs in the case of the $A(T)$ constant, corresponding to the TMD. Bearing in mind this assumption we analyze the glass-crystal transformation of $Ge_{0.08}Sb_{0.15}Se_{0.77}$ semiconductor glass in accordance with theory developed in "Basic theory" section.

With the aim to analyze the crystallization kinetics of the above-mentioned semiconductor glass, the experimental values of the quantities described by the thermograms corresponding to the different heating rates, quoted in "Experimental part" section, are obtained and given in Table 1, where T_i, and T_p are the temperatures at which the crystallization begins and that corresponding to the maximum crystallization rate, respectively, and ΔT is the width

Table 1 Characteristic temperatures and enthalpies of the crystallization processes of the $Ge_{0.08}Sb_{0.15}Se_{0.77}$ semiconductor glass

Quantity	Experimental value, β (K/min)				
	4	8	16	32	64
T_g (K)	401.6	419.7	424.8	430.2	433.0
T_i (K)	508.0	514.0	519.7	526.1	531.9
T_p (K)	537.4	547.5	557.6	565.8	572.8
ΔT (K)	48.0	59.1	65.7	69.5	79.8
ΔH (mJ/mg)	26.9	25.8	27.3	25.2	24.0

of the peak of the DSC trace. The crystallization enthalpy ΔH is also evaluated for each of the heating rates.

The area under the peak of DSC curve is directly proportional to the total amount of alloy crystallized. The quotients between the ordinates of the quoted peak and the total area of the same give the corresponding crystallization rates, which allow to plot the curves of $\mathrm{d}x/\mathrm{d}t$ versus T for the different heating rates represented in Fig. 4. It should be noted that the $(\mathrm{d}x/\mathrm{d}t)|_{\mathrm{p}}$ values increase in the same proportion that the heating rate, a property which has been widely discussed in the literature [38].

Table 2 Crystallized fractions corresponding to various temperatures for different heating rates

Temperature (K)	Experimental value, β (K/min)				
	4	8	16	32	64
532	0.308242	0.085741	0.011331	0.011133	0.000000
534	0.380421	0.118403	0.018103	0.016599	0.000096
536	0.469327	0.155584	0.028704	0.024192	0.000557
538	0.563753	0.201494	0.041530	0.034387	0.001767
540	0.657892	0.258368	0.058866	0.049406	0.004022
542	0.746798	0.330997	0.081341	0.067088	0.007022
544	0.824772	0.406162	0.113593	0.089514	0.011225
546	0.888266	0.486450	0.150274	0.117624	0.016985
548	0.935775	0.579395	0.195102	0.156456	0.024739
550	0.967190	0.662130	0.255004	0.198955	0.036402
552	0.985053	0.739512	0.317839	0.249172	0.050223
554	0.995376	0.808276	0.388361	0.314009	0.067708

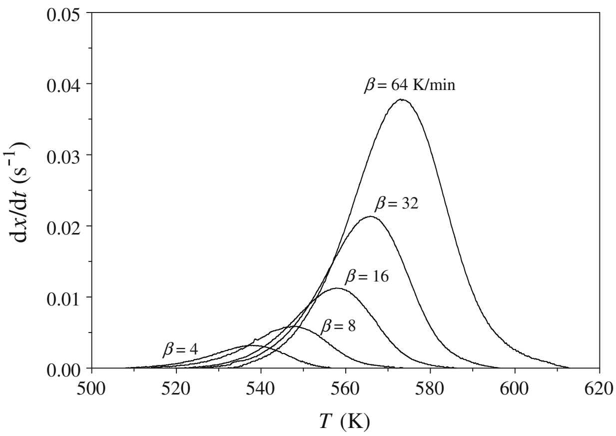

Fig. 4 Crystallization rate versus temperature for the exothermal peak at different heating rates

From the experimental data, x and T, it is possible to construct the Table 2 for the chalcogenide glass studied at the different heating rates, quoted in "Experimental part" section. It is necessary to remark that the quoted data give curves with the typical sigmoid shape, as appearing quite frequently in the literature [39, 40]. In order to find values of the kinetic exponent for different temperatures and to know the variation of the quoted exponent with the temperature, we have taken various values of this quantity with the step-size of 2 K and the corresponding crystallized fractions for each heating rate, which are given in the already quoted Table 2. According to the mentioned table, representing $T_{\mathrm{r}} = T - 1$ and $T_{\mathrm{s}} = T + 1$ and varying T from 533 to 553 K, the corresponding values of F_{rs} can be obtained by using Eq. 6, the value of $\langle \delta_{\mathrm{i}} \rangle = 1.59$, calculated in accordance with Eq. 32 of Ref. [29] (see Table 3) and different values of the n-exponent for each value of the temperature. Taking the quoted different n values for each pair T_{r}, T_{s} and bearing in mind Eq. 5, we find a number of point distributions, F_{rs} versus $1/\beta$, for each temperature, which is equal than the number of n values considered. The straight lines corresponding pass through the computed points $(1/\beta, F_{\mathrm{rs}})$ and the origin of the axes, because as it has been already mentioned, the intercepts of the quoted straight lines have to be zero. By means of a computer program and using different values of the kinetic exponent for each temperature the regression straight lines corresponding are fitted to the above-mentioned point distributions by the least square method, choosing as more suitable kinetic exponent the value corresponding to the larger correlation coefficient. Bearing in mind that it is important for the integral method studied to show as figures the relationships F_{rs} versus $1/\beta$ and $\ln \frac{\beta}{T_{\mathrm{s}} - T_{\mathrm{r}}}$ vs. $1/\bar{T}$ to obtain the kinetic parameters n and E, respectively, we have chosen as an illustrative example for the case of the kinetic exponent, n, the Fig. 5, which shows the plots of F_{rs} versus $1/\beta$ for $T = 541$ K and the corresponding straight regression line for $n = 2.25$, value of the kinetic exponent corresponding to the larger correlation coefficient, $r = 0.9943$, for the above-mentioned temperature. Considering that the kinetic exponent depends on the temperature, Fig. 6 shows the plots of n versus T for the $\mathrm{Ge}_{0.08}\mathrm{Sb}_{0.15}\mathrm{Se}_{0.77}$ chalcogenide glass, where it is observed that the already quoted variation of the kinetic exponent with the temperature is evident. According to the corresponding fitting, we have obtained that between $T = 533$ and 543 K, the correlation coefficients are larger or equal than 0.99. For the quoted temperatures, the corresponding values of the kinetic exponent are in the interval $1.75 \leq n \leq 2.5$. On the other hand, by means of Eq. 34 of Ref. [29], we have calculated the n values for the different heating rates given in "Experimental part" section, whose mean value is $\langle n \rangle = 1.95$ (see Table 3). It should be noted that this mean value is within the above-mentioned interval of values corresponding to kinetic exponent. These facts reveal that, although the quoted exponent varies with the temperature, it is possible to take as n value for the glass-crystal transformation of the $\mathrm{Ge}_{0.08}\mathrm{Sb}_{0.15}\mathrm{Se}_{0.77}$ glassy semiconductor the value corresponding to TMD.

Table 3 Maximum crystallization rate, $(\mathrm{d}x/\mathrm{d}t)|_p$, corresponding temperature, T_p, and crystallized fraction, x_p, kinetic exponent, n, and impingement factor, δ_i, for different heating rates of the $Ge_{0.08}Sb_{0.15}Se_{0.77}$ semiconductor glass

Alloy	β (K min^{-1})	Experimental data			TMD			
		$10^3(\mathrm{d}x/\mathrm{d}t)\|_p(\mathrm{s}^{-1})$	T_p (K)	x_p	δ_i	n	$\langle\delta_i\rangle$	$\langle n\rangle$
As-quenched	4	3.21	537.4	0.5351	1.4982	2.12		
	8	5.90	547.5	0.5513	1.8752	1.92		
	16	11.24	557.6	0.5361	1.5176	1.99	1.5904	1.95
	32	21.34	565.8	0.5529	1.9213	1.82		
	64	37.79	572.8	0.5121	1.1398	1.90		
Reheated	4	2.91	523.3	0.5676	2.4471	2.10		
	8	5.64	543.4	0.5817	3.2415	2.04		
	16	9.52	551.9	0.5457	1.1788	1.97	2.2831	1.94
	32	18.21	563.4	0.5712	2.6145	1.82		
	64	30.31	574.5	0.5288	1.3836	1.79		

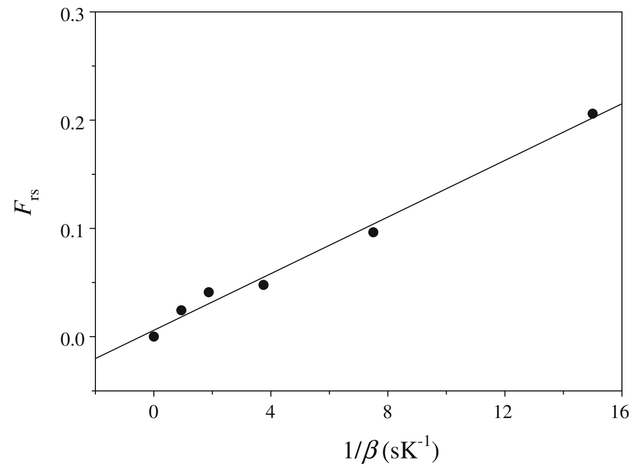

Fig. 5 Variation of F_{rs} function with the reciprocal heating rate, $1/\beta$, for $T = 541$ K in the case of $n = 2.25$

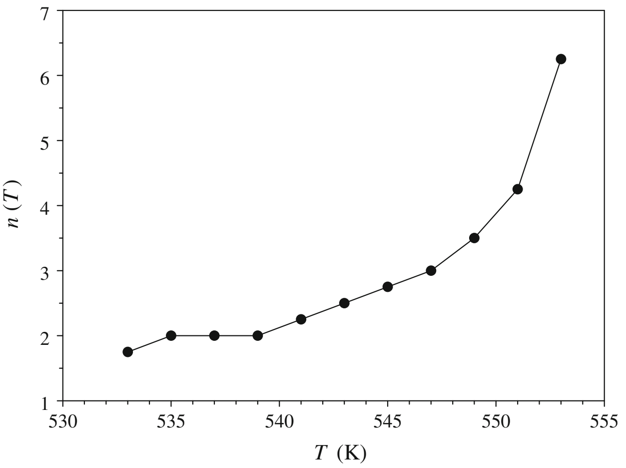

Fig. 6 Variation of the kinetic exponent with the temperature during the non-isothermal crystallization of the $Ge_{0.08}Sb_{0.15}Se_{0.77}$ glassy alloy

Bearing in mind that the value of the kinetic exponent, n, for the as-quenched material ranges from 1.82 to 2.12, as it is shown in Table 3, which means a glass-crystal transformation with two-dimensional growth in case of "site saturation" or bulk nucleation with one-dimensional growth in case of "continuous nucleation", it seems interesting to clarify the thermal process type which happens. It is well known that both process types can be distinguished by means of DSC experiments. Thus, according to the literature [38, 41], the reheating of a glassy solid at the nucleation temperature (slightly higher than the glass transition temperature, T_g) allows to know the process type. If the kinetic exponent, n, does not change with reheating, a large number of nuclei already exist in the as-quenched material, a case of "site saturation". However, if n changes with reheating, not so many nuclei exist in the as-quenched solid and this nucleates during the reheating, which is a case of continuous nucleation. Accordingly, the quoted glassy semiconductor has been reheated up to a temperature somewhat larger than the larger value of the glass transition temperature corresponding to the larger heating rate during the necessary time to form a sufficiently big number of nuclei. Subsequently, the reheated material has been scanned at the same heating rates (4, 8, 16, 32, and 64 K/min) that the as-quenched material, to obtain the necessary experimental data to calculate the corresponding kinetic exponents, given also in Table 3. In this table it is observed that the value of the quoted exponent for the reheated alloy ranges from 1.79 to 2.10, whose mean value is $\langle n\rangle = 1.94$. By comparison of the values of the already mentioned exponent for the material both as-quenched and reheated it is evident that kinetic exponent does not change with the reheating and accordingly, it is clear that the thermal process type is “site saturation” with two-dimensional growth.

Next, to calculate values of the activation energy, E, and of the pre-exponential frequency, A_0, for different transformed fractions, x, and to know the variation of the E and A_0 quantities with x, we have taken various values of this quantity with the step-size of 0.06 and the corresponding temperatures for each heating rate. Representing $x_r = x - 0.03$ and $x_s = x + 0.03$ and varying x from 0.09 to 0.93, for each pair x_r, x_s corresponding to each heating rate, we obtain a point distribution $\ln \frac{\beta}{T_s - T_r}$ vs. $1/\bar{T}$ that, according Eq. 20, represents a straight line, whose slope and intercept allow to obtain the activation energy and pre-exponential frequency, respectively, corresponding to each x value considered. As an illustrative example, the Fig. 7 shows $\ln \frac{\beta}{T_s - T_r}$ vs.$1/\bar{T}$ for $x = 0.63$ with the corresponding straight regression line, whose correlation coefficient is $r = 0.9980$ for the quoted crystallized fraction. The above-mentioned values of x and the corresponding values of the kinetic parameters E and A_0 are plotted in Fig. 8a and b, which show the variation of the effective activation energy and of the pre-exponential frequency, respectively, with the crystallized fraction. In the case of the graph E versus x, Fig. 8a, it is obvious that the E value decreases of form almost linear with increasing x. The corresponding regression straight line has a correlation coefficient $r = 0.996$ and the values of the above-mentioned energy in kJ mol^{-1} are included in the interval $189.7 \geq E \geq 162.5$. With regard to the graph A_0 versus x, Fig. 8b, it is observed that the value of A_0 indicates an exponential decay throughout the whole range of x. Moreover, by means of Eq. 33 of Ref. [29], recently published, corresponding to the TMD, we obtain from the experimental data (see Table 1) for the activation energy $E = 184.3$ kJ mol^{-1}. It is observed that this value of energy is within the quoted value interval for this quantity, obtained by means of Eq. 20 of this study. Bearing in mind these considerations it is possible to affirm that although the activation energy is a function of the crystallized fraction, also it can be taken as a suitable value of the quoted energy the corresponding result obtained from of the above-mentioned TMD.

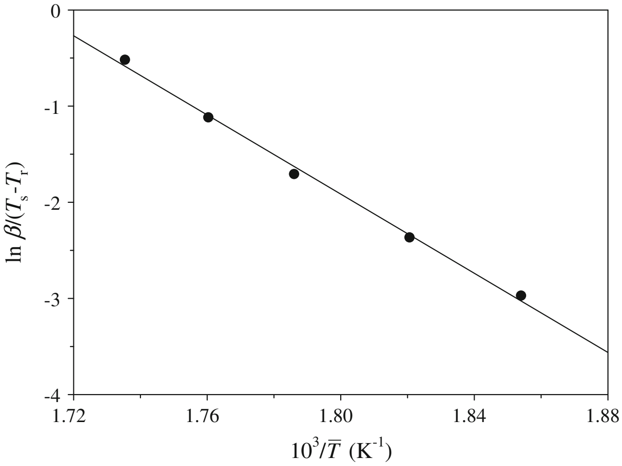

Fig. 7 Variation of $\ln \frac{\beta}{T_s - T_r}$ with $1/\bar{T}$ for the crystallized fraction $x = 0.63$

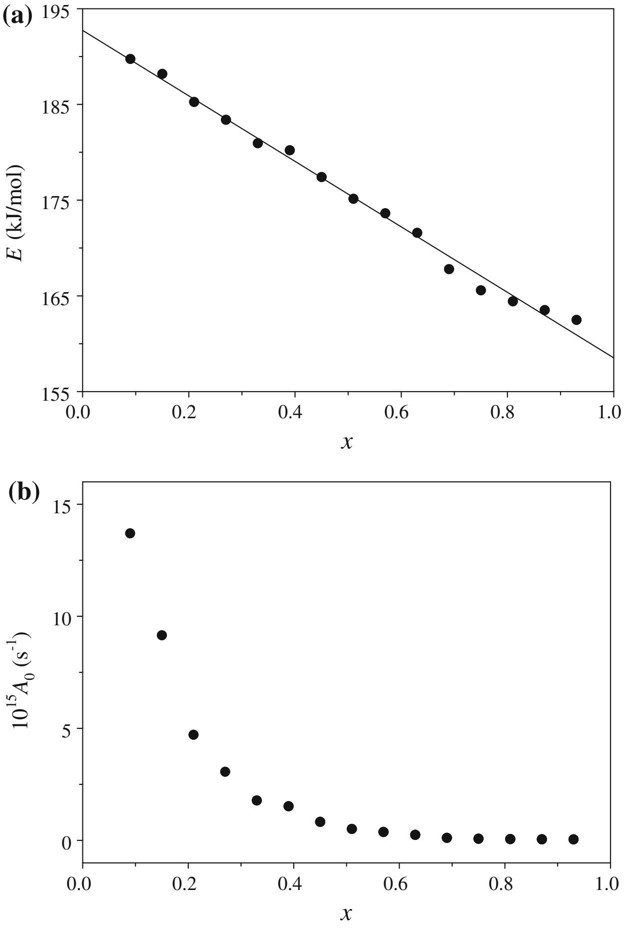

Fig. 8 Variations of the activation energy (**a**) and of the pre-exponential frequency (**b**) with the crystallized fraction during the non-isothermal glass-crystal transformation of the $Ge_{0.08}Sb_{0.15}Se_{0.77}$ alloy

Given that the values of the above quoted interval of the activation energy show a relatively substantial variation of E with the crystallized fraction, x, as it is observed in Fig. 8a, and accordingly, with temperature, it appears interesting to interpret the quoted variation in terms of a multi-step mechanism. In this sense, it is possible to say, in accordance with the literature [42], that the E values decrease with the increasing temperature, which simply indicates that the crystallization rate increases as the temperature increases. This behavior demonstrates that the rate of crystallization is determined by the rates of the nucleation and crystal growth processes [43]. Given that both mechanisms are likely to have different activation energies, the effective activation

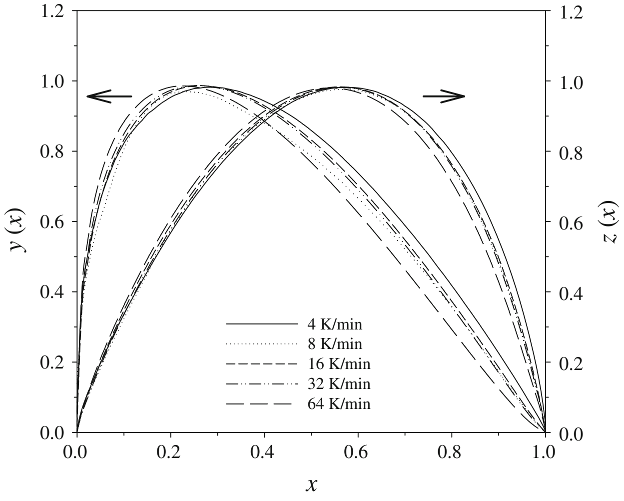

Fig. 9 Plots of the normalized $y(x)$ and $z(x)$ functions obtained from experimental data corresponding to the non-isothermal glass-crystal transformation of the $Ge_{0.08}Sb_{0.15}Se_{0.77}$ semiconductor glass

energy of the transformation will vary with temperature [44]. This physical interpretation is based on the nucleation theory proposed by Fisher and Turnbull [45].

Finally, with the aim of displaying the reliability of the $f(x)$ function, corresponding to TMD, to reflect the transformation mechanism of $Ge_{0.08}Sb_{0.15}Se_{0.77}$ glassy alloy, we have used the functions: $y(x) \propto (dx/dt)\exp(E/RT)$ and $z(x) \propto T^2(dx/dt)$, defined in "Basic theory" section of this manuscript. The quoted normalized functions corresponding to the experimental data of the quoted alloy are shown in Fig. 9 for the different heating rates, quoted in "Experimental part" section. In the above-mentioned figure it is observed that all the curves of each quoted function have almost identical shapes with maximum values, which correspond to values of x within the range $0.23 \leq x_q \leq 0.28$ for the $y(x)$ function and within the range of $0.54 \leq x_p \leq 0.57$ for the $z(x)$ function. On the other hand, by using Eqs. 32 and 34 of Ref. [29] from the experimental data, given in Table 3, we have calculated the values of the parameters: impingement factor, δ_i, and kinetic exponent, n, given also in Table 3, together with its mean values $\langle\delta_i\rangle = 1.59$ and $\langle n\rangle = 1.95$. From these mean values and by using Eqs. 15 and 18 of this study, the results $x_q = 0.28$ and $x_p = 0.54$, corresponding to the maximum values of the $y(x)$ and $z(x)$ functions, respectively, have been obtained. It should be noted that, these x_q and x_p values are within the above-mentioned ranges of x values corresponding to the maximum values of the $y(x)$ and $z(x)$ functions, respectively, and obtained from the experimental data at different heating rates. This fact confirms again the reliability of the quoted $f(x)$ function, corresponding to the TMD to analyze the glass-crystal transformation kinetics of the $Ge_{0.08}Sb_{0.15}Se_{0.77}$ chalcogenide glass.

Conclusions

The theoretical procedure developed enables us to study the glass-crystal transformation kinetics and to calculate the corresponding parameters: kinetic exponent, activation energy, and pre-exponential frequency of glassy alloys, by using experimental data obtained through DSC under non-isothermal regime. It is dealt with an integral procedure, which is based on a transformation rate independent of the thermal history of the material and assumes that the quoted rate can be expressed as the product of two separable functions of absolute temperature, $A(T)$, and the transformed fraction, $f(x)$. This $f(x)$ function corresponds to the TMD that we have recently published. Considering the same pair temperatures for the different heating rates, one obtains a constant value for temperature integral and, therefore, a plot of a function of the transformed fraction versus the reciprocal of the heating rate leads to a straight line with an intercept of zero, if the value of kinetic exponent is correctly chosen. By using different values of kinetic exponent for each of the possible lines, it is taken the best correlation coefficient to choose the quoted exponent more suitable. Besides, by using the first mean value theorem to approach the temperature integral, one obtains a relationship between a function of the temperature and other function of the transformed fraction. The logarithmic form of the quoted relationship leads to a straight line, whose slope and intercept allow the obtaining of the activation energy and the pre-exponential frequency, respectively.

The theoretical procedure developed has been applied to the study of the crystallization kinetics of the $Ge_{0.08}Sb_{0.15}Se_{0.77}$ semiconductor glass resulting in ranges of variation both of the kinetic exponent, n, with the temperature and of the activation energy, E, with the crystallized fraction, which contain the values of n and E, obtained according to the TMD, that we have recently published. This fact shows the reliability of the theoretical procedure developed in this study, to analyze the glass-crystal transformation kinetics of glassy alloys.

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