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A study on non-isothermal transformation kinetics Application to the crystallization of the $Ge_{0.18}Sb_{0.23}Se_{0.59}$ glassy alloy

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Abstract

A theoretical method is derived for the progress of a nucleation and growth-controlled reaction during heating at a constant rate. The kinetic parameters have been obtained assuming that the reaction rate constant is a time function through its Arrhenian temperature dependence. Besides, it has been shown that the different models, used in the literature for analyzing the glass-crystal transformation, are particular cases of the general expression deduced for the actual volume fraction transformed. The model is applied to the DSC data of crystallization kinetics of the $Ge_{0.18}Sb_{0.23}Se_{0.59}$ glassy alloy, thus obtaining values for the kinetic parameters that agree satisfactorily with the calculated results by the Austin–Rickett kinetic equation, under non-isothermal regime. This fact shows the reliability of the theoretical method developed.

Keywords: Glassy alloy; Glass-crystal transformation; Differential scanning calorimetry; Extended volume; Impingement effect; Kinetic parameters

1. Introduction

Chalcogenide glasses are transparent visible or near infrared region up to 15 μm. Germanium has very interesting optical properties with very high refractive index and very low chromatic dispersion. There are very few materials which are transparent in the 8–12 μm region and which are environmentally stable enough for outdoor applications [1–2].

An important commercial application for chalcogenide glasses concerns optical lenses for infrared transmission. They are mainly used for infrared radiometry. Recently, moulding technology has been developed, making possible the economical production of very complex and high efficient lenses, which are necessary for thermal imaging application [3–4]. Infrared transmitting glasses based on Ge-Sb-Se are technologically important because they are good transmitters of radiation in the 2–16 μm wavelength region. The applications include fabrication of optical components like IR lenses, windows and filters used in thermal imaging systems. They are less sensitive to the presence of impurities. The Ge-Sb films are sensitive for the UV radiation, and exhibit mechanical, optical and structural changes [5–6]. Glass-forming regions in the Ge-Sb-Se system were studied by several authors [7–12].

In the present work, a theoretical method has been developed for obtaining an evolution equation with time for the actual volume fraction transformed, bearing in mind the mutual interference of regions growing from separated nuclei (impingement effect). From the quoted equation the kinetic parameters and the glass-crystal transformation mechanism have been deduced by means of differential scanning calorimetry (DSC), using non-isothermal regime. In addition, this paper applies the developed method to the analysis of the crystallization kinetics of the $Ge_{0.18}Sb_{0.23}Se_{0.59}$ glassy semiconductor. The values obtained for the quoted parameters are in good agreement with the calculated results by other

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kinetic equations. As an example, the above mentioned agreement with the obtained results by the Johnson–Mehl–Avrami (JMA) equation under non-isothermal regime can be quoted.

The treatment of condensed systems was adapted from the classical theory of the vapour–liquid transition by Turnbull and Fisher [13]. A full development of the theory is given by Christian [14] and a relatively recent review published by Kelton [15]. The last decades have seen a strong theoretical and practical interest in the application of calorimetric analysis techniques to the study of phase transformations [16–18]. This analysis is very quick and needs very small quantities of glass samples to obtain kinetic parameters of the quoted transformation. Two thermal analysis regimes are employed: one is the isothermal regime [19,20] in which glass samples are quickly heated up and held at a temperature of interest, above glass transition temperature. In this regime, the glasses crystallize a constant temperature. The other is so-called non-isothermal regime [21–25] in which glass samples are heated up at a fixed heating rate. Generally, an isothermal experiment takes longer time than a non-isothermal experiment, but isothermal experimental data can be interpreted by the well-established JMA kinetic equation [26–29]. In the non-isothermal experiments themselves are rather simple and quick, but assumptions are usually required for data interpretation because there is no uniquely accepted equation available for non-isothermal regime. Therefore, the utilization of the non-isothermal regime has produced a large number of mathematical treatments for analyzing thermal process data. While all of the treatments are based on the formal theory of transformation kinetics, they differ greatly in their assumptions, and in some cases they lead to contradictory results. It was suggested by Henderson [29], in a notable work, that many of the treatments are based on an incomplete understanding of the formal theory of transformation kinetics. Thus, many authors applied the JMA kinetic equation to the non-isothermal crystallization process [30], and although sometimes they appeared to get reasonable activation energies, this procedure is not appropriate when their expressions are deduced from the JMA equation considering isothermal transformation conditions [31].

2. Theoretical background

2.1. Nucleation, crystal growth and volume fraction transformed

The theoretical basis for interpreting DTA or DSC results is provided by the formal theory of transformation kinetics [26–29,32,33]. This theory supposes that the crystal growth rate, in general, is anisotropic, and therefore the volume of a region originating at time $t=\tau$ (τ being the nucleation period) is then

$$v_\tau = g\prod_i \int_\tau^t u_i(t')\,\mathrm{d}t' \tag{1}$$

where the expression $\prod_i \int_\tau^t u_i(t')\,\mathrm{d}t'$ condenses the product of the integrals corresponding to the values of the above quoted subscript i and g is a geometric factor, which depends on the dimensionality and shape of the crystal growth, and therefore its dimension equation can be expressed as

$$[g]=[L]^{3-i} \quad ([L]\text{ is the length}).$$

Defining an extended volume of transformed material and assuming spatially random nucleation [21,34,35], the elemental extended volume fraction, $\mathrm{d}x_\mathrm{e}$, in terms of nucleation frequency per unit volume, $I_\mathrm{V}(\tau)$, is expressed as

$$\mathrm{d}x_\mathrm{e} = v_\tau I_\mathrm{V}(\tau)\,\mathrm{d}\tau = gI_\mathrm{V}(\tau)\left(\prod_i \int_\tau^t u_i(t')\,\mathrm{d}t'\right)\mathrm{d}\tau. \tag{2}$$

When the crystal growth rate is isotropic, $u_i=u$, an assumption which is in agreement with the experimental evidence, since in many transformations the reaction product grows approximately as spherical nodules [14], Eq. (2) can be written as

$$\mathrm{d}x_\mathrm{e} = gI_\mathrm{V}(\tau)\left(\int_\tau^t u(t')\,\mathrm{d}t'\right)^m \mathrm{d}\tau \tag{3}$$

where m is an exponent related to the dimensionality of the crystal growth and the mode of transformation.

For the important case of isothermal transformation with nucleation frequency and growth rate independent of time, Eq. (3) can be integrated, resulting in

$$x_\mathrm{e} = gI_\mathrm{V}u^m\int_0^t (t-\tau)^m\,\mathrm{d}\tau = g'I_\mathrm{V}u^m t^n = (Kt)^n \tag{4}$$

where $n=m+1$ for $I_\mathrm{V}\neq 0$, g' is a new shape factor and K is defined as the effective overall reaction rate constant, which is usually assigned an Arrhenian temperature dependence:

$$K = K_0 \exp\left(\frac{-E}{RT}\right) \tag{5}$$

where E is the effective activation energy, describing the overall transformation process. It should be observed that K^n is proportional to $I_\mathrm{V}\ u^m$. Hence assumption of an Arrhenian temperature dependence for K is appropriate when I_V and u vary in an Arrhenian manner with temperature.

In general, the temperature dependence of the nucleation frequency is far from Arrhenian, and the temperature dependence of the crystal growth rate is also not Arrhenian when a broad range of temperature is considered [35]. Over a sufficiently limited range of temperature (such as the range of transformation peaks in DTA or DSC experiments), both I_V and u may be described in zeroth-order approximation by

$$I_\mathrm{V} \approx I_{\mathrm{V}0} \exp\left(\frac{-E_\mathrm{N}}{RT}\right) \tag{6}$$

and

$$u \approx u_0 \exp\left(\frac{-E_G}{RT}\right) \tag{7}$$

where E_N and E_G are the effective activation energies for nucleation and growth, respectively.

Combining Eqs. (4)–(7) results in

$$K_0^n \exp\left(\frac{-nE}{RT}\right) \propto I_{V0}u_0^m \exp\left[\frac{-(E_N+mE_G)}{RT}\right] \tag{8}$$

and the overall effective activation energy for the transformation is expressed as

$$E = \frac{E_N+mE_G}{n} \tag{9}$$

Eqs. (4) and (5) have served as the basis of nearly all treatments of transformation in DTA or DSC experiments. It should be noted, however, that Eq. (4) strictly applies only to isothermal experiments, where an integration of the general expression of Eq. (3) is straightforward. Accordingly, for analyzing glass-crystal transformations in heating continuous regime it is more accurate to integrate Eq. (3) under non-isothermal conditions, according to the literature [22,35,36].

In the present work, a theoretical method has been developed to integrate Eq. (3) under the above mentioned conditions and to obtain a general expression for the extended volume fraction, x_e, for each value of the m exponent. In this sense, the case when nucleation and crystal growth occur simultaneously has been considered. Both the nucleation frequency, Eq. (6), and crystal growth rate, Eq. (7), may still be approximately described by Arrhenius- type laws at temperatures lower than the peak temperatures for both quantities. In this case, the temperature dependence of extended volume fraction involves a range of particles that are nucleated at different temperatures and, thus, grow to different final sizes when the sample is subjected to continuous heating. By considering the quoted fact of nucleation and crystal growth simultaneous, which agrees with literature [22], and a constant heating rate, $\beta = \mathrm{d}T/\mathrm{d}t$, Eq. (3) becomes

$$\mathrm{d}x_e = pI_1^m\, \mathrm{e}^{-E_N/RT_\tau}\, \mathrm{d}T_\tau \tag{10}$$

where p is a parameter equal to $gI_{V0}u_0^m\beta^{-(m+1)}$, T_τ the temperature at time τ and I_1 is a temperature integral defined by

$$I_1 = \int_{T_\tau}^{T} \mathrm{e}^{-E_G/RT'}\, \mathrm{d}T' \tag{11}$$

By using the substitution $z' = E_G/RT'$, the integral I_1 is transformed in an exponential integral of order two, which is a particular case of that order r, which can be expressed, according to literature [37], by the sum of the alternating series

$$S_r(z_\tau, z) = \left[\frac{\mathrm{e}^{-z'}}{z'^r}\sum_{k=0}^{\infty}\frac{(-1)^k(k+r-1)!}{(r-1)!z'^k}\right]_z^{z_\tau} \tag{12}$$

Accordingly, taking $r = 2$ in Eq. (12) and considering that in this type of series the error produced is less than the first term neglected, Eq. (11) becomes

$$I_1 = \frac{R}{E_G}\left[T^2\,\mathrm{e}^{-E_G/RT} - T_\tau^2\,\mathrm{e}^{-E_G/RT_\tau}\right] \tag{13}$$

bearing in mind that in most crystallization reactions $E_G/RT' \gg 1$, usually $E/RT' \geq 25$, it is possible to use only the first term of the above mentioned series without making any appreciable error.

Substituting Eq. (13) into Eq. (10), by using the expansion of the binomial-potential series and integrating the resulting expression one obtains an equation with an exponential integral of order $2s + 2$, which is again evaluated according to Eq. (12), yielding

$$x_e = pR\left(\frac{R}{E_G}\right)^m\left[\sum_{s=0}^{m}(-1)^s\binom{m}{s}(E_N+sE_G)^{-1}\right]T^{2m+2} \times \exp\left[\frac{-(E_N+mE_G)}{RT}\right] \tag{14}$$

if it is assumed that $T_0 \ll T$, (T_0 is the starting temperature). This assumption is justifiable for any heating treatment that begins at a temperature where nucleation and crystal growth are negligible, i.e., below T_g (glass transition temperature) for most glass-forming systems [35].

Introducing in Eq. (14) the parameter

$$Q = R\left(\frac{R}{E_G}\right)^m\sum_{s=0}^{m}(-1)^s\binom{m}{s}(E_N+sE_G)^{-1}$$

and defining the reaction rate constant

$$K_V = K_{V0}\exp\left[\frac{-(E_N+mE_G)}{(m+1)RT}\right], \quad K_{V0} = (gI_{V0}u_0^m)^{1/(m+1)} \tag{15}$$

with an Arrhenian temperature dependence, the extended volume fraction, under heating continuous regime, is expressed as

$$x_e = Q\left(\frac{K_V T^2}{\beta}\right)^{m+1} \tag{16}$$

which, as can be observed is a general expression for all possible values of the m exponent, which, as it is well know, depends on the dimensionality of the crystal growth. Besides, given that in the present work Eqs. (6) and (7) have been considered valid, the exponent $m + 1$ equals the so-called kinetic exponent n.

It should be noted that the frequency factor $K_{V0} = (gI_{V0}u_0^m)^{1/(m+1)}$, of Eq. (15) can be expressed by the relationship $K_{V0} = (I'_{V0}u'^m_0)^{1/(m+1)}$, which includes the shape factor, g, and where the dimension equation of each of the quantities I'_{V0} and u'_0 is $[T]^{-1}$.

The graphical representation of Eq. (16) shows the typical parabolic curve of the extended volume fraction as a func-

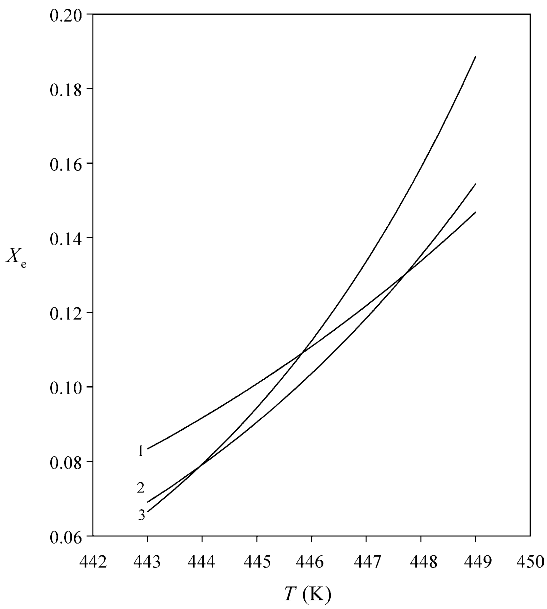

Fig. 1. Extended volume fraction transformed as function of temperature calculated from Eq. (16), with $I'_{V0} = 6\times10^6\ \mathrm{s}^{-1}$, $E_N = 20\ \mathrm{kcal\ mol}^{-1}$, $u'_0 = 4.8\times10^4\ \mathrm{s}^{-1}$, $E_G = 14\ \mathrm{kcal\ mol}^{-1}$, $\beta = 0.13\ \mathrm{K\ s}^{-1}$ and for crystal growth in one (1), two (2) and three (3) dimensions.

tion of temperature in crystallization reactions. Fig. 1 shows the representation of the quoted equation for some selected kinetic parameters and for crystal growth in one, two and three dimensions. It should be noted that x_e function tends to infinity for T increasing and their corresponding curves for several m values intercept at different temperatures.

Finally, as an illustration of the use of Eq. (16), a reaction with $m = 3$ (e.g. valid for recrystallization), nucleation frequency and crystal growth rate according to Eqs. (6) and (7), respectively, has been considered. Then Eq. (16) shows that, for an experiment at constant heating rate, x_e increases approximately in proportion to $t^{2(m+1)} = t^8$. For comparison, in an isothermal experiment, x_e increases in proportion to $t^{m+1} = t^4$.

2.2. Effect of impingement

To obtain a general kinetic equation for the volume fraction transformed, the mutual interference of regions growing from separated nuclei must be considered. When two such regions impinge on each other it is possible that the two regions develop a common interface, over which growth ceases, although it continues normally elsewhere. This happens in most solid transformations. The problem is primarily geometrical and through the concept of extended volume may thus be separated from the kinetic laws of nucleation and growth. We have now to find a relation between the extended volume, V_e, and the actual volume, V_b. Consider any small random region, of which a fraction $(1–V_b/V)$ remains untransformed at time t, and where V is the volume of the whole assembly. During a further time dt, the extended volume will increase by dV_e, and the true volume by dV_b. Of the new elements of volume, which make up dV_e, a fraction $(1 - V_b/V)^{\gamma_i}$ on the average will lie in previously untransformed material, and thus contribute to dV_b, whilst the remainder of dV_e will be in already transformed material. Note that γ_i will be termed the impingement exponent. The above quoted result clearly follows only if dV_e can be treated as a completely random volume element. Accordingly, bearing in mind the hypothesis of random nucleation it is possible to write the relation between V_b and V_e in the form

$$\mathrm{d}V_b = \left(1 - \frac{V_b}{V}\right)^{\gamma_i} \mathrm{d}V_e = (1-x)^{\gamma_i}\,\mathrm{d}V_e \tag{17}$$

where $x = V_b/V$ is the actual volume fraction transformed and with $\mathrm{d}V_e = V\,\mathrm{d}x_e$, Eq. (17)can be expressed as

$$(1-x)^{-\gamma_i}\,\mathrm{d}x = \mathrm{d}x_e. \tag{18}$$

Defining an impingement factor, $\delta_i = (\gamma_i - 1)^{-1}$, the general solution of the preceding differential equation is given as

$$x = 1 - (1 + x_e\delta_i{}^{-1})^{-\delta_i} \tag{19}$$

It should be noted that the Eq. (19) includes different models used in the literature when the glass-crystal transformation is analyzed, namely:

(i) Case of no impingement, $\gamma_i = 0$, $x = x_e$.
(ii) If the impingement exponent, $\gamma_i = 1$, $\delta_i \to \infty$ and Eq. (19) becomes

$$x = 1 - \lim_{\delta_i\to\infty}\left[1 + \left(\frac{\delta_i}{x_e}\right)^{-1}\right]^{-\delta_i}$$
$$= 1 - \exp(-x_e) = 1 - \exp[-(Kt)^n] \tag{20}$$

(iii) When $\gamma_i = 2$, $\delta_i = 1$ and Eq. (19) can be written as

$$x = 1 - (1 + x_e)^{-1} = 1 - [1 + (Kt)^n]^{-1}. \tag{21}$$

Both in Eq. (20) and in Eq. (21) an isothermal transformation has been considered, and therefore, the extended volume fraction is given by Eq. (4), resulting in the JMAK equation and the Austin–Rickett (AR), respectively.

Finally, by substituting Eq. (16) into Eq. (19), one obtains

$$x = 1 - \left[1 + \frac{1}{\delta_i} Q\left(\frac{K_V T^2}{\beta}\right)^{m+1}\right]^{-\delta_i} \tag{22}$$

a general expression for the actual volume fraction transformed in a non-isothermal process.

2.3. Deducing the kinetic parameters

The usual analytical methods, proposed in the literature [35] for analyzing the crystallization kinetics in glass-forming liquids, assume that the reaction rate constant can be defined by an Arrhenian temperature dependence. In order for this condition to hold, the present work assumes that both the nucleation frequency, I_V, and crystal growth rate, u, have Arrhenian temperature dependences. From this point of view, the crystallization rate is obtained by deriving the actual volume fraction crystallized [Eq. (22)] with respect to time, bearing in mind the fact that, in non-isothermal processes, the reaction rate constant is a function of time through its above mentioned Arrhenian temperature dependence. Moreover, if in the resulting equation, the expression in square brackets is substituted by its value given in Eq. (22), one obtains

$$\frac{dx}{dt} = \frac{Q(m+1)}{\beta}\left(\frac{K_V T^2}{\beta}\right)^m (1-x)^{(\delta_i+1)/\delta_i} \times \left(T^2\frac{dK_V}{dt} + 2T\beta K_V\right). \quad (23)$$

The maximum crystallization rate is found making $dx^2/dt^2 = 0$, resulting in

$$\frac{\delta_i+1}{\delta_i}(1-x_p)^{1/\delta_i} Q\left[\frac{K_V|_p T_p{}^2}{\beta}\right]^{m+1} = 1 - \frac{1}{m+1}\left[T_p^2\left(\left.\frac{dK_V}{dt}\right|_p\right)^2 + 2\beta^2(K_V|_p)^2 - T_p^2 K_V|_p \left.\frac{d^2K_V}{dt^2}\right|_p\right] \times \left[T_p\left.\frac{dK_V}{dt}\right|_p + 2\beta K_V|_p\right]^{-2}, \quad (24)$$

where the subscript p denotes the quantity values corresponding to the maximum crystallization rate.

Taking the first and the second derivative of the reaction rate constant, K_V, with respect to time, substituting both into Eq. (24), assuming that the overall effective activation energy, E, is given by Eq. (9), and that $n = m + 1$, as already stated, the quoted Eq. (24) can be rewritten as

$$\frac{\delta_i+1}{\delta_i}(1-x_p)^{1/\delta_i} Q\left[\frac{K_V|_p T_p^2}{\beta}\right]^{n} = 1 - \frac{2}{n}\left(1+\frac{E}{RT_p}\right)\left(2+\frac{E}{RT_p}\right)^{-2} \quad (25)$$

which relates the crystallization kinetic parameters E, n and δ_i to the quantity values that can be determined experimentally, and which correspond to the maximum crystallization rate. Bearing in mind that in most transformation reactions $E/RT_p \gg 1$ (usually $E/RT_p \geq 25$), already quoted assumption, Eq. (25) becomes

$$\frac{\delta_i+1}{\delta_i}(1-x_p)^{1/\delta_i} Q\left[\frac{K_V|_p T_p^2}{\beta}\right]^{n} = 1 \quad (26)$$

and the error introduced is not greater than 2.5%.

Substituting in Eq. (26) the expression $Q\left(K_V|_p T_p^2\beta^{-1}\right)^n$ taken from Eq. (22) and by making explicit the quantity $1–x_p$, one obtains

$$1 - x_p = \left(\frac{\delta_i}{\delta_i+1}\right)^{\delta_i} \quad (27)$$

an expression from which, the impingement factor, δ_i, can be evaluated in a set of exotherms taken at different heating rates, by using a method of successive approximations (e.g. secant method). The corresponding mean value may be taken as the most probable value of the impingement factor in the glass-crystal transformation process.

Substituting Eq. (27) into Eq. (26) and taking the logarithm in the resulting expression leads to the relationship

$$\ln\frac{T_p^2}{\beta} = \frac{E}{RT_p} - \ln q \quad (28)$$

which is a linear function, whose slope and intercept give the overall effective activation energy, E, and the factor $q = Q^{1/n}K_{V0}$ [Eq. (22)], which is related to the probability of effective collisions for the formation of the activated complex. About the physical meaning of the overall effective activation energy of Eq. (28) it can be explained by analyzing the expression of the reaction rate constant, $(K_V)|_p$, given by Eq. (15). According to the quoted equation and following the literature [35], the above-mentioned activation energy is expressed by Eq. (9). From this equation it is immediate that the activation energy in Eq. (28), means physically a combination of the effective activation energies for the nucleation, E_N, and for the crystal growth, E_G, respectively, which agrees satisfactorily with the literature [35] (see page 255).

Finally, substituting in Eq. (23) for the maximum crystallization rate, the expression $Q(K_V|_p T_p{}^2\beta^{-1})^n$ taken from Eq. (22), introducing Eq. (27) into the resulting expression and considering the above quoted assumption $E/RT_p \gg 1$, one obtains

$$n = RT_p^2\left.\frac{dx}{dt}\right|_p\left[(1-x_p)^{(\delta_i+1)/\delta_i}\beta E\right]^{-1} \quad (29)$$

an expression which permits the kinetic exponent, n, to be calculated in a set of exotherms taken at different heating rates. The corresponding mean value may be considered as the most probable value of the kinetic exponent of the transformation process.

Eqs. (27) and (29) give information about the mechanism of the transformation through the parameters δ_i and n. Moreover, it should be noted that when the δ_i parameter is taken as infinity, Eqs. (22)–(24) for the maximum crystallization rate become exactly the equations corresponding to the JMAK model, in the case of glass-crystal transformations under non-isothermal regime, namely

$$x_p = 1 - \exp[-Q(K_V|_p T_p^2\beta^{-1})^n] \quad (30)$$

$$\left.\frac{dx}{dt}\right|_p = nQ(K_V|_p T_p^2\beta^{-1})^n(1-x_p)\beta T_p^{-1}[2 + E(RT_p)^{-1}] \quad (31)$$

$$Q[K_V|_p T_p^2 \beta^{-1}]^n = 1 - 2n^{-1}[1 + E(RT_p)^{-1}][2 + E(RT_p)^{-1}]^{-2}. \qquad (32)$$

The present fact shows again that the JMAK evolution equation for the volume fraction transformed under non-isothermal regime is a particular case, $\gamma_i = 1$, of the more general transformation equation, which considers the impingement effect between regions growing from separated nuclei.

3. Experimental procedures

The $Ge_{0.18}Sb_{0.23}Se_{0.59}$ glassy alloy was made from their components of 99.999% purity, which were pulverized to less than 64 μm, mixed in adequate proportions, and introduced into a quartz glass ampoule. The content of the ampoule (7 g per batch) was sealed under a vacuum of 10^{-2} Pa and heated in a rotating furnace at around 1223 K for 52 h, submitted to longitudinal rotation of 1/3 rpm in order to ensure the homogeneity of the molten material. It was then immersed in a receptacle containing water in order to solidify the material quickly, avoiding crystallization of the compound. The amorphous state of the material was confirmed by a diffractometric X-ray scan, in a Siemens D500 diffractometer. The homogeneity and composition of the solid were verified through scanning electron microscopy in a JEOL, scanning microscope JSM-820. The calorimetric measurements were carried out in 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 indium and zinc supplied with the instrument. Powdered samples weighing about 10 mg (particle size around 40 μm) were crimped in aluminium pans, and scanned at room temperature through their T_g at different heating rates of 2, 4, 8, 16, 32 and 64 K min^{-1}. An empty aluminium pan was used as reference, and in all cases, a constant 60 ml min^{-1} flow of nitrogen was maintained in order to provide a constant thermal blanket within the DSC cell, thus eliminating thermal gradients and ensuring the validity of the applied calibration standard from sample to sample. Moreover, the nitrogen purge allows to expel the gases emitted by the reaction, which, without affecting the DSC peaks, are highly corrosive to the sensory equipment installed in the DSC furnace. The glass transition temperature was considered as a temperature corresponding to the inflection point of the lambda-like trace on the DSC scan, as shown in the Fig. 2. The volume fraction crystallized, x, at any temperature T is given as $x = A_T/A$, where A is the total area of the exotherm between the temperature T_i, where the crystallization is just beginning and the temperature T_f, where the crystallization is completed and A_T is the area between the initial temperature and a generic temperature T, see Fig. 2.

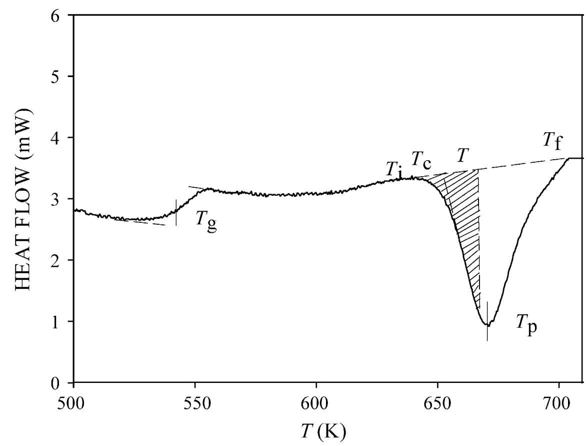

Fig. 2. Typical DSC trace of $Ge_{0.18}Sb_{0.23}Se_{0.59}$ glassy alloy at a heating rate of 32 K min^{-1}. The hatched area shows A_T, the area between T_i and T.

4. Results

The typical DSC trace of $Ge_{0.18}Sb_{0.23}Se_{0.59}$ chalcogenide glass obtained at a heating rate of 32 K min^{-1} and plotted in Fig. 2 shows three characteristic phenomena, which are resolved in the temperature region studied. The first one (T = 545.4 K) corresponds to the glass transition temperature, T_g, the second (T = 653.4 K) to the extrapolated onset crystallization temperature, T_c, and the third (T = 671.0 K) to the peak temperature of crystallization, T_p, of the above mentioned chalcogenide glass. This DSC trace shows the typical behaviour of a glass-crystal transformation. The DSC data for the different heating rates, β, quoted in Section 3, 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 [38]. The ratio between the ordinates and the total area of the peak gives the corresponding crystallization rates, which make it possible to plot the curves of the exothermal peaks represented in Fig. 3. It may be observed that the $(dx/dt)|_p$ value increases in the same proportion as the heating rate, a property which has been widely discussed in the literature [38].

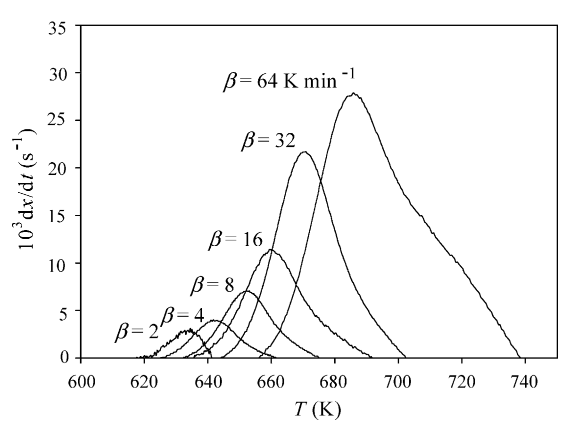

Fig. 3. Crystallization rate vs. temperature of the exothermal peaks at different heating rates.

Table 1
Characteristic temperatures and enthalpies of the crystallization process of the $Ge_{0.18}Sb_{0.23}Se_{0.59}$ glassy alloy

Parameter	Experimental value
T_g (K)	536.8–553.2
T_i (K)	617.5–656.2
T_p (K)	634.6–686.1
ΔT (K)	23.9–82.3
ΔH (mcal mg^{-1})	2.5–6.1

Table 2
Maximum crystallization rate, corresponding temperature and volume fraction crystallized, kinetic exponent and impingement factor for the different heating rates

β (K min^{-1})	$10^3(\mathrm{d}x/\mathrm{d}t)\vert_p$ (s^{-1})	T_p (K)	x_p	δ_i	n
2	3.11	634.6	0.5862	3.5972	4.08
4	3.99	641.9	0.4577	0.6701	3.99
8	7.08	652.1	0.4660	0.7213	3.55
16	11.43	659.7	0.4284	0.5237	3.34
32	21.68	670.9	0.4725	0.7652	2.82
64	27.84	686.1	0.3629	0.3160	2.83

4.1. Glass-crystal transformation

The kinetic study of the glass-crystal transformations is related to the knowledge of the reaction rate constant, K_V, as a function of the temperature. In the present work it is assumed that the quoted constant has an Arrhenius type temperature dependence. Bearing in mind this assumption and that the nucleation frequency and crystal growth rate have also Arrhenian temperature dependences, the overall effective activation energy, E, for crystallization is given by Eq. (9). From this point of view, and considering that in most crystallization processes $E \gg RT$, the crystallization kinetics of the alloy $Ge_{0.18}Sb_{0.23}Se_{0.59}$ may be analyzed according to the theory developed in Section 2.

With the aim of analyzing the above mentioned kinetics, the variation intervals of the quantities described by the thermograms for the different heating rates quoted in Section 3 are obtained and given in Table 1, where T_i and T_p are the temperatures at which crystallization begins and that corresponding to the maximum crystallization rate, respectively, and ΔT is the width of the crystallization peak. The crystallization enthalpy, ΔH, is also determined for each heating rate. The data of $\ln(T_p^2/\beta)$ and $10^3/T_p$ are fitted to a linear function by least squares fitting and shown in Fig. 4. From the slope and intercept of this fit, according to Eq. (28), both the overall effective activation energy, E, and the pre-exponential factor, q, of the transformation are obtained. The results are the following:

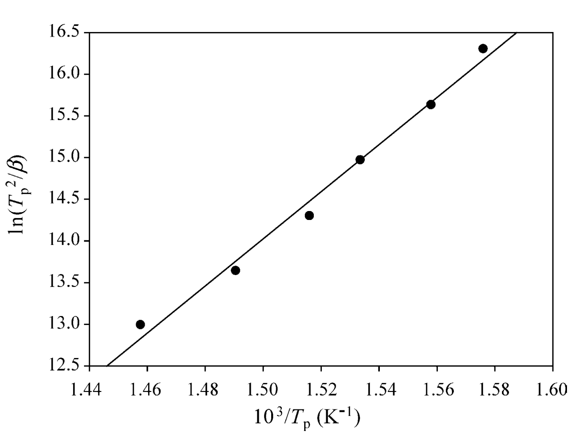

Fig. 4. Experimental plots of $\ln(T_p^2/\beta)$ vs. $10^3/T_p$ and straight regression line of $Ge_{0.18}Sb_{0.23}Se_{0.59}$ alloy (β in K s^{-1}).

$E = 56.5$ kcal mol^{-1}and $q = 2.11 \times 10^{12}$ (Ks)$^{-1}$. Moreover, the experimental data T_p, x_p and $(\mathrm{d}x/\mathrm{d}t)|_p$, shown in Table 2 allow to obtain the parameters: impingement factor, δ_i, and kinetic exponent, n. By using Eq. (27) and following the secant method of successive approximations, the impingement factor has been evaluated for each heating rate. The calculation of the kinetic exponent has been carried out for each heating rate, by using Eq. (29) and from the quoted experimental data, together with the above mentioned value of the activation energy and the corresponding results of the impingement factor. The values both for δ_i and for n are also given in Table 2. With the aim of explaining why the lowest heating rate, 2 K min^{-1}, gives the highest δ_i and n values, the Eqs. (27) and (29) have been related, yielding

$$nf(\delta_i) = n\left(\frac{\delta_i}{\delta_i + 1}\right)^{\delta_i+1} = \frac{RT_p^2(\mathrm{d}x/\mathrm{d}t)|_p}{\beta E}$$

an expression where the product $nf(\delta_i)$ is inversely proportional to heating rate. From the data given in Table 2, the values of the product $h_p = T_p^2(\mathrm{d}x/\mathrm{d}t)|_p$ are obtained. It should be noted that the quotient, $c = (h_p)_{i+1}/(h_p)_i$, in general, increases with the value of the subscript $i = 1, 2, 3, \ldots$, keeping always minor values that the corresponding ratio of 2–1 of the heating rate. By means of this fact it is possible to explain why the lowest heating rate gives the highest δ_i and n values. In addition, bearing in mind that the calorimetric analysis is an indirect method which only makes it possible to obtain mean values for the parameters that control the mechanism of a reaction, the quoted mean values have been calculated, resulting in: $\langle\delta_i\rangle = 1.10$ and $\langle n\rangle = 3.43$. It should be noted that the preceding value of the impingement factor suggests that the Austin–Rickett kinetic equation ($\gamma_i = 2$, $\delta_i = 1$), is more adequate than the JMA equation ($\gamma_i = 1$, $\delta_i \to \infty$) to describe the mechanism of the glass-crystal transformation of the semiconducting $Ge_{0.18}Sb_{0.23}Se_{0.59}$ glass. Of course, by using both equations under non-isothermal regime. This fact explains that the experimental x_p values range from 0.3629 to 0.5862 (see Table 2) results which are relatively different of $x_p = 0.63$, an approximately constant value, as it is required by JMA kinetic equation. With the aim of making comment on the validity of the model represented by Eq. (22) to analyze the kinetics of different non-isothermal transformations it must be considered the Eq. (27), which relates the parameters: volume fraction transformed, x_p, and impingement factor, δ_i. The values obtained for the quoted parameters by means of the developed model are compared with the calculated results by other kinetic equations, and they allow to check the validity of the quoted model. Accordingly, it is interesting to emphasize that when the x_p value is close to 0.5, the Austin–Rickett equation is more adequate, whereas if the quoted value of x_p tends to 0.63, the JMA kinetic equation is more suitable to describe the corresponding non-isothermal transformation. For this purpose, we have applied the present model at the analysis of the crystallization kinetics of a glassy alloy set, corresponding to the Sb-As-Se and Ge-Sb-Se systems, and we have examined the kinetic parameters, which control the glass-crystal transformation, checking the validity of the described model. In this sense, it should be noted that the mean value both of the volume fraction transformed, $\langle x_p \rangle$, and of the impingement factor, $\langle \delta_i \rangle$, for the quoted alloys, range from 0.4399 to 0.5348 and from 0.6198 to 1.5366, respectively. These results oscillate around the theoretical values: $x_p = 0.5$ and $\delta_i = 1$, and, therefore, the developed model proposes the Austin–Rickett kinetic equation, under non-isothermal regime to describe the mechanism of the glass-crystal transformation of the quoted alloys.

Besides, from the mean value of the kinetic exponent, $\langle n \rangle = 3.43$, of the semiconducting $Ge_{0.18}Sb_{0.23}Se_{0.59}$ glass it is possible to postulate a crystallization reaction mechanism of the quoted glass. Mahadevan et al. [39] have shown that n may be 4, 3, 2, or 1, which are related to different glass-crystal transformation mechanisms: $n = 4$, volume nucleation, three- dimensional growth; $n = 3$, volume nucleation, two-dimensional growth, $n = 2$, volume nucleation, one-dimensional growth; $n = 1$, surface nucleation, one-dimensional growth from surface to the inside. Bearing in mind that the material is grained (Section 3), according to the literature [40,41], it can be supposed that the most likely nucleation site of the studied glass is the free surface of the grain, arising a concentration of nuclei growing into the grain. These nuclei are formed during the process of temperature rise at temperatures lower than that required for the onset of crystal growth, and, therefore, the number of nuclei remains almost constant during the growth stage. This fact allows considering that the site saturation occurs at initial stage of the transformation for the $Ge_{0.18}Sb_{0.23}Se_{0.59}$ glassy alloy. With the aim of confirming the possible site saturation, the material was reheated up to a temperature slightly higher than the glass transition temperature. The reheated samples were subjected to the same calorimetric scans that the as-quenched samples. The values of the kinetic exponent, n, for reheated samples are similar to the corresponding data of the as-quenched material, given in Table 2. Matusita et al. [42] have shown that if n does not changes with the reheating, a large number of nuclei already exists in the specimen when the crystal growth begins. Accordingly, it is confirmed that the site saturation happens at initial stage of the glass-crystal transformation of the alloy studied.

5. Conclusions

The developed theoretical method enables us to study the evolution with the time of the actual volume fraction transformed and to analyze the glass-crystal transformation mechanisms in semiconducting glass systems involving formation and growth of nuclei. This method assumes the concept of the extended volume of transformed material and the condition of randomly located nuclei, together with the assumption of mutual interference of regions growing from separated nuclei. By using these assumptions we have obtained a general expression for the actual volume fraction transformed, as a function of the temperature in non-isothermal crystallization processes. In the quoted expression the kinetic exponent depends on both the nucleation frequency and the dimensionality of the crystal growth. It should be noted that the above mentioned expression also depends on the impingement factor. The kinetic parameters have been deduced by using the following considerations: the condition of the maximum crystallization rate and the quoted maximum rate.

The theoretical method developed has been applied to the experimental data corresponding to the crystallization kinetics of the $Ge_{0.18}Sb_{0.23}Se_{0.59}$ glassy alloy. The results obtained for the kinetic parameters agree satisfactorily with the calculated values by other mathematical treatments, confirming the reliability of the method developed.

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