



# On the glass–crystal transformation kinetics by using differential scanning calorimetry under non-isothermal regime

## Application to the crystallization of the $\text{Ag}_{0.16}\text{As}_{0.46}\text{Se}_{0.38}$ semiconductor glass

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### ABSTRACT

A procedure has been developed to obtain an evolution equation with the temperature for the actual transformed volume fraction under non-isothermal regime, to calculate the kinetic parameters and to analyze the glass–crystal transformation mechanisms in solid systems where a large number of nuclei already exists and no other new nuclei are formed during the thermal treatment. In this case, it is assumed that the nuclei only grow, “site saturation”, during the thermal process. Once an extended volume of transformed material has been defined and spatially random transformed regions have been assumed, a general expression of the extended volume fraction has been obtained as a function of the temperature. Considering the mutual interference of regions which grow from separate nuclei (impingement effect) and from the quoted expression, the actual transformed volume fraction has been deduced. The kinetic parameters have been obtained, by assuming that the reaction rate constant is a time function through its Arrhenian temperature dependence. The developed theoretical method has been applied to the crystallization kinetics of the  $\text{Ag}_{0.16}\text{As}_{0.46}\text{Se}_{0.38}$  glassy alloy as-quenched and previously reheated. In accordance with the corresponding results, it is possible to establish that in the considered alloy the nuclei were dominant before the thermal treatment, and because of it the reheating does not change in a considerable way the number of the pre-existing nuclei in the material, which is a case of “site saturation”. The comparison of the quoted results with the values obtained by means of Matusita method confirms the reliability of the theoretical method developed (TMD). Moreover, the obtained values for the kinetic parameters coincide in a satisfactory way with the results calculated by means of the Austin–Rickett (AR) equation under non-isothermal regime. Besides, the experimental curve of the transformed fraction shows a better agreement with the theoretical curves of the developed method and of the Austin–Rickett model than with the corresponding curve of the Avrami model. Accordingly, it seems appropriate to choose the Austin–Rickett equation in order to describe the crystallization mechanism of the above-mentioned glassy alloy.

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## 1. Introduction

Traditionally, solid-state physics has meant crystal physics. Solidity and crystallinity have been considered as synonymous in texts on condensed matter. However, at present one of the most active fields of solid-state research 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. Solid-state phase transformations play an important role in the production of many materials. Therefore, the last decades have seen the strong impulse that research community has given at the study of a general description of the kinetics of phase transformations [1] and accordingly, during the last 60 years the theoretical and practical interest in the

application of calorimetric analysis techniques to the study of the quoted transformations has notably increased [2–4]. Thus, the formal theory of nucleation and crystal growth has been developed during the last half century with the notable work performed by Christian [5] and a relatively recent review published by Kelton [6]. The calorimetric analysis techniques are quick and need small quantities of glass samples to obtain the kinetic parameters of a transformation. There are two thermal analysis regimes: isothermal and non-isothermal. The first one is in most cases more accurate and the data can be interpreted by the Johnson–Mehl–Avrami (JMA) equation [7–10], however, the non-isothermal thermoanalytical methods have several advantages. The rapidity with which non-isothermal experiments can be performed makes this type of experiments more attractive. Moreover, the industrial processes often depend on the kinetic behaviour of systems undergoing phase transformations under non-isothermal conditions. Accordingly, the use of non-isothermal techniques to study solid-state

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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 study of crystallization kinetics in amorphous materials by differential scanning calorimetry (DSC) methods has been widely discussed in the literature [6–18]. There is a large variety of theoretical models and theoretical functions proposed to explain the crystallization kinetics. The application of each of them depends on the type of amorphous material studied and how it was made.

It is well known that the JMA equation and the Arrhenian temperature dependence for the reaction rate constant have served as the basis on nearly all treatments of glass-crystal transformation in DSC experiments [19]. It should be noted, however, that the quoted equation strictly applies only to isothermal experiments, where an integration of its general expression is straightforward. Nevertheless, the JMA equation has been extensively used to derive expressions describing non-isothermal crystallization processes. Even though it is true that the experimental data interpreted on the basis of such expressions have often indicated good agreement between the overall effective activation energy calculated by means of the quoted expressions and activation energies obtained by other methods, also it is true that the quoted expressions have been deduced under isothermal conditions, whereas the studied transformation is a non-isothermal process [19]. Moreover, the most of theoretical methods developed on the basis of the formal theory of transformation kinetics are particular cases. Thus, it is possible to quote, as an illustrative example, the JMA equation, which is a particular case of the mentioned formal theory when both isothermal regime and the exponent of impingement effect equal to the unit are considered. For this reason it seems necessary to develop a new theoretical method more general on the basis, of course, of the formal theory. Thus, the theoretical method developed (TMD) in the present work obtains an evolution equation with the temperature for the actual transformed volume fraction, bearing in mind the mutual interference of regions growing from separated nuclei with variable impingement  $\gamma_i$ -exponent. Besides, the quoted method considers the non-isothermal crystallization of an as-quenched glass, which contains a large number of nuclei, a case of “site saturation” [20]. The quoted conditions of this method add a larger generality to the same, constituting an important advantage of the new method. This advantage allows the reader to use the quoted method under different theoretical and experimental conditions. The kinetics parameters and the glass-crystal transformation mechanism have been deduced from DSC experiments, using the quoted evolution equation and assuming a non-isothermal regime.

Moreover, this work applies the TMD to the analysis of the crystallization kinetics of the  $\text{Ag}_{0.16}\text{As}_{0.46}\text{Se}_{0.38}$  glassy semiconductor. The material was reheated to research the applicability of the mentioned method, obtaining for the kinetic exponent similar values before and after reheating. This result confirms the presence of a sufficient number of nuclei in the as-quenched glass, representing a case of “site saturation”.

On the other hand, the TMD has been compared with the Matusita model [21] to ascertain the conclusions which both methods provide about the transformation type, continuous nucleation or “site saturation”, for the analyzed alloy in the present work. Both methods give for the kinetic exponent of the as-quenched and the reheated material enough close values each other and, therefore, the conclusion obtained from both methods about the transformation type is the same, “site saturation”.

Finally, the variability of the impingement exponent in the TMD allows identify different kinetic models used in the literature. Thus, the mean values of the transformed volume fraction in the peak,  $\langle x_p \rangle = 0.4864$ , and of the impingement factor,  $\langle \delta_i \rangle = 0.8984$ , have been obtained for the as-quenched  $\text{Ag}_{0.16}\text{As}_{0.46}\text{Se}_{0.38}$  glassy alloy.

It should be noted that the above quoted mean values are very close to the values  $x_p = 0.5$  and  $\delta_i = 1$  that, according to the developed method, correspond to the Austin–Rickett (AR) model under non-isothermal regime [22]. In this sense, the AR equation can be considered as the more adequate to describe the crystallization mechanism of the studied glassy alloy. Therefore, it must be marked that the possibility on the part of the developed method to choose the kinetic equation more appropriate for analyzing the crystallization process of a glass is a fact which seems to advise clearly the use of the new method for studying the non-isothermal transformation of a glassy alloy.

## 2. Theoretical development

### 2.1. Deducing the actual volume fraction transformed

It is well known that the theoretical basis for interpreting DSC results is provided by the formal theory of transformation kinetics [7–10,18,23,24]. In accordance with this theory, it is possible to define an extended volume,  $V_e$ , of transformed material assuming spatially random transformed regions [12,19,25] and considering an isotropic growth rate,  $u$ , since in many transformations the reaction product grows approximately as spherical nodules [5] and, therefore, the elemental extended volume fraction,  $dx_e$ , is expressed as

$$dx_e = g \left[ \int_{(1-\alpha)\tau}^t u(t') dt' \right]^m dN \quad (1)$$

where  $\tau$  is the nucleation period,  $\alpha$  is a parameter equal to zero in the case of continuous nucleation and equal to unit in the case of “site saturation” [20], the  $m$ -exponent and the  $g$ -geometric factor are related to the dimensionality of the crystal growth and  $dN$  is the elemental number of nuclei existing per unit volume.

It should be noted that for continuous nucleation the quoted number of nuclei,  $dN$ , in terms of the nucleation frequency per unit volume,  $I_V(\tau)$ , is written as  $dN = I_V(\tau) d\tau$  and Eq. (1) becomes:

$$dx_e = g I_V(\tau) \left[ \int_{\tau}^t u(t') dt' \right]^m d\tau \quad (2)$$

whereas for “site saturation” Eq. (1) is written as

$$dx_e = g \left[ \int_0^t u(t') dt' \right]^n dN \quad (3)$$

since in this case, according to the literature [21], the kinetic exponent is  $n = m$ .

The Arrhenian temperature dependence for the glass-crystal transformation is often used in the literature [19,26] and, therefore, it is necessary to justify this use on the basis of the elementary processes of transformation. Thus, according to the literature [19], 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. Nevertheless, over a sufficiently limited range of temperature (such as the range of crystallization peaks in DSC experiments), both  $I_V$  and  $u$  may be described in a zeroth-order approximation by

$$I_V \approx I_{V0} \exp\left(-\frac{E_N}{RT}\right) \quad (4)$$

and

$$u \approx u_0 \exp\left(-\frac{E_G}{RT}\right) \quad (5)$$

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

Considering a constant heating rate,  $\beta = dT/dt$  [27], and integrating Eq. (3), according to the literature [28,29], the extended volume fraction, under non-isothermal regime in the case of “site saturation”, is expressed as

$$x_e = P(KT^2\beta^{-1})^n \quad (6)$$

which, as it can be observed, is a general expression, function of the kinetic exponent which, as it has been already said, depends on the dimensionality of the crystal growth. In Eq. (6),  $P = (R/E_G)^n$  and  $K = (gN_0)^{1/n} u_0 \exp(-E_G/RT) = K_0 \exp(-E_G/RT)$  is the reaction rate constant with an Arrhenian temperature dependence.

Next, with the aim of obtaining an evolution equation with the temperature for the actual transformed volume fraction, we have to consider the impingement effect. In this sense, following the literature [5,30], the quoted fraction is given as

$$x = 1 - (1 + x_e \delta_i^{-1})^{-\delta_i} \quad (7)$$

with the impingement factor  $\delta_i = (\gamma_i - 1)^{-1}$  and  $\gamma_i$  being the impingement exponent.

It should be noted that Eq. (7) includes different models used in the literature when a glass-crystal transformation is analyzed. Thus, for  $\gamma_i = 0 \Rightarrow \delta_i = -1$ ,  $x = x_e$ ; when  $\gamma_i = 1 \Rightarrow \delta_i \rightarrow \infty$ ,  $x = 1 - \exp(-x_e)$  (JMA model) and if  $\gamma_i = 2 \Rightarrow \delta_i = 1$ ,  $x = 1 - (1 + x_e)^{-1}$  (AR model) [22].

Finally, by substituting Eq. (6) into Eq. (7), one obtains:

$$x = 1 - \left[ 1 + \frac{1}{\delta_i} P \left( \frac{KT^2}{\beta} \right)^n \right]^{-\delta_i} \quad (8)$$

a general expression for the actual transformed volume fraction in a non-isothermal process with “site saturation”.

## 2.2. Calculating kinetic parameters

The usual methods, proposed in the literature [19] to analyze the crystallization kinetics in glass-forming liquids, assume that the reaction rate constant can be defined by Arrhenian temperature dependence, an assumption clearly justified in Section 2.1. In order to hold this assumption, the present work assumes that the crystal growth rate,  $u$ , has Arrhenian temperature dependence (see Section 2.1). From this point of view, the crystallization rate is obtained by taking the derivative with respect to time of the actual crystallized volume fraction [Eq. (8)], bearing in mind that in non-isothermal processes the reaction rate constant is a function of time through its above-mentioned Arrhenian temperature dependence. Thus, in a transformation with “site saturation”, by means of a similar development to the used way in the literature [30], one obtains:

$$\frac{dx}{dt} = \frac{Pn}{\beta} \left( \frac{KT^2}{\beta} \right)^{n-1} (1-x)^{(\delta_i+1)/\delta_i} \left( T^2 \frac{dK}{dt} + 2T\beta K \right) \quad (9)$$

The maximum crystallization rate is found making  $d^2x/dt^2 = 0$ , yielding:

$$\frac{\delta_i + 1}{\delta_i} (1 - x_p)^{1/\delta_i} P \left( \frac{K_p T_p^2}{\beta} \right)^n = 1 \quad (10)$$

an expression which relates the crystallization kinetic parameters  $E_G$ ,  $n$  and  $\delta_i$  to the quantity values that can be experimentally determined, and which correspond to the maximum crystallization rate.

According to the literature [30], one obtains:

$$1 - x_p = \left( \frac{\delta_i}{\delta_i + 1} \right)^{\delta_i} \quad (11)$$

an equation from which, the impingement factor,  $\delta_i$ , can be evaluated in a set of exotherms taken at different heating rates, by using a method of successive approximations (e.g. secant method).

Combining Eqs. (10) and (11), the logarithmic form of the resulting expression leads to the relationship:

$$\ln \frac{T_p^2}{\beta} = \frac{E_G}{RT_p} - \ln p \quad (12)$$

which is a linear function, whose slope and intercept give the effective activation energy,  $E_G$ , for the crystal growth, and the factor  $p = P^{1/n} K_0$  [see Eq. (8)], which is related to the probability of effective collisions for the formation of the activated complex.

Finally, following again Ref. [30] results in

$$n = RT_p^2 \frac{dx}{dt} \bigg|_p \left[ (1 - x_p)^{(\delta_i+1)/\delta_i} \beta E_G \right]^{-1} \quad (13)$$

an expression which allows to calculate the kinetic exponent,  $n$ , from 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 in a glass-crystal transformation process.

## 3. Experimental details

The  $Ag_{0.16}As_{0.46}Se_{0.38}$  glassy semiconductor was prepared in our laboratory in bulk form by the standard melt quenching method. High purity (99.999%) silver, arsenic and selenium in appropriate atomic percentage proportions were weighed into a quartz glass ampoule (6 mm diameter). The content of the ampoule (7 g per batch) was sealed at a pressure of  $10^{-2}$  Pa, heated in a rotating furnace at around 1125 K for 120 h and submitted to a 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 with ice in order to solidify the material quickly, avoiding the crystallization of the compound. The amorphous state of the material was checked through a diffractometric X-ray scan, in a Siemens D500 diffractometer. The thermal behaviour was investigated using a Perkin-Elmer DSC7 differential scanning calorimeter with an accuracy of  $\pm 0.1$  K. The temperature and energy calibrations of the instrument were performed, for each heating rate, by using the well-known melting temperatures and melting enthalpies of high-purity zinc and indium supplied with the instrument [31]. The samples weighing about 10 mg were crimped in aluminium pans and scanned from room temperature through their glass transition temperature,  $T_g$ , 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. 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. 1.

The crystallized fraction,  $x$ , corresponding to an exothermic peak at any temperature,  $T$ , is given by  $x = A_T/A$ , where  $A$  is the total area limited by the exotherm of the quoted peak between the temperature,  $T_i$ , where the crystallization just begins 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. 1.

## 4. Results

The typical DSC trace of  $Ag_{0.16}As_{0.46}Se_{0.38}$  semiconductor glass obtained at a heating rate of 32 K  $min^{-1}$  and plotted in Fig. 1 shows three characteristic phenomena, which are resolved in the temperature region studied. The first one ( $T = 434.3$  K) corresponds to the glass transition temperature,  $T_g$ , the second one ( $T = 483.0$  K) to the extrapolated onset crystallization temperature,  $T_c$ , and the last one ( $T = 513.5$  K) to the peak temperature of crystallization,  $T_p$ , of

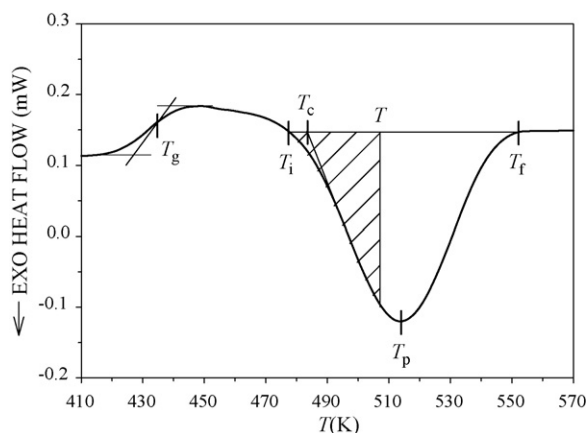


Fig. 1. Typical DSC trace of  $\text{Ag}_{0.16}\text{As}_{0.46}\text{Se}_{0.38}$  semiconductor alloy at a heating rate of  $32 \text{ K min}^{-1}$ . The hatched area shows  $A_T$ , the area between  $T_i$  and  $T$ .

the above-mentioned semiconductor glass. The quoted DSC trace shows the typical behaviour of a glass-crystal transformation. The data of the thermograms for the different heating rates,  $\beta$ , quoted in Section 3, show values of the quantities  $T_g$ ,  $T_c$  and  $T_p$ , which increase with increasing  $\beta$  as it is observed in Fig. 2, a property which has been reported in the literature [32].

The area limited by the DSC curve is directly proportional to the total amount of crystallized alloy. The quotient between the ordinates of the quoted curve and the total area of the peak gives the corresponding crystallization rates, which allow plot the curves of the exothermal peaks represented in Fig. 3. It may be observed that the values of the quantity  $(dx/dt)_p$  increase in the same proportion that the heating rate, a property which has been widely discussed in the literature [32,33]. Besides, in the quoted Fig. 3, it can be immediately verified that the initial temperature of the peak corresponding to the heating rate,  $\beta = 64 \text{ K min}^{-1}$ , is  $T_i = 483.6 \text{ K}$ , a larger value than all initial temperatures corresponding to the lower heating rates, which vary in the temperature interval (459.8–477.1) K. A similar explanation can be achieved for the  $T_c$ -onset crystallization temperature which is not commented in this manuscript for simplicity reasons. Moreover, according to Fig. 3 it is possible to verify clearly that initial temperature corresponding to the heating rate,  $\beta = 2 \text{ K min}^{-1}$ , is approximately  $T_i = 459.8 \text{ K}$  which, of course, is in the temperature interval (459.8–483.6) K as it is observed in Table 1, which is commented in the following section.

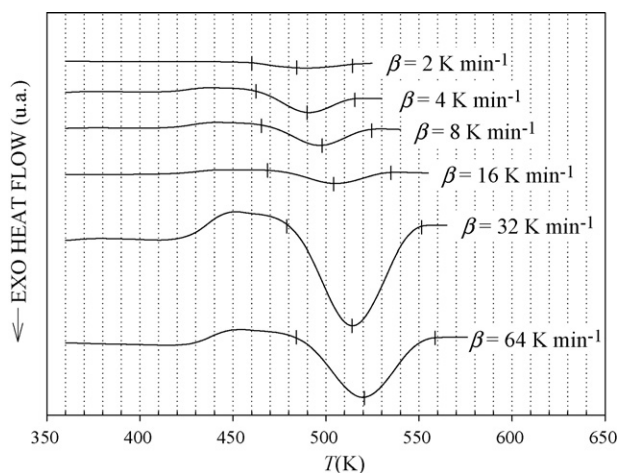


Fig. 2. Continuous heating DSC plots of  $\text{Ag}_{0.16}\text{As}_{0.46}\text{Se}_{0.38}$  glassy alloy.

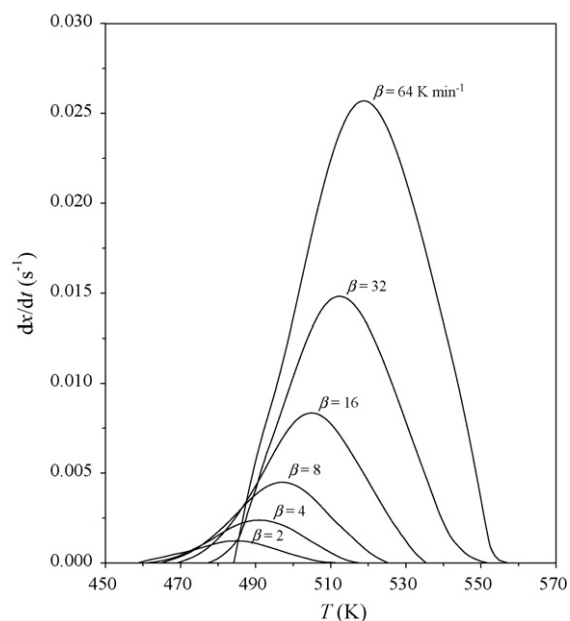


Fig. 3. Crystallization rate vs. temperature for the as-quenched glass at different heating rates.

#### 4.1. Glass-crystal transformation

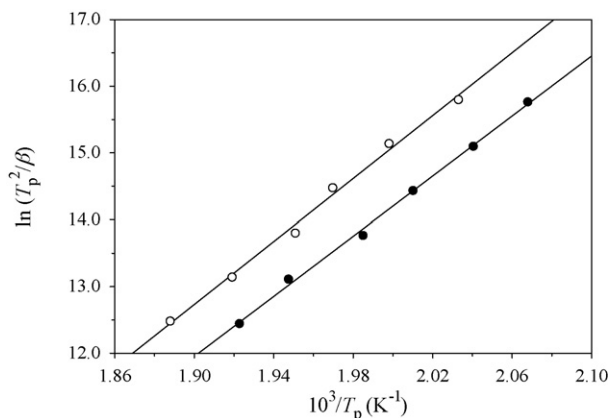
The kinetic analysis of the crystallization reactions is related to the knowledge of the reaction rate constant as a function of the temperature. The usual analytical methods, proposed in the literature to describe the above-mentioned reactions, assume that the reaction rate constant can be represented by means of an Arrhenius type temperature dependence [19,26]. Bearing in mind this assumption and that the nucleation frequency is practically negligible in “site saturation” as it is supposed in this work, the overall effective activation energy of the process is represented by the activation energy for the crystal growth [19]. From this point of view, and considering that in most crystallization processes the overall activation energy is much larger than the product  $RT$ , the glass-crystal transformation kinetics of the  $\text{Ag}_{0.16}\text{As}_{0.46}\text{Se}_{0.38}$  alloy may be analyzed in accordance with the theory developed in Section 2.

The analysis of the transformation kinetics of the above-mentioned alloy involves know the experimental values of the quantities, which are obtained from the thermograms corresponding to the heating rates, quoted in Section 3. The values of the mentioned quantities are 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  $\Delta T$  is the width of the crystallization peak. The crystallization enthalpy  $\Delta H$  is also determined for each of the heating rates. It should be noted that the enthalpy values for as-quenched and for reheated samples range from 18.3 to 20.8 mJ/mg and from 23.3 to 26.7 mJ/mg, respectively.

To research the correct application of the preceding theory, the material was reheated up to 447 K (a temperature slightly higher than  $T_g$ ) for 90 min in order to form a large number of nuclei. It was ascertained by X-ray diffraction that no crystalline peaks were detected after the reheating. The reheated samples were subjected to the same calorimetric scans that the as-quenched samples. The data of  $\ln(T_p^2/\beta)$  and  $1/T_p$ , both for the as-quenched and for the reheated glass, are fitted to linear functions by least squares fitting and shown in Fig. 4. The activation energy,  $E_G$ , and the pre-exponential factor,  $p$ , are obtained, in accordance with Eq. (12), from the slope and intercept of the corresponding straight regression lines. The results are the

**Table 1**  
Characteristic temperatures and enthalpies of the crystallization process of the  $\text{Ag}_{0.16}\text{As}_{0.46}\text{Se}_{0.38}$  glassy alloy.

Material	Quantity	Experimental value $\beta$ ( $\text{K min}^{-1}$ )					
		2	4	8	16	32	64
As-quenched	$T_g$ (K)	423.0	427.9	429.1	431.7	434.3	444.0
	$T_i$ (K)	459.8	461.8	464.9	468.8	477.1	483.6
	$T_p$ (K)	483.6	490.1	497.5	503.8	513.5	520.1
	$\Delta T$ (K)	53.7	53.8	59.1	66.1	74.4	74.6
	$\Delta H$ (mJ/mg)	18.3	18.8	19.2	19.2	20.8	20.4
Reheated	$T_g$ (K)	420.3	426.3	434.1	439.3	445.5	451.1
	$T_i$ (K)	463.7	464.2	465.9	469.0	478.0	479.7
	$T_p$ (K)	491.9	500.5	507.7	512.6	521.1	529.7
	$\Delta T$ (K)	54.9	68.2	71.1	77.0	79.7	84.9
	$\Delta H$ (mJ/mg)	26.7	23.3	25.8	25.4	26.7	24.6



**Fig. 4.** Experimental plots of  $\ln(T_p^2/\beta)$  vs.  $10^3/T_p$  and straight regression lines of the  $\text{Ag}_{0.16}\text{As}_{0.46}\text{Se}_{0.38}$  alloy ( $\beta$  in  $\text{K s}^{-1}$ ): (●) as-quenched glass; (○) reheated glass.

following:  $E_G = 187.5$  kJ/mol and  $p = 2.39 \times 10^{13}$  ( $\text{K s})^{-1}$  for the as-quenched glass, and  $E_G = 196.7$  kJ/mol and  $p = 8.43 \times 10^{13}$  ( $\text{K s})^{-1}$  for the reheated glass. Moreover, the experimental data  $(dx/dt)_p$ ,  $T_p$  and  $x_p$  shown in Table 2 allow to obtain the parameters: impingement factor,  $\delta_i$ , and kinetic exponent,  $n$ , that, as it is well-known, give information about the glass-crystal transformation mechanism. By using Eq. (11) and following the secant method of successive approximations, the impingement factor has been evaluated for each heating rate both in the case of the as-quenched glass and of the reheated glass. The calculation of the kinetic exponent has been carried out for each heating rate both for the as-quenched and for reheated material, by using Eq. (13), from the quoted experimental data, together with the above-mentioned values of the corresponding activation energy and the respective results of the impingement factor. The values both for  $\delta_i$  and for  $n$  are also given in Table 2. Bearing in mind that the calorimetric analysis is an indirect method which solely allows to obtain mean values for the parameters which control the mechanism of a reaction, impingement factor and kinetic exponent, the mentioned mean values have been calculated, resulting in:  $\langle \delta_i \rangle = 0.8984$ ,  $\langle n \rangle = 1.49$  for the as-quenched glass and  $\langle \delta_i \rangle = 1.1883$ ,  $\langle n \rangle = 1.33$  for the reheated glass. Allowing for the

experimental error, these values of the kinetic exponent,  $n$ , are near to 1. Matusita et al. [21] have shown that if  $n$  does not change with reheating, a large number of nuclei already exists in the specimen, and when  $n$  decreases with reheating, not so many nuclei exist in the specimen. Accordingly, it is possible to affirm that a large number of nuclei already exists in the as-quenched material analyzed in this work, given that  $n$  has not changed with reheating, by representing a case of “site saturation”.

On the other hand, Matusita technique has been applied to the experimental data of  $\text{Ag}_{0.16}\text{As}_{0.46}\text{Se}_{0.38}$  glassy alloy, with the aim of confirming the reliability of the TMD in the present article. In the quoted technique, according to the literature [21,34] the following equations:

$$\ln[-\ln(1-x)] = -n \ln \beta - 1.053 \frac{mE}{RT} + \text{constant} \quad (14)$$

and

$$\ln \frac{T_p^2}{\beta^n} = 1.053 \frac{mE}{RT_p} + \text{constant} \quad (15)$$

allow to obtain the parameter values: kinetic exponent,  $n$ , and activation energy,  $E$ , both for the as-quenched and for the reheated material. Thus, by representing  $\ln[-\ln(1-x)]$  vs.  $\ln \beta$  at different fixed temperatures, the values of the kinetic exponent are obtained, and it is observed that the correlation coefficients of the corresponding straight regression lines show a maximum value for a given temperature, which has been considered as the most appropriate one for the calculation of the quoted exponent. Fig. 5 shows the relation between  $\ln[-\ln(1-x)]$  and  $\ln \beta$  for as-quenched glass at 507.5 K and for reheated glass at 525.5 K. According to Eq. (14) the slopes of these lines give the  $n$ -values, and it has been found that  $n = 0.98$  for the as-quenched glass and  $n = 0.93$  for the reheated glass with correlation coefficients 0.9967 and 0.9972, respectively. With these values it can be said that both for the as-quenched and for the reheated sample the  $n$ -value is near to 1 and, therefore, it is possible to conclude that a large number of nuclei already exists in the as-quenched material, representing a case of “site saturation”. Accordingly,  $m = 1$ , that is, the crystal particles grow one-dimensionally. It should be noted that the comparison of the TMD with other methods (e.g. Matusita method) leads to the same

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

$\beta$ ( $\text{K min}^{-1}$ )	As-quenched					Reheated				
	$10^3(dx/dt)_p$ ( $\text{s}^{-1}$ )	$T_p$ (K)	$x_p$	$\delta_i$	$n$	$10^3(dx/dt)_p$ ( $\text{s}^{-1}$ )	$T_p$ (K)	$x_p$	$\delta_i$	$n$
2	1.33	483.6	0.4808	0.8288	1.73	1.24	491.9	0.4897	0.9013	1.58
4	2.45	490.1	0.4714	0.7595	1.68	2.45	500.5	0.4900	0.9042	1.61
8	4.55	497.5	0.5207	1.2559	1.38	4.20	507.7	0.4923	0.9262	1.41
16	8.49	503.8	0.4629	0.7015	1.59	7.30	512.6	0.5532	1.9294	1.06
32	14.90	513.5	0.5011	1.0122	1.30	14.10	521.1	0.5052	1.0578	1.22
64	26.10	520.1	0.4813	0.8326	1.25	26.50	529.7	0.5304	1.4111	1.10

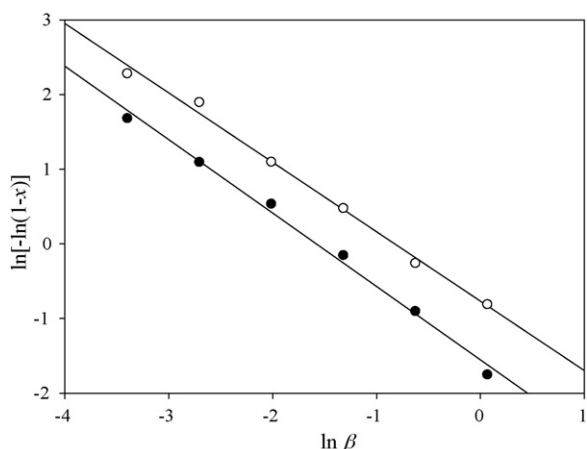


Fig. 5. Variation of  $\ln[-\ln(1-x)]$  with logarithm of heating rate ( $\beta$  in  $\text{K s}^{-1}$ ): (●) as-quenched glass at 507.5 K; (○) reheated glass at 525.5 K.

conclusions about the glass-crystal transformation type, i.e.: “site saturation”, for  $\text{Ag}_{0.16}\text{As}_{0.46}\text{Se}_{0.38}$  glassy alloy. This fact confirms the reliability of the developed method in this work.

Moreover, once the crystallization mechanism is known by the calculated  $n$  and  $m$  values, according to Eq. (15) it is possible to draw in Fig. 6 the plots, which show the variation of  $\ln(T_p^2/\beta^n)$  vs.  $1/T_p$ . The slopes of the corresponding straight regression lines give the activation energy for crystal growth: 177.9 kJ/mol for the as-quenched glass and 185.8 kJ/mol for the reheated glass with correlation coefficients 0.9987 and 0.9972, respectively. Likewise, according to Eq. (14), by making explicit the quantity  $\ln \beta$  one obtains the expression:

$$\ln \beta = -1.053 \frac{m}{n} \frac{E}{RT} - \frac{1}{n} \ln[-\ln(1-x)] + \text{constant} \quad (16)$$

which allow to plot  $\ln \beta$  vs.  $1/T$  for a fixed value of the transformed volume fraction. Fig. 7 shows the relation between  $\ln \beta$  and  $1/T$  at which  $x$  reaches 0.3, 0.5 and 0.7 values. According to Eq. (16), the slopes of the corresponding straight regression lines give the  $E$ -values, both for as-quenched and for reheated glass, which are shown in Table 3.

It can be observed that the activation energies obtained by means of the TMD, 187.5 kJ/mol for the as-quenched glass and 196.7 kJ/mol for the reheated glass, already quoted, are in enough good agreement with the activation energies given in Table 3 and obtained by the Matusita alternative method. This fact confirms again the reliability of the developed method in this work to study

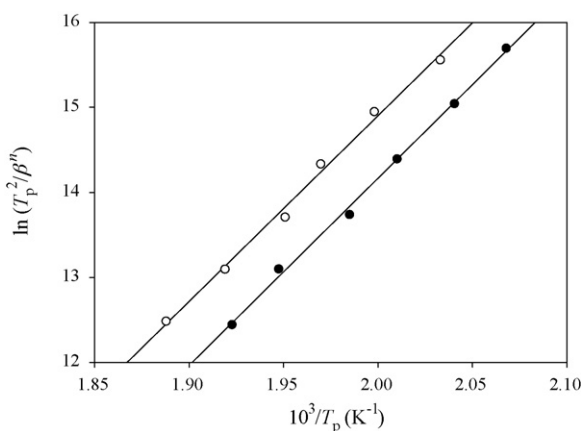


Fig. 6. Experimental plots of  $\ln(T_p^2/\beta^n)$  vs.  $10^3/T_p$  and straight regression lines of the  $\text{Ag}_{0.16}\text{As}_{0.46}\text{Se}_{0.38}$  alloy ( $\beta$  in  $\text{K s}^{-1}$ ): (●) as-quenched glass; (○) reheated glass.

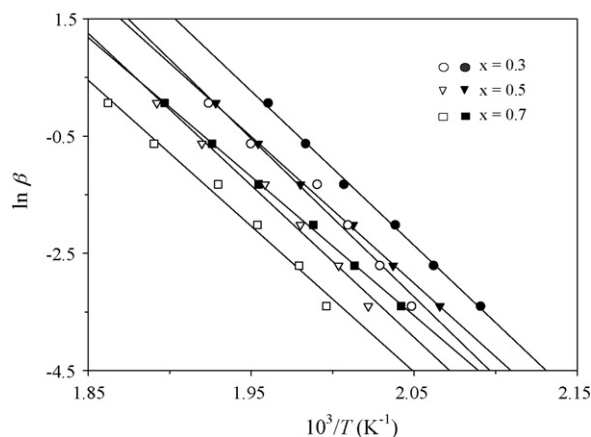


Fig. 7. Plot of  $\ln \beta$  vs.  $10^3/T$  for the values of the crystallized volume fraction equal to 0.3, 0.5 and 0.7 ( $\beta$  in  $\text{K s}^{-1}$ ): (●, ▼, ■) as-quenched glass; (○, ▽, □) reheated glass.

Table 3

Activation energy obtained from the plot of  $\ln \beta$  vs.  $1/T$  for fixed values of the transformed volume fraction.

Transformed volume fraction, $x$	As-quenched glass		Reheated glass	
	$E$ (kJ/mol)	$r$	$E$ (kJ/mol)	$r$
0.3	208.3	0.9989	213.8	0.9895
0.5	198.3	0.9995	205.4	0.9927
0.7	187.9	0.9995	197.1	0.9926

$r$  is the correlation coefficients.

the non-isothermal glass-crystal transformation kinetics in the case of “site saturation”.

Once the comparison of the TMD with the Matusita method confirms that both methods lead to the same conclusion about the transformation type of the alloy studied, we explain the reasons for the better fitting of the TMD by the AR model in comparison with the JMA model. Firstly, we examine the mean values of the transformed volume fraction,  $\langle x_p \rangle = 0.4864$ , and of the impingement factor,  $\langle \delta_i \rangle = 0.8984$ , for the as-quenched glass, obtained by means of the TMD, with the aim of correctly choosing the more suitable model to describe the crystallization kinetics of the  $\text{Ag}_{0.16}\text{As}_{0.46}\text{Se}_{0.38}$  semiconductor glass. It should be noted that the above quoted mean values are very close to the theoretical values:  $x_p = 0.5$  and  $\delta_i = 1$ , corresponding to the AR kinetic equation, whereas the above-mentioned mean values are very different of the theoretical values:  $x_p = 0.63$  and  $\delta_i \rightarrow \infty$ , which correspond to the JMA model (see Section 2). This is the first reason why it is recommended the AR model under non-isothermal regime to describe the glass-crystal transformation kinetics of the quoted semiconductor glass. Next, considering Eq. (8), from which the AR and JMA kinetic equations are particular cases, we obtain the expressions of the theoretical transformed volume fraction,  $x$ , as functions of the temperature corresponding to the as-quenched material, by using both the TMD and the AR and JMA models, which are given in Table 4 for  $\beta = 16 \text{ K min}^{-1}$ . To obtain the quoted expressions it is necessary to know the kinetic exponent values, which correspond to the above-mentioned models. Accordingly, given that the AR and JMA models

Table 4

Theoretical expressions of the transformed volume fraction for the TMD and for AR and JMA models when  $\beta = 16 \text{ K min}^{-1}$ .

Model	Equation
TMD	$x = 1 - [1 + 6.84 \times 10^{20} T^{2.98} \exp(-33,525/T)]^{-0.8984}$
AR	$x = 1 - [1 + 1.23 \times 10^{20} T^{2.88} \exp(-32,400/T)]^{-1}$
JMA	$x = 1 - \exp[-2.48 \times 10^{13} T^{1.92} \exp(-21,600/T)]$

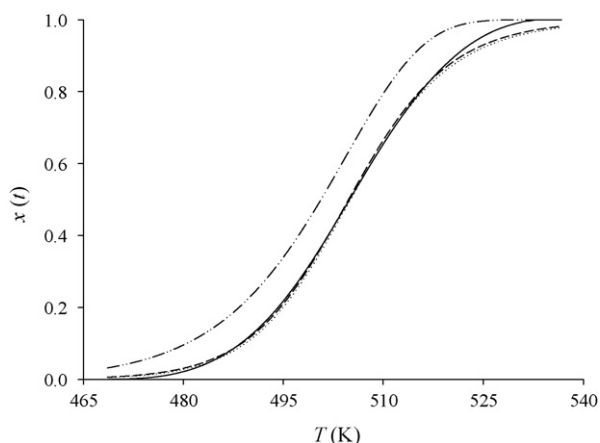


Fig. 8. Transformed volume fraction,  $x$  vs.  $T$  for  $\beta = 16 \text{ K min}^{-1}$ : (—) experimental data; (····) TMD; (---) AR model; (-·-·) JMA model.

are particular cases of the TMD, the values of the kinetic exponent of both models are calculated from Eq. (13), taking  $x_p = 0.5$  and  $\delta_i = 1$  for the AR model and  $x_p = 0.63$  and  $\delta_i \rightarrow \infty$  for the JMA model. Thus, we obtain for the quoted exponent the following mean values:  $\langle n \rangle = 1.44$  for the first model and  $\langle n \rangle = 0.96$  for the second model.

As an illustrative example, which contributes other reason to recommend the TMD to the analysis of the  $\text{Ag}_{0.16}\text{As}_{0.46}\text{Se}_{0.38}$  alloy, we represent in Fig. 8 the experimental curve and the theoretical curves  $x$  vs.  $T$  corresponding to the TMD and the AR and JMA models. In this figure, it is observed a very satisfactory agreement between the experimental curve and the theoretical curves of the TMD and of the AR model, whereas the theoretical curve of the JMA model shows an enough large disagreement with the experimental curve. This fact is the second reason which advises to recommend the TMD in order to analyze the non-isothermal glass-crystal transformation kinetics of as-quenched materials with “site saturation”.

Finally, once we have confirmed that the studied alloy has undergone a non-isothermal transformation with “site saturation” by means of the comparison of the TMD with the Matusita method, it is possible to postulate the corresponding mechanism for the quoted transformation. In this sense, from the mean value of the kinetic exponent, which is near to 1, according to the Avrami theory of nucleation and crystal growth [8–10,19], it is possible to state that in the quoted mechanism there is a diffusion controlled growth, coherent with the basic formalism used and with the crystal particles growing one-dimensionally.

## 5. Conclusions

The theoretical method developed enables us to study the evolution with the temperature of the actual transformed volume fraction, and to analyze the glass-crystal transformation mechanisms in solid systems where a large number of nuclei already exists and no other new nuclei are formed in the thermal treatment, assuming that the nuclei solely grow, “site saturation”. This method assumes the concept of 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 transformed volume fraction, as a function of the temperature in non-isothermal crystallization processes. It should be noted that the above-mentioned expression 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 max-

imum rate. The theoretical method developed has been applied to the experimental data corresponding to the crystallization kinetics of the  $\text{Ag}_{0.16}\text{As}_{0.46}\text{Se}_{0.38}$  glassy alloy as-quenched and previously reheated. In accordance with the study carried out, it is possible to establish that the reheating does not cause the appearance of nuclei, but that the as-quenched material already contains a sufficient number of them. The method developed gives for the quoted alloy values of kinetic parameters, which agree in a very satisfactory way with the results calculated by Matusita alternative method, as it is observed in Section 4.1. This fact confirms the reliability of TMD in order to analyze a non-isothermal glass-crystal transformation with “site saturation”. Moreover, the mean values of  $x_p$  and  $\delta_i$  for alloy studied are very close to the theoretical values 0.5 and 1, respectively, that corresponding to the Austin–Rickett model. Also, the experimental curve  $x$  vs.  $T$  agrees very satisfactory with the theoretical curves of the method developed and of the Austin–Rickett model, as it is observed in Fig. 8. These facts advise to consider the Austin–Rickett equation under non-isothermal regime as the more adequate kinetic equation to study the glass-crystal transformation of the above-mentioned alloy.

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