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Crystallization of $Ge_{0.08}Sb_{0.15}Se_{0.77}$ glass studied by DSC

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Abstract

A theoretical method has been considered for deriving the evolution equation with time of the actual volume fraction transformed, for integrating the above mentioned equation under non-isothermal regime, and for deducing the kinetic parameters of the glass–crystal transformations in solid systems where a large number of nuclei already exists and no 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. By defining an extended volume of transformed material and assuming spatially random transformed regions, a general expression of the extended volume fraction has been obtained as a function of the temperature. Considering the impingement effect and from the above mentioned expression the actual volume fraction has been deduced. The kinetic parameters have been obtained, assuming that the reaction rate constant is a time function through its Arrhenian temperature dependence. The theoretical method considered has been applied to the crystallization kinetics of the $Ge_{0.08}Sb_{0.15}Se_{0.77}$ glassy alloy with and without previous reheating. According to the study carried out, it is possible to state that in the considered alloy the nuclei were dominant before thermal analysis, and therefore the reheating did not appreciably change the number of pre-existing nuclei in the material, which constitutes a case of 'site saturation'.

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1. Introduction

The last decades have seen a strong interest in the study of the glass–crystal transformation. An understanding of the kinetics of crystallization in glasses is important for the manufacturing of glass-ceramics and in preventing devitrification. Nucleation and crystallization rates are sometimes measured directly in the microscope [1] but this method could not be applied to glasses in which nucleation and crystallization occurred in times below 1h. Differential scanning calorimetry (DSC) is valuable for the quantitative study of crystallization in different glassy systems. This study of crystallization kinetics has been widely discussed in the literature [2–4], and thus many authors applied the Johnson–Mehl–Avrami (JMA) [5] equation to the non-isothermal crystallization process [6]. 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 crystallization conditions [7].

In this work, according to literature [2,8–11], a theoretical method is considered for analyzing the non-isothermal crystallization kinetics on the basis of nucleation and crystal growth processes, in the case of an as-quenched glass, which contains a large number of nuclei, 'site saturation' [12]. In addition, the present paper applies the quoted method to the analysis of the crystallization kinetics of the $Ge_{0.08}Sb_{0.15}Se_{0.77}$ glassy semiconductor. The material was reheated to research

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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.

2. Theoretical background

2.1. Deducing volume fraction transformed

The theoretical basis for interpreting DSC results is provided by the formal theory of transformation kinetics [4,5,9,13]. This theory supposes that the crystal growth rate, in general, is anisotropic, and in the case of an as-quenched glass where a large number of nuclei already exists and no new nuclei are formed during the thermal treatment (site saturation) [12], the volume of a transformed region is then

$$v = g\prod_i \int_0^t u_i(t')\mathrm{d}t', \tag{1}$$

where the expression $\prod_i \int_0^t u_i(t')\mathrm{d}t'$ 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. Defining an extended volume of transformed material and assuming spatially random transformed regions [14], the elemental extended volume fraction, $\mathrm{d}x_\mathrm{e}$ is expressed as

$$\mathrm{d}x_\mathrm{e} = v\mathrm{d}N' = g\left(\prod_i \int_0^t u_i(t')\mathrm{d}t'\right)\mathrm{d}N'. \tag{2}$$

$\mathrm{d}N'$ being the number of nuclei existing in a volume element of material. When the crystal growth rate is isotropic, $u_i = u$, an assumption which is agreement with the experimental evidence, since in many transformations the reaction product grow approximately as spherical nodules [14], Eq. (2) can be written as [9,15]

$$\mathrm{d}x_\mathrm{e} = g\left[\int_0^t u(t')\mathrm{d}t'\right]^m \mathrm{d}N', \tag{3}$$

where m is an exponent related to the dimensionality of the crystal growth. In the considered case 'site saturation' [12] the kinetic exponent is $n = m$, assuming an Arrhenian temperature dependence for u [9], and a constant heating rate, $\beta = \mathrm{d}T/\mathrm{d}t$ [2], Eq. (3) becomes

$$x_\mathrm{e} = gN_0u_0^n\beta^{-n}\left(\int_{T_0}^{T} \mathrm{e}^{-E_\mathrm{G}/RT'}\,\mathrm{d}T'\right)^n = qI^n, \tag{4}$$

where E_G is the effective activation energy for crystal growth and N_0 is the number of pre-existing nuclei per unit volume.

By using the substitution $z' = E_\mathrm{G}/RT'$ the integral I can be represented, according to the literature [16], by the sum of the alternating series

$$S(z') = \frac{-\mathrm{e}^{-z'}}{z'^2}\sum_{k=0}^{\infty}\frac{(-1)^k(k+1)!}{z'^k}.$$

Considering that in this type of series the error produced is less than the first term neglected and bearing in mind that in most crystallization reactions $z' = E_\mathrm{G}/RT' \gg 1$, usually $E_\mathrm{G}/RT' \geqslant 25$ [17], it is possible to use only the first term of this series, without making any appreciable error, and the above mentioned integral can be written as

$$I = \frac{E_\mathrm{G}}{R}\mathrm{e}^{-z}z^{-2} = RT^2E_\mathrm{G}^{-1}\exp\left(-\frac{E_\mathrm{G}}{RT}\right), \tag{5}$$

if it is assumed that $T_0 \ll T$ (T_0 is the starting temperature), so that z_0 can be taken as infinity. This assumption is justifiable for any thermal treatment that begins at a temperature where crystal growth is negligible, i.e. below the glass transition temperature, T_g [17].

Substituting Eq. (5) into Eq. (4), introducing the parameter $P = (R/E_\mathrm{G})^n$ and defining the reaction rate constant $K_\mathrm{R} = (gN_0)^{1/n}u_0\exp(-E_\mathrm{G}/RT)$, with an Arrhenian temperature dependence, the extended volume fraction, under non-isothermal regime, is expressed as

$$x_\mathrm{e} = P(K_\mathrm{R}T^2\beta^{-1})^n, \tag{6}$$

which, as can be observed, is a general expression for all possible values of the n exponent, which depends on the dimensionality of the crystal growth.

The extended volume fraction gives information about the kinetic laws which govern the crystal growth, however, a general kinetic equation must also consider the geometrical problem of the impingement between regions growing from separated nuclei. In this sense, we will simply state that a relationship between the actual fraction transformed, x, and the extended, x_e can be written as

$$\mathrm{d}x = (1 - x)\mathrm{d}x_\mathrm{e}, \tag{7}$$

when the termed impingement exponent, $\gamma_i = 1$, according to the literature [18]. Bearing in mind Eq. (6) the general solution of Eq. (7) is given as

$$x = 1 - \exp[-P(K_\mathrm{R}T^2\beta^{-1})^n], \tag{8}$$

an expression from that the kinetic parameters can be obtained.

2.2. Calculating kinetic parameters

The usual analytical methods, proposed in the literature [17] for analyzing the transformation kinetics, 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 the crystal growth rate, u, has an Arrhenian temperature dependence [9], and over the temperature range where the thermoanalytical measurements are carried out, the nucleation rate is negligible (i.e. the condition of site saturation) [9,12]. From this point of view, the crystallization rate is obtained by deriving Eq. (8) with respect to time [2], yielding

$$dx/dt = nP(K_R T^2 \beta^{-1})^{n-1}(1-x)(K_R E_G R^{-1} + 2K_R T), \tag{9}$$

where it is assumed that the reaction rate constant is a time function through its Arrhenian temperature dependence.

The maximum crystallization rate is found by making $d^2x/dt^2 = 0$ [2], thus obtaining the relationship

$$P[(K_R)|_p T_p^2 \beta^{-1}]^n = 1 - \left(\frac{2}{n}\right)\left(1 + \frac{E_G}{RT_p}\right)\left(2 + \frac{E_G}{RT_p}\right)^{-2}, \tag{10}$$

where the subscript p denotes the quantity values corresponding to the maximum crystallization rate. Assuming the above mentioned hypothesis $E_G/RT_p \gg 1$; the logarithmic form of Eq. (10) is written as

$$\ln\left(\frac{T_p^2}{\beta}\right) = \frac{E_G}{RT_p} - \ln(P^{1/n}K_{R0}), \tag{11}$$

equation of a straight line, whose slope and intercept give the activation energy, E_G, and the factor $p = P^{1/n}K_{R0}$, which is related to the probability of effective collisions for the formation of the activated complex.

On the other hand, the quoted assumption, $E_G/RT_p \gg 1$, together with Eqs. (8)–(10) for $d^2x/dt^2 = 0$, allows us to express the maximum crystallization rate by the relationship

$$\left.\frac{dx}{dt}\right|_p = 0.37\beta E_G n (RT_p^2)^{-1}, \tag{12}$$

which makes it possible to obtain, for each heating rate, a value of the kinetic exponent, n. The corresponding mean value may be taken as the most probable value of the quoted exponent.

2.3. Single-scan technique

It has been indicated in the literature [3,9,19] that a single temperature scan can be used to determine the kinetic parameters, E, n, of the glass–crystal transformation. The JMA transformation rate equation

$$\frac{dx}{dt} = nK(1-x)[-\ln(1-x)]^{(n-1)/n} = nKf(x), \tag{13}$$

can be integrated, obtaining an expression which logarithm form is expressed as

$$\ln[-\ln(1-x)] - 2n\ln T = n\ln\frac{K_0 R}{\beta E} - \frac{nE}{RT}. \tag{14}$$

Moreover, taking logarithm in Eq. (13) results in

$$\ln\left(\frac{dx}{dt}\right) = \ln(nK_0) + \ln[f(x)] - \frac{E}{RT}. \tag{15}$$

Eqs. (14) and (15) are linear functions assuming, in the former, that over a temperature range of 100 K the contribution of the term, $2n\ln T$, can be ignored without causing a substantial error in the calculated slope. Regarding the second equation, the function $\ln[f(x)]$ may be considered constant, provided $0.25 < x < 0.75$. Bearing in mind this assumptions, the slopes of Eqs. (14) and (15) allow us to obtain the product nE and E, respectively.

3. Experimental procedures

The semiconducting $Ge_{0.08}Sb_{0.15}Se_{0.77}$ glassy was prepared in bulk form by the standard melt quenching method. High-purity (99.999%) germanium, antimony and selenium in appropriate atomic percent proportions were weighed (7 g per batch) and introduced into a quartz glass ampoule (6 mm diameter). The content of the quoted ampoule was sealed under a vacuum of 10^{-2} Pa, heated in a rotating furnace at around 1225 K for 60 h and then quenched in water with ice to avoid crystallization. The amorphous state of the material was checked through a diffractometric X-ray scan in a Siemens D500 diffractometer. The homogeneity and composition of the samples were verified through scanning electron microscopy (SEM) in a JEOL, scanning microscope JSM 820. The calorimetric measurements were carried out in a Perkin-Elmer DSC7 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 [20]. Powdered samples weighing about

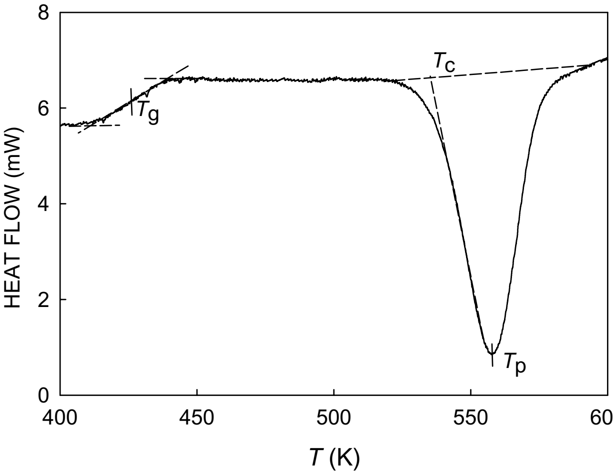

Fig. 1. Typical DSC trace of $Ge_{0.08}Sb_{0.15}Se_{0.77}$ semiconducting alloy at a heating rate of $16\,K\,min^{-1}$.

20 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 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 of the lambda-like trace on the DSC scan, as shown in Fig. 1.

4. Results

The typical DSC trace of $Ge_{0.08}Sb_{0.15}Se_{0.77}$ semiconductor glass obtained at a heating rate of 16 K min^{-1} and plotted in Fig. 1 shows three characteristic phenomena which are resolved in the temperature region studied. The first one ($T = 425.6 \pm 1.8$ K) corresponds to the glass transition temperature, T_g the second ($T = 538.7 \pm 2.3$ K) to the extrapolated onset crystallization temperature, T_c and the third ($T = 557.6 \pm 2.4$ K) to the peak temperature of crystallization, T_p of the quoted semiconductor glass. This DSC trace shows the typical behavior of the 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 [21].

4.1. Glass–crystal transformation

The kinetic study of the glass–crystal transformations is related to the knowledge of the reaction rate constant, K, as a function of the temperature. In the present work it is assumed that the constant K, has an Arrhenius type temperature dependence [9]. By considering this hypothesis and that the nucleation frequency is practically negligible ('site saturation'), as supposed in this article, the overall effective activation energy of the process is represented by the activation energy for the crystal growth. From this point of view, and bearing in mind, that in most glass–crystal transformations $E \gg RT$, the crystallization kinetics of the alloy $Ge_{0.08}Sb_{0.15}Se_{0.77}$ may be analyzed according to the theory developed in Section 2.

With the aim of analyzing the quoted 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 of the heating rates. The area under the DSC curve is directly proportional to the total amount of alloy crystallized. The ratio between the ordinates and the total area of the peak gives the

Table 1
Characteristic temperatures and enthalpies of the crystallization process of the alloy $Ge_{0.08}Sb_{0.15}Se_{0.77}$

Parameters	Experimental value	
	As-quenched	Reheated
T_g (K)	414.4–433.1	413.5–423.3
T_i (K)	508.5–521.8	508.3–520.6
T_p (K)	529.0–572.8	525.3–574.5
ΔT (K)	34.5–79.8	32.7–90.5
ΔH (mcal mg^{-1})	5.3–6.4	2.7–5.2

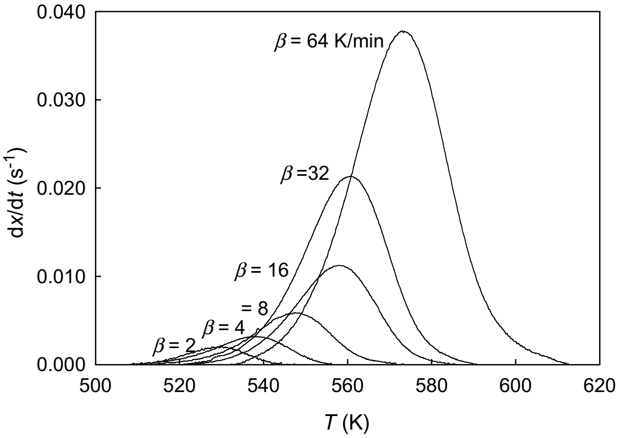

Fig. 2. Crystallization rate versus temperature for the as-quenched glass at different heating rates.

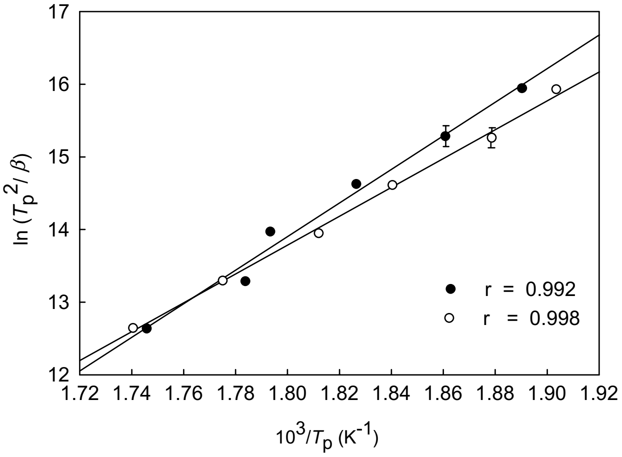

Fig. 3. Experimental plots of $\ln(T_p^2/\beta)$ versus $10^3/T_p$ and straight regression lines of the $Ge_{0.08}Sb_{0.15}Se_{0.77}$ alloy (β in K s^{-1}): (●), as-quenched glass; (○), reheated glass.

Table 2
Maximum crystallization rate, corresponding temperature, and kinetic exponent for the different heating rates

β (K min^{-1})	As-quenched			Reheated		
	10^3 $(\mathrm{d}x/\mathrm{d}t)\|_p$ (s^{-1})	T_p (K)	n	10^3 $(\mathrm{d}x/\mathrm{d}t)\|_p$ (s^{-1})	T_p (K)	n
2	2.05	529.0	1.98	1.78	525.3	2.01
4	3.21	537.4	1.60	2.54	532.3	1.47
8	5.90	547.5	1.53	4.94	543.4	1.49
16	11.24	557.6	1.51	8.42	551.9	1.31
32	21.34	560.6	1.45	16.04	563.4	1.30
64	37.79	572.8	1.34	26.58	574.5	1.12

corresponding crystallization rates, which make it possible to plot the curves dx/dt versus T for each scan, which are represented in Fig. 2. It may be observed that the values of the quantity dx/dt increase in the same proportion as the heating rate, a property which has been discussed in the literature [21].

To research the correct applicability of the preceding theory, the material was reheated up to 488 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 $10^3/T_p$ both for the as-quenched and for reheated glass, are fitted to linear functions by least squares fitting and shown in Fig. 3. From the slope and intercept of these fits, according to Eq. (11), the activation energy, E_G and logarithm of the pre-exponential factor, p, are obtained. The results are the following: $E_G = 47.0 \pm 1.7\,\mathrm{kcal\,mol^{-1}}$ and $\ln p = 27.7 \pm 0.5$ (p in (Ks)$^{-1}$) for the as-quenched glass, and: $E_G = 39.7 \pm 1.4\,\mathrm{kcal\,mol^{-1}}$ and $\ln p = 21.9 \pm 0.4$ for the reheated glass. Moreover, the experimental data T_p and $(\mathrm{d}x/\mathrm{d}t)|_p$ shown in Table 2, both for the as-quenched glass and for the reheated glass, together with the quoted values of the corresponding activation energies, allow us to determine the kinetic exponent, n. The values of the mentioned exponent calculated for each heating rate by means of Eq. (12) are also given in Table 2. The mean values were calculated, resulting: $\langle n \rangle = 1.57 \pm 0.18$ for the as-quenched glass and $\langle n \rangle = 1.45 \pm 0.17$ for the reheated glass. Allowing for experimental error, these values of the exponent n are close to 1.5. Matusita et al. [22] 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, no 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 of this work, given that n has not changed with reheating, by representing a case of 'site saturation'. Moreover, the single scan technique has been applied with a heating rate of 8 K min^{-1}. The variation intervals considered of the quantities: temperature, transformed fraction and transformation rate have been respectively the following: $537.8\,\mathrm{K} \leqslant T \leqslant 546.6\,\mathrm{K}$, $0.1959 \leqslant x \leqslant 0.5141$ and $3.5 \times 10^{-3}\,\mathrm{s^{-1}} \leqslant \mathrm{d}x/\mathrm{d}t \leqslant 7.2 \times 10^{-3}\,\mathrm{s^{-1}}$. The slopes of the linear regressions of these sets of data, according to Eqs. (14) and (15), give: $nE = 79.6 \pm 2.9\,\mathrm{kcal\,mol^{-1}}$ and $E = 48.2 \pm 1.8\,\mathrm{kcal\,mol^{-1}}$, respectively. The parameters E and n, calculated by means techniques of single-scan and multiple-scan, were compared, finding that the error between them is less than 5%, which in agreement with the literature [10]. Finally, from the mean value of the kinetic exponent, n, it is possible to postulate a crystallization reaction mechanism. Mahadevan et al, [23] have shown that n may be 4, 3, 2 or 1, which are related to different crystallization 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. Given that in the studied alloy the 'site saturation', $n = m$, is presented, the mean values obtained for the kinetic exponent are relatively consistent with a two-dimensional growth mechanism.

5. Conclusions

The considered theoretical method assumes the concept of the extended volume of transformed material and the condition of randomly located nuclei. Using these assumptions a general expression of the actual volume fraction crystallized, as a function of the temperature in non-isothermal crystallization processes is obtained. The kinetic parameters have been deduced by using the techniques of single-scan and multiple-scan. In the second technique it has been considered the following assumptions: the condition of the maximum crystallization rate and the quoted maximum rate.

The theoretical method considered has been applied to the crystallization kinetics of the $\mathrm{Ge_{0.08}Sb_{0.15}Se_{0.77}}$ glassy alloy with and without previous reheating. According to the study carried out, it is possible to establish that the reheating did not cause the appearance of nuclei, but that the as-quenched material already contains a sufficient number of them. The method for the thermal analysis of the quoted alloy has given results in good agreement with the characteristics of the glass–crystal transformation of the material under study and representative of a crystal growth process.

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