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A theoretical method for resolving overlapping peaks in differential scanning calorimetry

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In this work the sum of two Gaussian functions is fitted to exothermal peaks obtained through differential scanning calorimetry of amorphous semiconducting alloys. The aforementioned approximation is used to resolve overlapping peaks by a numerical method. In this procedure the experimental values are approximated by an adequate theoretical function, obtaining parameters by least-squares adjustment from certain initial values. Once the overlapping peaks are resolved, the crystallization kinetics of the semiconducting glassy alloy $Cu_{0.10}As_{0.45}Te_{0.45}$ was studied, using the maximal-values method for calculating the kinetic parameters (activation energy, E, reaction order, n, and frequency factor, K_0) of the different stages of the process.

1. Introduction

Chalcogenide glasses have recently drawn attention because of their use in various solid state devices. In recent years we have seen a growing interest in the theory and practical aspects of the application of experimental analysis techniques to the study of the crystallization of glasses. Two popular techniques, isothermal and non-isothermal, have been widely used [1-4]. While isothermal experimental analysis techniques are in most cases more definite, non-isothermal techniques have several advantages. The speed with which non-isothermal experiments can be performed makes them attractive. Many phase transformations occur too rapidly to be measured under isothermal conditions, because of transients inherently associated with the experimental devices. Non-isothermal experiments can be used to extend the temperature range of measurements beyond the range accessible to isothermal experiments. Thus non-isothermal analysis of the crystallization kinetics of glasses has become increasingly attractive.

The crystallization kinetics of glass-forming materials are controlled by nucleation and growth mechanisms which can be characterized by kinetic constants. In the late '30s, Johnson, Mehl and Avrami [5-7] developed a formal theory of transformation kinetics, relating the volume fraction of crystals to kinetic parameters, which has proven to be very useful in describing the behaviour of the crystallization processes that glasses undergo.

Certain glassy alloys exhibit several stages of crystallization, affecting more of the elementary compounds chemically produced during the reaction. These stages of crystallization generally exhibit overlap which can vary between minimum overlap, in which the second process begins when the first is finished, or a high degree of overlap, in which both processes occur nearly simultaneously. The present paper proposes a method to solve the problem of overlapping exothermic peaks. In order to ascertain its validity, the method is applied to the crystallization process of the chalcogenide glassy alloy $Cu_{0.10}As_{0.45}Te_{0.45}$, using the maximal-values method [3].

2. Experimental procedure

High purity (99.999%) copper, arsenic and tellurium, in appropriate atomic % proportions, were weighed into a quartz glass ampoule (6 mm diameter). The contents of the ampoules (7 g total) were sealed at a pressure of 10^{-4} Torr (0.01 N m^{-2}) and heated in a rotating furnace at around 900°C for 5 h. The melt was quenched in ice water, which sup-

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plied the necessary cooling rate to obtain the glass.

The thermal behaviour was investigated using a Thermoflex (Rigaku Co.) differential scanning calorimeter (DSC) keeping a constant flow of 60 cm^3 min^{-1} of inert gas inside the oven. The temperature and energy calibrations of the instrument were performed using the melting temperatures and melting enthalpies of high purity indium, tin and lead supplied with the instrument.

The crystallization thermograms were recorded as the temperatures of the samples were increased at a uniform rate. Typically, 20 mg of sample, in powdered form (particle size ≈ 54 μm), was placed in standard aluminum pans and crimped (but not hermetically sealed) and the temperature scanned over a range from room temperature to about 600 K at uniform heating rates, β, of 2, 4, 8, 16 and 32 K min^{-1}. An empty aluminum pan was used as reference.

The 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 onset-temperature, T_0, at which crystallization just begins and the temperature, T_f, at which the crystallization is completed; A_T is the area between T_0 and T [8].

3. Theoretical background

The experimental determination of the magnitudes of the physical changes through analog methods often leads to graphic data whose shape allows them to be given the generic name of peaks. An analysis of the variables represented in the ordinates in relation to the values corresponding to the abscissae, based on a certain theoretical formalism, makes it possible finally to gain a knowledge of the mechanism governing the measured phenomenon. However, it often happens that because the phenomenon is complex or difficult to isolate or because the measurement technique itself causes intrinsic interactions, the experimental data consist of two or more overlapping peaks. For these cases, theoretical conclusions reached for a single process are not applicable, since there is an abscissa interval in which no experimental data are available for the magnitude of the single property being measured within the overlapping region. The problem is generically called overlapping, and to determine the contribution of each one of the phenomena to the value of the ordinate in the common abscissa interval, one has to resolve the different peaks. This obviously presents various degrees of difficulty, depending on the degree of overlap.

The abovementioned problem, which is common to a great variety of physical problems, will be confined in this work to differential scanning calorimetry (DSC) experimental techniques, carried out by continuous heating, and applied to the study of the crystallization kinetics of bulk amorphous materials. This DSC technique gives curves whose abscissae correspond to temperatures (times), and whose ordinates register the instantaneous energy that the sample requires so as to maintain the programmed thermal growth. When the crystallization process begins, implying an exothermic reaction, the power required varies, depending on the amount of glassy material that is gradually crystallizing; thus, a typical exothermal peak is recorded which goes from the start of the crystallization to the end of crystallization of the whole sample. Certain glassy solids exhibit several stages of crystallization; therefore, the data will likely exhibit the abovementioned behaviour in the overlap of crystallization peaks.

A relatively broad, though not complete analysis of cases such as glassy alloy systems: Cu–As–Se [9] and Sn–As–Se [10], seems to make it advisable to express each experimental peak throught the sum of two Gaussian functions which best fit the experimental data obtained by the DSC techniques. These two Gaussian functions should have the same maximum peak value, a, and different widths, b, for bear in mind the existence of asymmetry of the abovementioned peaks. This sum of functions $f(T)$ is defined by

$$f(T)=a\{H(T_p-T)\exp[-b_1(T-T_p)^2]$$
$$+H(T-T_p)\exp[-b_2(T-T_p)^2]\}, \qquad (1)$$

where $H(T_p-T)$ and $H(T-T_p)$ are forms of the Heaviside unit function [11], T is the temperature and T_p is the value of the temperature at which the crystallization rate is at a maximum.

Once the mathematical function, $f(T)$, representing one exothermic crystallization peak is found, the resolution of the overlapping peaks is theoretically simple. Let us consider an experimental curve such as the one given in fig. 1a, the result of various, M, stages of the crystallization process which overlap at certain intervals of temperature (time). The experimental measurement of the ordinate, over such an interval, is the sum of those supplied by different stages, and the aim is to find the fraction corresponding to each individual stage. Thus, to fit the experimental curve, the function $F(T)$ is defined as

$$\begin{aligned} F(T) &= \sum_{j=1}^{M} f_j(T) \\ &= \sum_{j=1}^{M} a_j \{ H(T_{pj} - T) \exp[-b_{1j}(T - T_{pj})^2] \\ &\quad + H(T - T_{pj}) \exp[-b_{2j}(T - T_{pj})^2] \} , \end{aligned} \tag{2}$$

where M is the number of stages of the crystallization process, T_{pj} is the temperature at which stage j reaches the maximum value of the crystallization rate, $\mathrm{d}x/\mathrm{d}t$, a_j is the value of this maximum and b_{1j} and b_{2j} are the parameters that describe the width of the Gaussian branches of stage j. The values of parameters a_j, T_{pj}, b_{1j}, and b_{2j}, for $j=1$ to M have to be determined so that the mean square deviation denoted by S^2,

$$S^2 = \sum_{i=1}^{N} (y_i - F(T_i))^2 , \tag{3}$$

is at a minimum; y_i are the ordinates corresponding to the N abscissae T_i of the experimental curve. The solution of the problem implies the fitting of $4M$ parameters which is carried out in two steps, described below, to speed up the numerical calculations.

In the first step, the M peaks that make up the experimental curve are separated roughtly, fitting each one to the sum of the two Gaussian functions given by eq. (1). In the second step, the function (3) is minimized by a trial and error method taking as initial values those found in the first step.

The theoretical method described above, was applied to the semiconducting glassy alloy $\mathrm{Cu_{0.10}As_{0.45}Te_{0.45}}$, the thermograms of which exhibit three overlapping peaks ($M=3$). This number of peaks is large enough to show the validity of the method and small enough not to require excessive calculating time.

4. Application to glassy alloy $\mathrm{Cu_{0.10}As_{0.45}Te_{0.45}}$

Fig. 1a shows the crystallization rate versus temperature for the alloy $\mathrm{Cu_{0.10}As_{0.45}Te_{0.45}}$ at a heating rate of $\beta=8$ K min^{-1} resulting in three overlapping peaks, that are separated by means of the theoretical method described above. To carry out the initial separation one starts with the peak which shows less overlapping; in the case of the alloy $\mathrm{Cu_{0.10}As_{0.45}Te_{0.45}}$, peak 1 was chosen. To obtain the initial values that define peak 1, it was divided into two parts separated by their maximum value, whose corresponding abscissa was T_{p1}. The values to the left of T_{p1} were defined by experimental data (obtained through DSC techniques). The values to the right of T_{p1} (dotted line in fig. 1a) were initially defined by the symmetric part of the values to the left of the straight line $T=T_{p1}$. The values assigned to peak 1 are subtracted from the overall set of experimental data, obtaining thereby a set of data which we called residual data and which are shown in fig. 1b for the alloy under study.

Repeating the process described above for the first peak, a set of data points is obtained which is initially assigned to peak 2 and a residual set of results,

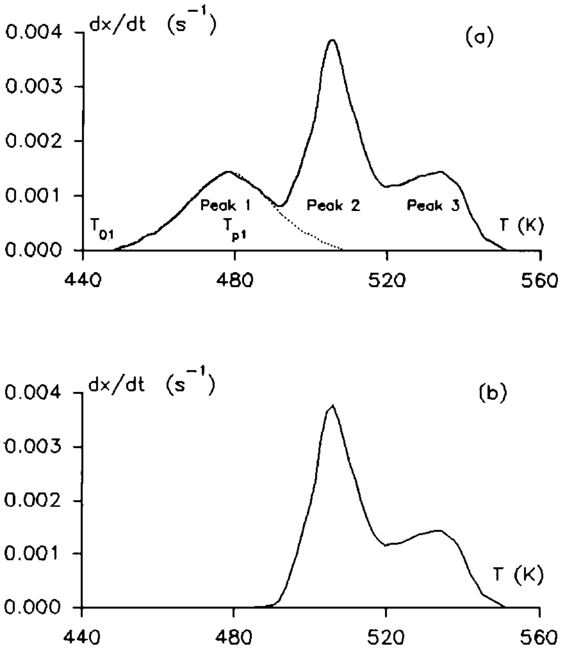


Fig. 1. Initial separation of the peaks.

which for the alloy $Cu_{0.10}As_{0.45}Te_{0.45}$ is assigned to peak 3.

To obtain the initial values of the parameters that define function (2), each of the three sets of data points is fitted to eq. (1). In table 1 are shown the abovementioned initial parameters for the alloy under study.

Next, the parameters that define the different Gaussian functions were varied simultaneously and the corresponding function $F(T)$ was calculated with the condition that expression (3) takes a lower value than before; this is done iteratively by a trial and error method until a minimum value for the function S^2 is obtained. The obtained correlation coefficient was $r=0.9983$. During the fitting process the variations of the parameters were fixed between 5 and 10% for the initial values, which was considered to be within the margin of experimental error. In table 1 are shown the final values of the parameters that define the theoretical Gaussian functions representative of the experimental data obtained by means of DSC for each of the three crystallization stages that exhibit the $Cu_{0.10}As_{0.45}Te_{0.45}$ alloy. Fig. 2 shows the crystallization rate for different heating rates versus temperature for each stage, obtained from the theoretical functions.

5. Kinetic parameters

Once the multiple peaks present in the thermograms of the alloy were separated, a crystallization kinetics analysis was performed for each of the separated peaks. Table 2 shows the characteristic temperatures of all the thermograms, as well as the enthalpies, for each reaction, calculated at the same heating rate at which the instrument was calibrated ($\beta=8$ K min^{-1}). In order to study the crystallization kinetics for the different stages of the overall process, the maximal-values method was used [2,3]. This method determines the crystallization rate, dx/dt, by taking the first derivative of x relative to t and imposing the condition of maximum, $d^2x/dt^2=0$, so as to locate the maximum crystallization rate. A satisfactory approximation was obtained from the following relationship

$$\ln\left.\frac{dx}{dt}\right|_p = \ln(0.37nK_0) - \frac{E}{R}\frac{1}{T_p}, \qquad (4)$$

which shows that there is a linear relationship, whose slope gives us the activation energy of the process, between the experimental values of the logarithm of the crystallization rate and the inverse temperature T_p (values measured at the instant when the maximum value is reached) corresponding to the different values of the heating rate. The other two kinetic parameters are obtained using the conditions [2]:

$$\frac{\beta E}{RK_pT_p^2} = 1 \quad \text{and} \quad \left.\frac{dx}{dt}\right|_p = 0.37nK_p, \qquad (5)$$

which are also derived using the aforementioned mathematical reasoning.

The crystallization kinetics for the various peaks were analyzed using the aforementioned method. From the values of $(dx/dt)|_p$ and T_p it is possible to draw the plot corresponding to eq. (4) and the best-fit straight line whose slope gives us the activation energy deduced by means of the equation predicted by the described method. Fig. 3 shows the plots and best-fit straight lines for the different peaks, and table 3 the computed activation energy values. By applying expressions (5) it is possible to calculate

Table 1
Parameters defining the theoretical Gaussian functions

	Peak 1		Peak 2		Peak 3	
	initial	final	initial	final	initial	final
T_p (K)	478.5	478.5	505.7	505.9	533.1	533.1
a (s^{-1})	1.447×10^{-3}	1.447×10^{-3}	3.782×10^{-3}	3.419×10^{-3}	1.436×10^{-3}	1.476×10^{-3}
b_1 (K^{-2})	5.638×10^{-3}	5.638×10^{-3}	2.244×10^{-2}	2.298×10^{-2}	3.805×10^{-3}	2.853×10^{-3}
b_2 (K^{-2})	5.638×10^{-3}	7.284×10^{-3}	2.244×10^{-2}	3.079×10^{-2}	1.686×10^{-2}	1.563×10^{-2}

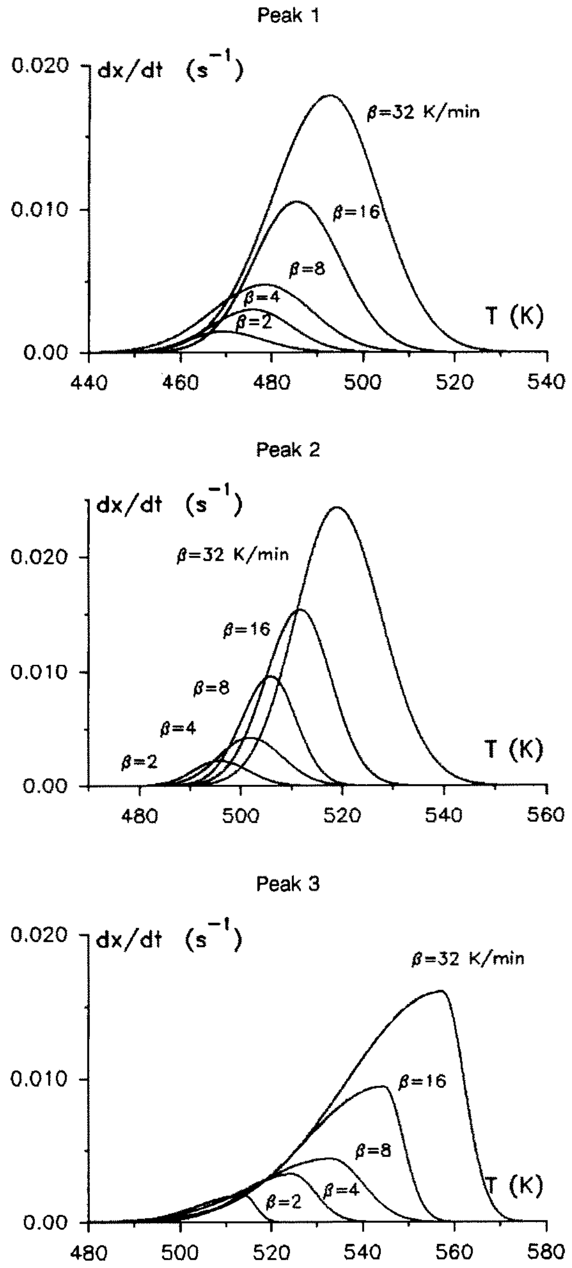


Fig. 2. Crystallization rate, versus temperature, found from the theoretical functions for each stage at the different heating rates.

the other two kinetic parameters, which are also shown in table 3.

The values obtained for the activation energy are in agreement with those found in the literature [12] for other alloys in this system. The Avrami index values which take into account the nucleation and growth mechanisms for solid state reactions that take place in each of the processes indicate diffusion controlled growth for the three stages [13]. For the first two peaks the reaction order suggests that both go through a surface nucleation [8,14] and in the third stage the aforementioned reaction order is very near the conditions required for one-dimensional growth [15].

Table 2
Intervals of glass transition temperature, T_g, initial peak temperature, T_0, maximum peak temperature, T_p, peak width, ΔT, corresponding to the different experimental heating rates, and calculated enthalpies

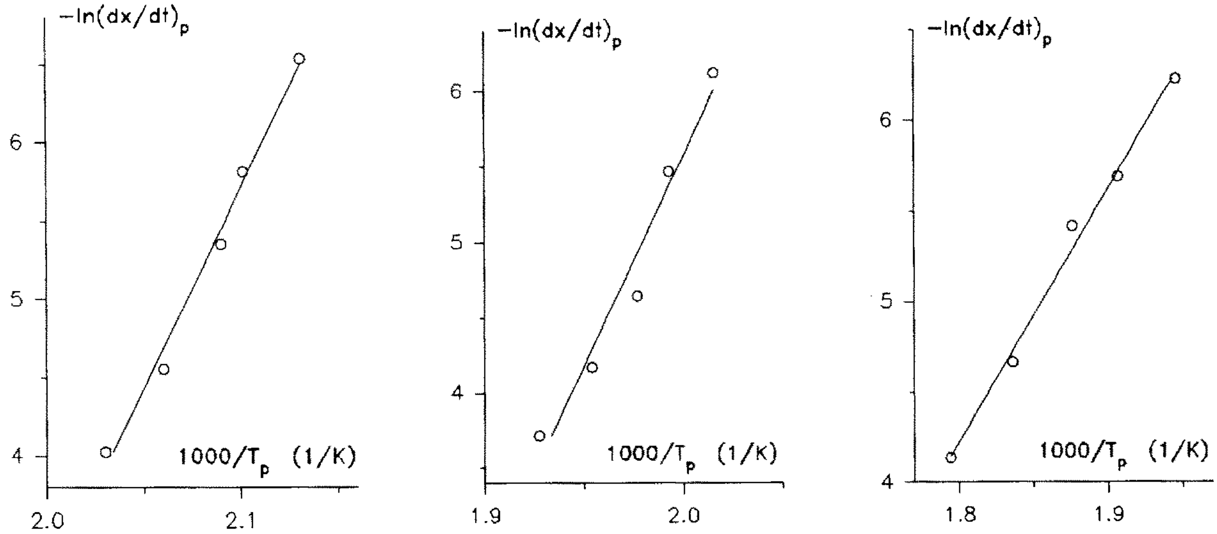
	Peak 1	Peak 2	Peak 3
T_g (K)	425–432		
T_0 (K)	443–463	479–493	484–496
T_p (K)	469–493	493–512	515–558
ΔT (K)	45–69	31–57	25–62
ΔH (mcal mg^{-1})	4.51	5.34	4.93

6. Conclusions

A relatively broad analysis of the crystallization kinetics of semiconducting glassy alloys, quoted in the literature, seems to confirm the validity of the sum of two Gaussian functions to describe the single peak of a crystallization process.

When the amorphous to crystal transformation results in DSC thermograms with various overlapping peaks, the previous description makes it possible to resolve them into various functions, like the abovementioned functions, and permits the calculation of the kinetic parameters describing each of the overlapping stages.

The maximal-values method, applied to the analysis of the crystallization kinetics of this alloy, gave results which were in good agreement with the nature of the alloy under study and which are representative of different nucleation and crystalline-growth processes, according to the values found for the reaction order.



PEAK 1 **PEAK 2** **PEAK 3**

Fig. 3. Experimental plots and compromise straight lines for the different peaks.

Table 3
Kinetic parameters calculated for different peaks of alloy $Cu_{0.10}As_{0.45}Te_{0.45}$

Peak	E (kcal mol^{-1})	n	K_0 (s^{-1})
1	50.84	0.96	2.05×10^{21}
2	55.55	1.51	1.32×10^{22}
3	28.24	2.2	2.40×10^{9}

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