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Effect of Te additions on the glass transition and crystallization kinetics of $(Sb_{15}As_{30}Se_{55})_{100-x}Te_x$ amorphous solids

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Abstract

Differential scanning calorimetry results under non-isothermal conditions of chalcogenide $(Sb_{15}As_{30}Se_{55})_{100-x}Te_x$ (where $0 \le x \le 10$ at.%) glasses are reported and discussed. The dependence of the characteristic temperatures "glass transition temperature (T_g), the crystallization onset temperature (T_c) and the crystallization temperature (T_p)" on the heating rate (β) utilized in the determination of the activation energy for the glass transition (E_g), the activation energy for crystallization (E_c), the glass thermal stability ($\Delta T = T_c - T_g$) and the Avrami exponent (n). The composition dependence of the T_g, E_g, and E_c were discussed in terms of the chemical bond approach, the average heats of atomization and the cohesive energy (CE). The diffractogram of the transformed material shows the presence of some crystallites of AsSb, Sb_4Te_6, As_2Se_3 and Sb_2Se_3 in the residual amorphous matrix.

Keywords: Glassy alloy; Non-isothermal process; Heating rate; Glass transition temperature; Crystallization kinetics; Crystalline phases

1. Introduction

Crystallization of chalcogenide glasses plays an important role in determining the transport mechanisms, thermal stability and practical applications [1–4]. The study of crystallization kinetics in amorphous materials by the DSC method has been widely discussed in the literature [5–10]. There are large varieties of theoretical models and functions proposed to explain the crystallization kinetics. The application of each depends on the type of amorphous material studied. In calorimetric measurements, two basic methods can be used, isothermal and non-isothermal method [8,10,11]. In the isothermal method, the sample is brought quickly to a temperature above the temperature of glass transition, T_g and the heat evolved during the crystallization process is recorded as a function of time. In the other method (non-isothermal), the sample is heated at a fixed rate and the heat evolved is again recorded as a function of temperature or time. The isothermal experiments are generally very time-consuming while, experiments performed at constant heating rate are a much more rapid way of studying a transformation. Furthermore, isothermal analysis is the impossibility of reaching a test temperature instantaneously and during the time, which the system needs to stabilize, no measurements are possible while, non-isothermal (constant heating rate) experiments do not have this drawback [8,10].

Tellurium additions to the later glasses would be expected to decrease their glass transition temperature and reduce their thermal stabilities [12]. According to Kastner [13], the addition of an element with a higher electropositive character than the elements in the host material will tend to the decrease of the activation energy for electrical conduction.

The present work study the effect of Te additions on both of the glass transition temperature T_g, the activation energy of glass transition E_g and crystallization kinetics of $(As_{30}Sb_{15}Se_{55})_{1-x}Te_x$ ($x = 0$, 2.5, 7.5, and 10 at.%) glasses.

2. Theoretical background

The theoretical bases for interpreting DTA or DSC results is provided by the formula theory of transformation kinetics as the volume fraction (χ) crystallized in time (t) by using the Johnson,

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Mehl and Avrami's equation [14].

$$\chi = 1 - \exp(-(kt)^n) \tag{1}$$

where n is an integer or half integer depends on the mechanism of growth and the dimensionality of the crystal, k is defined as the effective (overall) reaction rate, which is usually assumed to have an Arrhenian temperature dependence.

$$k = k_0 \exp\left(\frac{-E}{RT}\right) \tag{2}$$

where E is the effective activation energy describing the overall crystallization process.

2.1. Bansal's method

In a non-isothermal DSC experiment the rate constant K, changes continually with time due to the change of the temperature and Eq. (1) can be rewritten in the form [15]

$$\chi(t) = 1 - \exp\left[-\left(\int_0^t K[T(\bar{t})]\,\mathrm{d}\bar{t}\right)^n\right] = 1 - \exp(-I^n) \tag{3}$$

Deriving Eq. (3) with respect to time, the crystallization rate is obtained as

$$\dot{\chi} = nK(1-\chi)I^{n-1} \tag{4}$$

The maximum rate of crystallization occurs at the peak of the exotherm at time t_p and temperature T_p [14], the differentiation of Eq. (4) with respect to time yields

$$\ddot{\chi} = nK_\mathrm{p}(I^n)_\mathrm{p} - (n-1)K_\mathrm{p} - \frac{\beta E I_\mathrm{p}}{RT_\mathrm{p}^2} = 0 \tag{5}$$

The time integral in Eq. (3) is transformed to temperature integral yielding

$$I(T) = \frac{K_0}{\alpha}\int_{T_0}^{T} \exp\frac{-E}{R\bar{T}}\,\mathrm{d}\bar{T} \tag{6}$$

which is represented by several approximate analytical expressions [16–19] by the sum of the alternating series

$$S(\bar{y}) = \frac{\mathrm{e}^{-\bar{y}}}{\bar{y}^2}\sum_{k=0}^{k=\infty}\frac{(-1)^k(k+1)!}{\bar{y}^k} \tag{7}$$

where $\bar{y} = E/R\bar{T}$. Considering that, in this type of series the error produced is this less than the first term neglected and bearing in mind that, in most crystallization reactions $\bar{y} = E/R\bar{T} \gg 1$, it possible to use only the two first terms of this series and the error introduced is not greater than 1%. By assuming that,

$$T^2(1-2RT/E)\exp(-E/RT) \gg T_0^2(1-2RT_0/\bar{E})\exp(-E/RT_0)$$

Eq. (6) becomes

$$I = K_0E(\beta R)^{-1}\mathrm{e}^{-y}y^{-2}(1-2y^{-1}) \tag{8}$$

considering the assumptions used to get Eq. (8) and taking the logarithm of the quoted equation leads to an expression that in the range of values of $y = E/RT$, $25 \le y \le 55$, can be fitted very satisfactorily by a linear approximation (an additional assumption) yielding [20]

$$\ln[\mathrm{e}^{-y}y^{-2}(1-2y^{-1})] \cong -5.304 - 1.052y \tag{9}$$

Substituting into Eq. (8)

$$I = K_0E(\beta R)^{-1}\exp(-5.304 - 1.052y) \tag{10}$$

where the above-mentioned approximation might introduce 5.8% error in the value of $\mathrm{e}^{-y}y^{-2}(1-2y^{-1})$ in the worst cases.

Substituting for ($y = E/RT$) and ($K = K_0\exp(-E/RT)$) into Eq. (10) gives

$$I = RT^2K(\beta E)^{-1}\left(\frac{1-2RT}{E}\right) \tag{11}$$

if it is assumed that $T \gg T_0$ so that, y_0 can be taken as infinity, the last expression of the integral I is

$$I_\mathrm{p} = \left(\frac{1-2RT_\mathrm{p}}{nE}\right)^{1/n} \tag{12}$$

Substituting for I into Eq. (5) and taking the logarithmic form

$$\ln\left(\frac{T_\mathrm{p}^2}{\beta}\right) + \ln\left(\frac{K_0R}{E}\right) - \frac{E}{RT_\mathrm{p}} \approx \left(\frac{2RT_\mathrm{p}}{E}\right)\left(\frac{1-1}{n^2}\right) \tag{13}$$

note that, Eq. (13) reduces to the Kissinger's expression [6] for the case of $n = 1$ as one might have anticipated since this corresponds to the homogeneous reaction case. Thus, it can be seen that, the Kissinger's method is appropriate for the analysis not only for homogeneous reactions, but also for the analysis of heterogeneous reactions which are described by the JMA equation in the isothermal experiments [14]. The approximation in Eq. (13) RHS = 0 yielding,

$$\ln\left(\frac{T_\mathrm{p}^2}{\beta}\right) = \frac{-E_\mathrm{c}}{RT_\mathrm{p}} - \ln\left(\frac{K_0R}{E}\right) \tag{14}$$

where the quoted approximation might introduce a 3% error in the value of E/R in the worst cases.

Finally, it should be noted that, the term ($-2RT/E$) in Eq. (11) is negligible in comparison to the unity, since in most crystallization reactions $E/RT \gg 25$ [14]. Therefore, Eq. (11) may be rewritten

$$I = RT^2K(\beta E)^{-1} \tag{15}$$

Substituting for I into Eq. (4) gives

$$\dot{\chi}_\mathrm{p} = \frac{n(0.37\beta E_\mathrm{c})}{(RT_\mathrm{p}^2)} \tag{16}$$

That makes it possible to calculate kinetic exponent n.

2.2. Matusita's method

This theory describes the evolution with time, t, of the volume fraction crystallized, χ, by Eq. (3) according to the formula theory of transformation kinetics using the Johnson–Mehl and