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Glass transition and crystallization kinetics of $In_x(Se_{0.75}Te_{0.25})_{100-x}$ chalcogenide glasses

A.M. Abd Elnaeim [a,*], K.A. Aly [a], N. Afify [b], A.M. Abousehlly [a]

[a] Department of Physics, Faculty of Science, Al-Azhar University, Assiut Branch, Assiut 71542, Egypt
[b] Department of Physics, Faculty of Science, Assuit University, Assuit, Egypt

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ABSTRACT

The results of differential scanning calorimetry (DSC) under non-isothermal conditions of the chalcogenide $In_x(Se_{0.75}Te_{0.25})_{100-x}$ (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 peak temperature (T_p) on the heating rate (α) utilized in the determination of the activation energy for the glass transition (E_g), the activation energy for crystallization (E_c) and the Avrami's 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 (H_s) and the cohesive energy (CE). The diffractogram of the transformed material shows the presence of some crystallites of Se–Te and In–Se in the residual amorphous matrix.

1. Introduction

Chalcogenide semiconducting glasses have particular interest due to their wide range of applications as solid state devices both in scientific and technological fields. Se–In and Se–Te binary alloys have got several advantages over pure and amorphous Se [1,2]. The binary In–Se glassy alloys have drawn great attention because of their potential use in solar cells [3,4].

Amorphous Se–Te alloys have greater hardness, higher crystallization temperature, higher photosensitivity and smaller ageing effects than pure Se [1]. As these glasses have poor thermo-mechanical properties, in order to enlarge their domain of applications, it is necessary to increase their softening temperature and mechanical strength. The addition of a third element (In) which has a large electro-negativity difference with Se and Te, expands the glass forming area and also creates compositional and configurational disorder in the system, and also is found to modify the structure and thus the electrical and thermal properties of the Se–Te system [5–10].

There are number of papers [11–16] found in the literature deal the effect of addition of In into Se–Te glasses on the physical properties such as electrical-, photoelectrical-properties and thermal analysis. The thermal analysis of these alloys is important from an application point of view. The present work study in detail the effect of the additions of In content at the expense of Se and Te content on the glass transition, crystallization kinetics and the Avrami's exponent for different compositions of $In_x(Se_{75}Te_{25})_{100-x}$ ($x = 0$, 2, 4, 6, 8 and 10 at.%) chalcogenide 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, Mehl and Avrami's equation [17]

$$\chi = 1 - \exp\left[-(kt)^n\right] \tag{1}$$

where 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, n is the growth (Avrami) exponent and K_0 the rate constant, depend on the operating nucleation and growth modes [18,19].

* Corresponding author.
E-mail addresses: Alhosein2009@yahoo.com (A.M. Abd Elnaeim), Kamalaly2001@gamail.com (K.A. Aly).

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2.1. Afify method [20]

To determine the effective activation energy for crystallization, E_c, under isothermal or non-isothermal conditions, Eq. (1) can be written as

$$\ln(1-\chi) = -(kt)^n \quad (3)$$

the important condition in this method is at $\chi = 0.63205$ where $\ln(1-\chi) = -1$. This condition has been discussed in early work [21]. The advantage of this condition is that the results at $k_{0.63}$ are independent of the value of n, contrary to Avrami's method, which is dependent on the value of n. Eq. (3) at $\chi = 0.63205$, gives

$$1 = (k_{0.63} t_{0.63})^n \quad (4)$$

i.e.

$$k_{0.63} = \frac{1}{t_{0.63}} \quad (5)$$

The value of the effective overall reaction rate at $\chi = 0.63205$, ($k_{0.63}$), can be determined from Eq. (5), i.e. from the inverse of the time at $\chi = 0.63205$, ($1/t_{0.63}$). The values of $\chi = 0.63205$, $t_{0.63}$ has been determined using the partial area technique [22] described in the experimental techniques.

The effective overall reaction rate at $\chi = 0.63205$ ($k_{0.63}$) can be written as

$$k_{0.63} = k_0 \exp\left(\frac{-E}{RT_{0.63}}\right) \quad (6)$$

where E_c can be determined from the slope of $\ln(k_{0.63})$ vs. $1/T_{0.63}$ graphs, obtained from different thermograms. In the isothermal condition, the thermograms are carried out at different temperatures, but in case of non-isothermal condition, the thermograms are carried out at different heating rates.

To determine the reaction order, n, Eq. (3) can be written as

$$\ln[-\ln(1-\chi)] = n\ln(k) + n\ln(t) \quad (7)$$

At constant temperature (k is constant), the relation between $\ln[-\ln(1-\chi)]$ and $\ln(t)$ gives the reaction order, n. In the isothermal condition, the above graph is carried out from one thermogram, but in the case of non-isothermal condition, the graph is carried out, at constant temperature, from different thermograms, i.e. different heating rates.

2.2. 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 [23]

$$\chi(t) = 1 - \exp\left[-\left(\int_0^t K[T(\bar{t})]d\bar{t}\right)^n\right] = 1 - \exp(-I^n) \quad (8)$$

Deriving Eq. (8) with respect to time, the crystallization rate is obtained as

$$\dot{\chi} = nK(1-\chi)I^{n-1} \quad (9)$$

The maximum rate of crystallization occurs at the peak of the exotherm at time t_p and temperature T_p [17], the differentiation of Eq. (9) with respect to time yields

$$\ddot{\chi} = nK_p(I^n)_p - (n-1)K_p - \frac{\alpha E I_p}{RT_p^2} = 0 \quad (10)$$

The time integral in Eq. (8) is transformed to temperature integral yielding

$$I(T) = \frac{K_0}{\alpha}\int_{T_0}^{T} \exp\frac{-E}{R\bar{T}}d\bar{T} \quad (11)$$

which is represented by several approximate analytical expressions [24–27] by the sum of the alternating series

$$S(\bar{y}) = \frac{e^{-\bar{y}}}{\bar{y}^2}\sum_{k=0}^{k=\infty}\frac{(-1)^k(k+1)!}{\bar{y}^k} \quad (12)$$

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. (11) becomes

$$I = K_0E(\alpha R)^{-1}e^{-y}y^{-2}(1-2y^{-1}) \quad (13)$$

considering the assumptions used to get Eq. (13) 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 [28]

$$\ln[e^{-y}y^{-2}(1-2y^{-1})] \cong -5.304 - 1.052y \quad (14)$$

Substituting into Eq. (13)

$$I = K_0E(\alpha R)^{-1}\exp(-5.304 - 1.052y) \quad (15)$$

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

Substituting ($y = E/RT$) and ($K = K_0\exp(-E/RT)$) into Eq. (15) gives

$$I = RT^2K(\alpha E)^{-1}(1-2RT/E) \quad (16)$$

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

$$I_p = \left(\frac{1-2RT_p}{nE}\right)^{1/n} \quad (17)$$

Substituting I into Eq. (10) and taking the logarithmic form

$$\ln\left(\frac{T_p^2}{\alpha}\right) + \ln\left(\frac{K_0R}{E}\right) - \frac{E}{RT_p} \approx \left(\frac{2RT_p}{E}\right)\left(1-\frac{1}{n^2}\right) \quad (18)$$

note that, Eq. (18) reduces to the Kissinger's expression [29] 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 [17]. The approximation in Eq. (18) RHS = 0 yielding,

$$\ln\left(\frac{T_p^2}{\alpha}\right) = \frac{-E_c}{RT_p} - \ln\left(\frac{K_0R}{E}\right) \quad (19)$$

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. (16) is negligible in comparison to the unity, since in most crystallization reactions $E/RT \gg 25$ [17]. Therefore, Eq. (16) may be rewritten

$$I = RT^2K(\alpha E)^{-1} \quad (20)$$