An investigation of the kinetic transformation mechanism of Ge$_{12.5}$Te$_{87.5}$ chalcogenide glass under non-isothermal regime

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A B S T R A C T

Differential scanning calorimetry (DSC) technique was used to study the kinetics of amorphous to crystalline transformation in Ge$_{12.5}$Te$_{87.5}$ chalcogenide glass. The kinetic parameters of glassy Ge$_{12.5}$Te$_{87.5}$ under non-isothermal conditions are analyzed by the model-free and model-fitting approaches from a series of experiments at different constant heating rates (5–50 K/min). The effective activation energy of crystallization was determined by analyzing the data using the isoconversional methods of Kissinger–Akahira–Sunose (KAS), Tang, Starink, Flynn–Wall–Ozawa (FWO) and Vyazovkin. The analysis of the present data shows that the effective activation energy of crystallization is constant throughout the entire interval of conversions and hence with temperature. The transformation mechanism examined using the local Avrami exponents indicates that one mechanism (three-dimensional growth) is responsible for the transformation process for all heating rates used. The reaction model that may describe the transformation process of the Ge$_{12.5}$Te$_{87.5}$ chalcogenide glass is the Avrami–Erofeev model ($g(\alpha) = [-ln(1-\alpha)]^{1/n}$) with $n = 3$ for all heating range at the whole range of crystallized fraction ($\alpha = 0.05$–0.95). A good agreement between the experimental and the reconstructed (α–T) curves has been achieved. The transformation from amorphous to crystalline phase in Ge$_{12.5}$Te$_{87.5}$ chalcogenide glass demonstrates a single-step mechanism.

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1. Introduction

The variation of the effective activation energy with the degree of transformation is an important issue in the kinetics of amorphous to crystalline transformation [1]. As pointed out by Vyazovkin [1], this variation of the effective activation energy with the degree of transformation and hence with temperature can provide useful information about the different mechanisms involved in the transformation process. In order to reveal this variation, the isoconversional methods are widely used to determine the effective activation energy E of the crystallization process. The variation of the effective activation energy with the extent of conversion can be used to investigate different nucleation and growth mechanisms associated with this transformation [2–12]. The kinetics of isothermal transformation involving nucleation and growth is usually analyzed using the Johnson–Mehl–Avrami (JMA) model. According to the JMA model, the fraction of crystallites, α, is given by [13]

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

where n is the kinetic (growth) exponent that is associated with the nucleation and growth mechanisms and k is the reaction rate

constant. In this thermally activated process the rate constant is related to temperature, T, via the Arrhenius equation

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

where E is the effective activation energy of crystallization, A is the pre-exponential factor (frequency) and R is the gas constant. The kinetics of transformation in amorphous materials can be described by the following rate equation [9]

$$\frac{d\alpha}{dt} = A\ exp\left(\frac{-E}{RT}\right)f(\alpha), \tag{3}$$

where $f(\alpha)$ is the reaction model. Under non-isothermal conditions with a constant heating rate of $\beta = dT/dt$, Eq. (3) may be rewritten as:

$$\frac{d\alpha}{dT} = \frac{d\alpha}{dt}\left(\frac{1}{\beta}\right) = \frac{A}{\beta}\ exp\left(\frac{-E}{RT}\right)f(\alpha). \tag{4}$$

The integral form of the reaction model can be obtained by integrating Eq. (4) as follows:

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta}\int_{T_o}^T exp\left(-\frac{E}{RT}\right)dT = \frac{A}{\beta}I(E,T), \tag{5}$$

where T_o is the initial temperature. To solve the temperature integral in Eq. (5), several approximations were introduced. The isoconversional

procedures can be classified as linear or non-linear. In the linear procedures (Kissinger–Akahira–Sunose (KAS) [14–16], Tang [17], Starink [5,18] and Flynn–Wall–Ozawa (FWO) methods [19,20]) the activation energy is evaluated from the slope of a straight line, while in the integral (Vyazovkin method [9,21]) non-linear procedures the activation energy is evaluated from a specific minimum condition.

In general, all of these approximations lead to a direct isoconversional method in the linear form of:

$$ln\left(\frac{\beta_i}{T^\gamma(\alpha_i)}\right) = Const. - \frac{E(\alpha)}{RT(\alpha_i)}. \tag{6}$$

For each degree of the conversion fraction, α, a corresponding $T_{\alpha i}$ and heating rate are used to plot $ln(\beta_i/T^\gamma(\alpha_i))$ against $1/T^\gamma(\alpha_i)$, where γ is a constant. The effective activation energy, $E(\alpha)$, is then determined from the regression slope. However, the most popular models used for calculation of effective activation energy are :

1 — The Kissinger–Akahira–Sunose (KAS) method [14–16]:

$$ln\left(\frac{\beta_i}{T^2(\alpha_i)}\right) = C_K(\alpha) - \frac{E(\alpha)}{RT(\alpha_i)}, \tag{7}$$

2 — The Tang method [17]:

$$ln\left(\frac{\beta_i}{T^{1.894661}(\alpha_i)}\right) = C_T(\alpha) - 1.00145033\frac{E(\alpha)}{RT(\alpha_i)}, \tag{8}$$

3 — The Starink method [5,18]:

$$ln\left(\frac{\beta_i}{T^{1.92}(\alpha_i)}\right) = C_S(\alpha) - 1.0008\frac{E(\alpha)}{RT(\alpha_i)}, \tag{9}$$

4 — The Flynn–Wall–Ozawa (FWO) method [19,20]:

$$ln\beta_i = C_W(\alpha) - 1.0518\frac{E(\alpha)}{RT(\alpha_i)}, \tag{10}$$

5 — Vyazovkin method [9,21]:

$$\Omega = \sum_{i=1}^{l} \sum_{j\neq i}^{l} \frac{I[E(\alpha), T(\alpha_i)]\beta_j}{I[E(\alpha), T(\alpha_j)]\beta_i}, \tag{11}$$

where l is the number of heating rates. The effective activation energy can be determined at any particular value of α by finding the value of $E(\alpha)$ which minimizes the objective function Ω.

For non-isothermal experiments, model-fitting involves fitting of different models to $(\alpha-T)$ curves and simultaneously determining E and A [2,10,22]. One of these models proposed by the Kennedy–Clark method [23], is given by the following expression:

$$ln\left[\frac{\beta g(\alpha)}{T-T_0}\right] = ln(A) - \frac{E}{RT}, \tag{12}$$

where T_o is the initial temperature of the reaction. Plotting $ln[\beta g(\alpha)/(T-T_o)]$ versus $1/T$ gives a straight line of slope $(-E/R)$ and the intercept lnA for different reaction models of $g(\alpha)$. The most common reaction models used to describe the solid state reactions is listed in Ref. [2].

The other popular model is the Coats–Redfern method [24,25], which is given by the following expression:

$$ln\frac{g(\alpha)}{T^2} = ln\left(\frac{AR}{\beta E}\left[1-\left(\frac{2RT^*}{E}\right)\right]\right) - \frac{E}{RT}, \tag{13}$$

where T^* is the mean experimental temperature. Plotting $ln[g(\alpha)/T^2]$ versus $1/T$ gives a straight line. E and A will obtain from the slope and the intercept, respectively, for different reaction models of $g(\alpha)$.

The chalcogenide materials especially those containing Ge and Te are of importance in modern technology due to the large change in optical constants between crystalline and amorphous [26]. This indicates that it can be used as an optical recording material (in optical memory devices such as CD or DVD). The study of different properties of amorphous Ge–Te have been discussed in the literatures [3,26–40].

In the present work, the transformation kinetics are studied using the DSC technique under non-isothermal conditions at different heating rates, β, (5–50 K/min) for $Ge_{12.5}Te_{87.5}$ chalcogenide glass. The DSC data are analyzed using the isoconversional (model-free) and model-fitting methods to investigate the growth processes involved in the transformation. The dependence of transformation kinetic parameters ($E(\alpha), A(\alpha)$, and $g(\alpha)$) with the extent of conversion, α, for $Ge_{12.5}Te_{87.5}$ chalcogenide glass is discussed.

2. Experimental procedure

Bulk material was prepared by the well-established melt–quench technique. The high purity (99.999%) Ge and Te in appropriate at.% proportion were weighed in a quartz glass ampoule (12 mm diameter). The contents of the ampoule were sealed under a vacuum of 0.01 Pa and heated at around 1190 K for 24 h. During the melt process, the tube was frequently shaken to homogenize the resulting alloy. The melt was quenched in water at 273 K to obtain the glassy state.

The differential scanning calorimetry, DSC, was carried out on approximately 5 mg quantities of powder samples using a Shimadzu DSC-50 with sensitivity of $\pm10\,\mu W$. The accuracy of the heat flow is ±0.01 mW and the temperature precision as determined by the microprocessor of the thermal analyzer is ±0.1 K. The heating rates were varied from 5 to 50 K/min under dry nitrogen supplied at the rate 50 ml/min. To minimize the temperature gradient the samples were well granulated to form uniform fine powder and spread as thinly as possible on the bottom of the sample pan. Temperature and enthalpy calibration were checked with indium at heating rate 10 K/min ($T_m = 156.6\,^\circ C$ $\Delta H_m = 28.55$ J/g) as standard material supplied by Shimadzu. This calibration was also checked at different heating rates. The sample is pre-annealed for a period of time before each experimental run at temperature below the glass transition temperature, T_g, the condition of site saturation could be fulfilled to get an information about the growth mechanism separately from the nucleation process.

3. Results

The DSC curves were recorded at different heating rates, β, from 5 to 50 K/min for the $Ge_{12.5}Te_{87.5}$ chalcogenide glass and are shown in Fig. 1. The DSC curves shown in this figure are characterized by three temperatures effects. The glass transition temperature, T_g, as defined by the endothermic change in the DSC trace indicates a large change of viscosity, marking a transformation from amorphous solid phase to super-cooled liquid state. Second, it belongs to the extrapolation onset crystallization temperature, T_c. The last one is the exothermic peak temperature, T_P, used to identify the temperature at the maximum transformation rate. Values of T_g, T_c and T_P as well as the full width at half maximum of the crystallization peak, ΔT, are listed in Table 1. This behavior is typical for a glass–crystalline transformation. Generally, the three characteristic temperatures shift to higher temperatures with the increase of the heating rate.

4. Discussion

To get the information about the kinetic parameters such as the effective activation energy, $E(\alpha)$, pre-exponential factor, $A(\alpha)$, and reaction model, $g(\alpha)$, the differential scanning calorimetry, DSC, data will be analyzed using the isoconversional (model-free) with the help of the model-fitting method. The dependence of transformation kinetic