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Kinetics of the glass transition in $As_{22}S_{78}$ chalcogenide glass: Activation energy and fragility index

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ABSTRACT

Differential scanning calorimetry (DSC) has been used to probe the dynamics of the glass transition in $As_{22}S_{78}$ chalcogenide glass. Non-isothermal measurements were performed at different heating rates (5–35 K min^{-1}). The experimental result of this kinetic glass transition phenomenon was analyzed on the basis of the relaxation process occurring in the transition temperature range. The activation energy of the glass transition was determined from the heating rate dependence of the glass transition temperature. The fragility index m of the glass was estimated from the measurements of the activation energy of the relaxation process, which characterizes the glass transition. Different kinetic methods as well as isoconversional methods were used. Isoconversional analysis of the experimental data shows that the activation energy of glass transition process is varying with the degree of transformation (and hence with temperature) from the glassy to the supercooled phase.

1. Introduction

Semiconducting chalcogenide glasses have been widely used in device technology and the current interest in these materials centers on X-ray imaging [1] and photonics. The relevance of studying the structure relaxation of these materials has a technological aspect, since several physical properties change in the temperature range of utilization of the materials of interest. It is also of fundamental scientific interest, since one can obtain useful information on the elementary processes, which modify the structure of an amorphous system, eventually producing stable phases on crystallization.

Although the glass transition has been studied for many decades, there is still an ongoing discussion about the basic nature of the phenomenon [2–4]. Structural relaxation is a general phenomenon occurring when a glass is maintained at a temperature below its glass-transition temperature (T_g). Thus, a glassy material has at least two important characteristics: its glass-transition temperature and its sub-T_g relaxation kinetics. A classification of glass-forming liquids has been proposed according to the temperature dependence of their viscosity [5]. Liquids that exhibit an Arrhenius temperature dependence of the viscosity are defined as strong glass-forming liquids and those which exhibit a non-Arrhenius behavior (for instance described by a Vogel Tammann Fulcher equation) are declared fragile glass-forming liquids. To characterize this behavior, it was proposed to define a fragility index called m [6] and it was found that for strong glass forming liquids, the limit is reached for a low value of m ($m \approx 16$) [7], while for fragile glass-forming liquid, a high value of m is expected ($m \geq 200$) [8].

When an amorphous material is heated at a constant heating rate in a differential scanning calorimetry (DSC) experiment, the material undergoes structural changes and eventually crystallizes. In addition to the large exothermal crystallization peak, the DSC trace of some chalcogenide glasses shows an endothermic peak before crystallization occurs: the glass transition peak. This calorimetric glass transition is generally considered to be due to changes in the amorphous structure, which approaches a thermodynamic equilibrium state as the temperature of the system is increased [2,9,10]. The viscosity of glass-forming system changes dramatically near the glass transition. As a consequence, the time scale of the measurement determined where the characteristic changes occur which mark the transition to the glass. Like the crystallization peak, the position of the glass transition peak depends on the heating rate [11].

The kinetics of the glass transition as studied by the DSC method is important in investigating the nature the glass transformation process. The glass transition temperature, T_g, can be accurately determined by DSC measurements. Moreover, the kinetic aspect of the glass transition is evident from the strong dependence of T_g on the heating rate. This behavior can be used to identify different mechanisms involved in the transition process

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The dynamics of the structural relaxation above the glass transition temperature, T_g, can be characterized by the strong/fragile classification scheme for glass-forming liquids. At temperatures below T_g the relaxation time of a *glass* (τ) follows Arrhenius kinetics, while above T_g the system follows a relationship often described by the Vogel–Tamman–Fulcher (VTF) equation

$$\tau(T) = \tau_0 \exp\left[\frac{DT_0}{(T - T_0)}\right] \tag{1}$$

where T is the temperature and T_0 and τ_0 are the reference temperature and relaxation time. The parameter D is a constant which may be related to the fragility of the system.

The fragility is defined in terms of deviation of the temperature dependence of the relaxation time from Arrhenius behavior, it can be quantified by defining a dynamic fragility parameter (m) as:

$$m = \left.\frac{d \log \tau}{d(T_g/T)}\right|_{T_g} \tag{2}$$

Thus, it is necessary to choose an expression for the relaxation time. For a glass, the relaxation time (τ) is known to be dependent on the temperature and on some order parameters defining the structure of the glass. The most widely used model for the kinetics of structural relaxation is the Tool–Narayanaswamy–Moynihan (TNM) expression [12–14]

$$\tau(T, T_f) = A \exp\left[\frac{xE}{RT} + \frac{(1-x)E}{RT_f}\right] \tag{3}$$

where A is the pre-exponential factor and x is the non-linearity parameter ($0 \le x \le 1$), E the apparent activation energy, T_f the fictive temperature defined as the temperature at which the structure of the glass would be in equilibrium if instantaneously brought to it, and R is the gas constant. Based on the above model, the activation energy can be evaluated using the following expression [14]:

$$\frac{d \ln \beta}{d(1/T_g)} = -\frac{E}{R} \tag{4}$$

where β is the heating rate, knowing the value of the apparent activation energy, and according to relationship (2), the value of the fragility index can be obtained from [15–17]:

$$m = \frac{E}{(\ln 10)RT_g} \tag{5}$$

The activation energy of the glass transition can also be determined using the well-known Kissinger equation [18]. Although Kissinger equation was originally introduced to describe the kinetics of chemical reactions, it is widely used to determine the activation energy of crystallization. Recently, on the basis of the free volume model of glass transition, Ruitenberg [19] showed that Kissinger method can also be used to determine the glass transition activation energy. According to Kissinger method [18], the glass transition activation energy can be obtained using the following equation:

$$\frac{d \ln(\beta/T_g^2)}{d(1/T_g)} = -\frac{E}{R} \tag{6}$$

It should be mentioned here that in the original formalism of Kissinger method, T_g in the above equation is the peak temperature. In the present work we will apply Eq. (6) using the peak as well as the onset temperatures of the endothermic DSC output.

It is assumed in the framework of the TNM model that the activation energy is constant throughout the glass transition. Temperature dependence of the relaxation time deviates from the Arrhenian behavior as the glass transition temperature is approach on cooling. This complex non-Arrhenian relaxation causes the activation energy to vary with temperature. Different models have been proposed to describe this departure from Arrhenian behavior including the Vogel–Fulcher–Tammann (VFT) [20–22] and Williams–Landel–Ferry (WLF) [23] models. Such models predict a decrease of E as a function of temperature.

The variation of the activation energy throughout the glass transition region can also be revealed using the isoconversional methods. These methods were used to investigate the variation of the effective activation energy with extent of transformation and hence with temperature. This variation can be determined using the isoconversional method developed by Vyazovkin [24].

$$\Omega = \sum_{i=1}^{n}\sum_{j \ne i}^{n} \frac{I(E_\alpha, T_{\alpha i})\beta_j}{I(E_\alpha, T_{\alpha j})\beta_i}, \tag{7}$$

where n is the number of heating rates. The activation energy can be determined at any particular value of α by finding the value of E_α which minimizes the objective function Ω.

The variation of the activation energy throughout the glass transition region can also be determined using the isoconversional forms of Eqs. (4) and (6):

$$\frac{d \ln \beta_i}{d(1/T_{\alpha,i})} = -\frac{E_\alpha}{R} \tag{8}$$

$$\frac{d \ln(\beta_i/T_{\alpha,i}^2)}{d(1/T_{\alpha,i})} = -\frac{E_\alpha}{R} \tag{9}$$

where $T_{\alpha,i}$ is the set of temperatures related to a particular extent of conversion at different heating rates, β_i.

2. Experimental

The $As_{22}S_{78}$ chalcogenide glass was prepared using the standard melt-quench technique. High purity (99.999%) As, and S in appropriate atomic weight percentage were weighed and sealed in a quartz ampoule (12 mm diameter) under a vacuum of 10^{-6} Torr. The contents were heated at around 1100 K for 24 h. During the melting process, the tube was frequently shaken to homogenize the resulting alloy. The melt was quenched in ice water to obtain the glassy state. The structure of the sample was examined using Shimadzu XRD-6000 X-ray diffractometer using Cu Kα radiation (λ = 1.5418 Å). The surface microstructure was revealed by SEM (Shimadzu Superscan SSX-550). The content of the alloy was checked by Energy Dispersive X-ray (EDX) using the scanning electron microscope (Shimadzu Superscan SSX-550). The composition of the elements (As and S) was determined by EDX at different locations of the sample and average values were used.

Thermal behavior was investigated using Shimadzu DSC-60. The calorimetric sensitivity is ±10 μW and the temperature accuracy is ±0.1 K. Typically, 3 mg of sample in powder form was sealed in standard pans and heated at different rates 5, 7, 10, 15, 20, 25, 30, and 35 K min^{-1} under dry nitrogen supplied at the rate 35 ml min^{-1}. 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 was carried out with indium at heating rate 10 K min^{-1} (T_m = 156.6 C. ΔH_m = 28.55 J g^{-1}) as the standard material supplied by Shimadzu.

3. Results and discussion

The composition of as-prepared $As_{22}S_{78}$ bulk was analyzed using EDX. Fig. 1(a) shows the spectral distribution of the constituent elements. The atomic percentage ratios of As and S were found to be 22 and 78, respectively. The X-ray diffraction examination indicates the amorphous structure of the as-prepared specimen as shown in Fig. 1(b). Fig. 1(c) shows the SEM of a fractured as-prepared bulk specimen. Conchoidal contours of the fractured specimen indicate the glass structure.

DSC measurements were performed to study the kinetics of the glass transition in $As_{22}S_{78}$ chalcogenide glass. The DSC outputs showing the endothermic effects obtained at different heating rates are shown in Fig. 2. The glass transition temperature, T_g, is identified from the endothermic peak in the DSC signal. It is evident from Fig. 2 that T_g shifts to higher temperatures with increasing heating rate. The pronounced variation of T_g with heating rate is a