Evidence of intermediate phase in As_xSe_{100-x} chalcogenide glasses using isoconversional analysis of glass transition

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Abstract

The compositional and temperature dependence of the glass transition in As_xSe_{100-x} chalcogenide glasses were studied using differential scanning calorimetry (DSC). The temperature dependence of the glass transition activation energy was determined using an isoconversional kinetic analysis. The compositional trend of the activation energy provides evidence of a transition from floppy to rigid network regimes separated by an intermediate phase. The variations of the activation energy with respect to temperature at various compositions were presented and discussed.

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1. Introduction

It is well-known that a floppy-to-rigid phase transition occurs in covalent network glasses at a mean coordination number $r_c = 2.40$. According to Phillips and Thorpe [1–3], this rigidity percolation threshold occurs when the number of constraints per atom is equal to the number of degrees of freedom. More recently, Boolchand et al. [4] discovered the occurrence of two elastic phase transitions in network glasses. These two transitions define the limits of the intervening region or an intermediate phase

existing between the flexible floppy and the stressed rigid phases.

In a recent paper [5] henceforth cited as I, the compositional trend of the glass transition of As_xSe_{100-x} glasses was investigated using a DSC technique. Evidence for an intermediate phase from the compositional dependence of the activation energy was reported. In I, the activation energy of the glass transition in both aged and rejuvenated As_xSe_{100-x} glasses were determined from the heating rate dependence of T_g according to the well-known equation proposed by Bartenev and Ritland [6,7]:

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

where β is the heating rate, R is the gas constant, and E is the activation energy. Evidence of rigidity transitions were reported in I on the basis of the compositional dependence of the glass transition activation energy. Three distinct topological phases of the network glass were identified.

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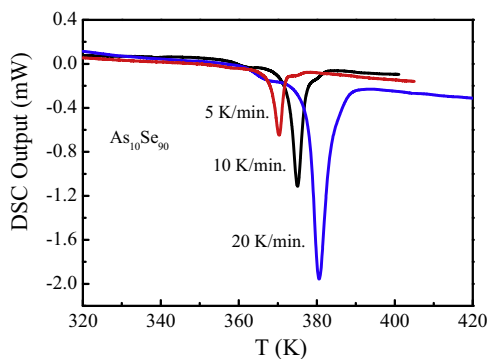
Fig. 1. DSC outputs of $As_{10}Se_{90}$ glass measured at heating rates varying between 5 and 20 K/min.

The effective activation energy of the glass transition can be determined by an isoconversional analysis of the experimental data of the extent of conversion (α) versus the temperature (Fig. 1) following the suggestion of Vyazovkin et al. [8]. Using an advanced isoconversional method developed by Vyazovkin [9], the effective activation energy can be determined for a series of n experiments carried out at different heating rates at any particular value of α by finding the value of E_α for which the objective function Ω is minimised, where

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

where the integral $I(E,T)$ is given by

$$I(E, T) = \int_{T_{\alpha-\Delta\alpha}}^{T_\alpha} \exp\left(\frac{-E}{RT}\right) dT \qquad (2)$$

The integral $I(E,T)$ can be numerically evaluated using the trapezoidal method. The activation energy E_α is the value that minimises Ω in Eq. (1) for a particular α.

2. Experiment

Bulk As_xSe_{100-x} chalcogenide glasses with $0 \leq x \leq 40$ were prepared using the standard melt-quench technique. High purity (99.999%) As and Se, in appropriate atomic weight percentages, were weighed and sealed in a quartz ampoule under a vacuum of 10^{-5} Torr. The contents were kept at a temperature of 1023 K for 24 h. During the melting process, the tube was frequently shaken to homogenise the resulting alloy. The melt was quenched in ice water to obtain a glassy state. The content of the alloy was checked with an Energy Dispersive X-ray (EDX) using a scanning electron microscope (Shimadzu Superscan SSX-550). The atomic percentages for arsenic were found to be 0,

5, 10, 20, 30, and 40 at.%. The samples were stored in the dark under normal conditions for 22 years.

The thermal behaviour was investigated using a Shimadzu DSC-60 calorimeter. Three mg of the samples in powder form were sealed in standard aluminium pans and heated at the following different rates: 5, 7, 10, 15, 20, and 25 K/min under dry nitrogen supplied at a rate of 35 ml/min. The temperature was measured within an accuracy of ±0.1 K. To minimise the temperature gradient, the samples were well granulated to form a uniform fine powder and were spread as thinly as possible on the bottom of the sample pan. Temperature and enthalpy calibration was carried out with indium at different heating rates.

3. Results and discussion

Examples of endothermic peaks corresponding to the glass transition in $As_{10}Se_{90}$ glass recorded at heating rates of 5, 10, and 20 K/min are shown in Fig. 1. The glass transition temperature T_g can be determined from the onset of the endothermic peak. Alternatively, the peak temperature of the endothermic curve can be used as an assignment for T_g. As evident from Fig. 1, T_g shifts to higher temperatures as the heating rate increases. This behaviour is a striking feature of the kinetic nature of the glass transition. It is worth mentioning that despite the fact that the kinetic aspect of the glass transition is pronounced, as indicated by the observed strong heating rate dependence of T_g, this cannot be taken as evidence that glass transition is purely a kinetic phenomenon. The possibility of a thermodynamic phase transition was addressed by Kauzmann [10], Adam and Gibbs [11], and many other investigators. The question of whether some phase transition underlies the glass transition is a matter of continuing research and debate [12]. The progress of transformation from the glassy state to the supercooled state during heating can be quantified by determining the extent of conversion (α) at any temperature T by using $\alpha = A_T/A$, where A is the total area of the endothermic peak between the temperature at the onset of the endotherm and the temperature where the transformation is completed and A_T is the area between the onset temperature and the temperature T. Fig. 2 shows α versus T for different heating rates. Using the data in Fig. 2, the effective activation energy as a function of α can be determined using the Vyazovkin isoconversional method described above. Fig. 3 shows E versus α for the As_xSe_{100-x} glasses of all compositions considered in this work. The temperature dependence of E can be obtained by replacing α with the corresponding temperature using the experimental data in Fig. 2. Figs. 4–9 show