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PHYSICAL AGING IN Bi_5Se_{95} CHALCOGENIDE GLASS: EFFECT OF ANNEALING TIME AND TEMPERATURE

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Physical aging in amorphous Bi_5Se_{95} system has been studied by using differential scanning calorimetry (DSC). The kinetics of physical aging was investigated by annealing the glass at ~ 20 °C below the glass transition temperature for different aging (annealing) times (t_a) ranging from 0.5 h to 163 h. It is observed that the endothermic enthalpic recovery temperature (T_p) and the enthalpy loss (ΔH) increase with increasing aging time. The effect of aging at different sub-T_g temperatures was studied and the usefulness of Kohlraush-Williams-Watts (KWW) function to describe the structural relaxation in Bi_5Se_{95} during aging was investigated. The kinetic parameters that are commonly used to describe the relaxation processes were determined.

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1. Introduction

Chalcogenide glasses are the target of extensive studies in recent years as they are promising materials for many applications. Due to their remarkable structural, thermal and optical properties they are widely used in infrared optics, xerography, photonics, and optical recording. Kinematical studies give important conclusions for the suitable usage of a chalcogenide glass in the proper application field [1-5]. However, because it is a characteristic feature of nonequilibrium glassy state, many physical properties in glasses change with time. Extensive research was devoted to this physical aging phenomenon because of its profound importance on commercial applications of glassy materials [6].

The kinetics of structural relaxation associated with physical aging in glassy materials is characterized by nonlinear and nonexponential behavior [7-10]. The nonexponential behavior is a consequence of the distribution of relaxation times. The most widely used equation for structural relaxation in glasses is the Kohlrausch-Williams-Watts (KWW) response function:

$$\phi(t) = \exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right] \tag{1}$$

where $\varphi(t)$ is the extent of relaxation at time t, τ is the mean relaxation time and β is the nonexponentiality parameter. When $\beta = 1$, the relaxation is characterized by a single relaxation time and can be described by exponential behavior. β is inversely related to the width of the distribution of relaxation times. The nonlinearity aspect of the physical aging is usually described by the Tool-Narayanaswamy-Moynihan (TNM) formulation [11-13]. According to this model, the relaxation time, τ, depends on temperature and the instantaneous structure of the glass characterized by the fictive temperature, T_f; as follows:

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$$\tau\left(T, T_f\right) = A \exp\left[\frac{xE_g}{RT} + \frac{\left(1-x\right)E_g}{RT_f}\right] \quad (2)$$

where A is the pre-exponential factor, R is the universal gas constant, E_g is the activation energy and x is the nonlinearity parameter ($0 \leq x \leq 1$) which determines the relative contributions of temperature and structure to the relaxation time.

BiSe glasses are interesting candidates for reversible optical recording application as the addition of Bi in Se facilitates crystallization. Many authors have investigated thermal and optical properties of BiSe glasses [14-16]. However, physical aging in these glasses has not been investigated.

The main objective of the present work is to study the structural relaxation of Bi_5Se_{95} chalcogenide glass annealed at different aging times at a temperature well below T_g. The applicability of the KWW stretched exponential function to describe physical aging in the present sample is discussed.

2. Experimental

Glassy Bi_5Se_{95} alloy was prepared by quenching technique. The exact proportions of high purity (99.999%) Se and Bi elements, in accordance with their atomic percentages were weighed. The materials were then sealed in evacuated (~ 10^{-5} Torr) quartz ampoules. The ampoule containing material was heated to 400 ^{o}C and was held at that temperature for 24 hours. During the melting process, the tube was frequently shaken to homogenize the resulting alloy. The obtained melt was cooled rapidly by removing the ampoules from the furnace and dropping them to ice-cooled water. The glassy nature of the alloy was checked by Energy Dispersive X-ray (EDX) using the scanning electron microscope (Shimadzu Superscan SSX-550).

DSC measurements were made using a Shimadzu DSC-60 calorimeter. Typically, 5 mg of samples in powder form were sealed in standard aluminum pans and heated at the following different rates: 1, 3, 5, 10, 15, 20, 30 and 40 K/min under dry nitrogen supplied at a rate of 35 ml/min. Temperature was measured with an accuracy of ±0.1 K. To erase the thermal history, the samples were heated to a rejuvenation temperature above T_g with a holding time of 5 minutes. The samples were then cooled to temperature of about 20 K below the onset T_g and immediately heated at a particular heating rate. In these runs, the cooling and subsequent heating were performed at the same rate.

3. Results and discussion

The DSC outputs showing the endothermic effects obtained at different heating rates (1 - 40 K/min) for Bi_5Se_{95} glasses are shown in Fig. 1. It is evident from Fig. 1 that the endothermic change marking the glass transition and enthalpic recovery shifts to higher temperatures with increasing heating rate. Two characteristics temperatures for this endothermic change can be identified from the DSC curves in Fig.1, namely the onset and peak temperatures, T_{onset} and T_p, respectively. The pronounced variation of these temperatures with heating rates is a manifestation of the kinetic nature of the glass transition. This strong heating rate dependence can provide important information on the relaxation processes. For example, the heating/cooling rate dependence of

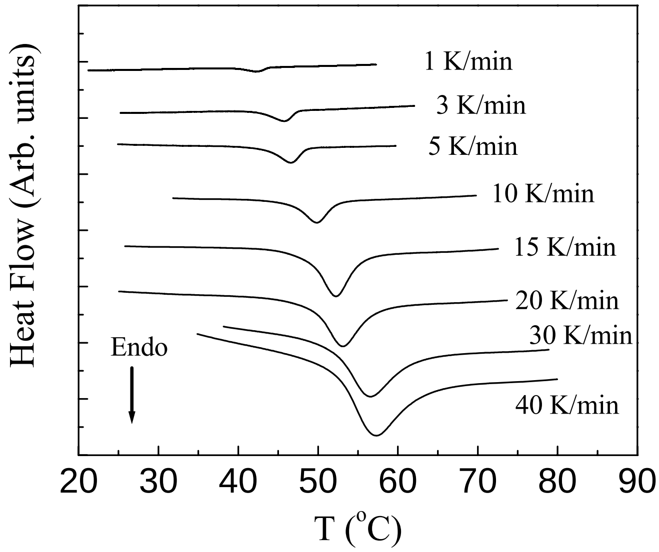

Fig. 1 DSC curves obtained for Bi_5Se_{95} chalcogenide glass at heating rates varying between 1 and 40 K/min. Only endothermic outputs are shown.

the apparent glass transition temperature T_g can be used to determine the activation energy of the transition from glassy to liquid state.

3.1 *The glass transition temperature*

Because the data in Fig.1 were obtained on heating, the onset temperatures of the endothermic peaks define a limiting fictive temperature T_f.
According to Lasocka [17], a useful assignment of the glass transition temperature (T_g) can be obtained from the heating rate dependence of T_f using the following expression:

$$T_f(q) = T_g^{'} + B \ln q \tag{3}$$

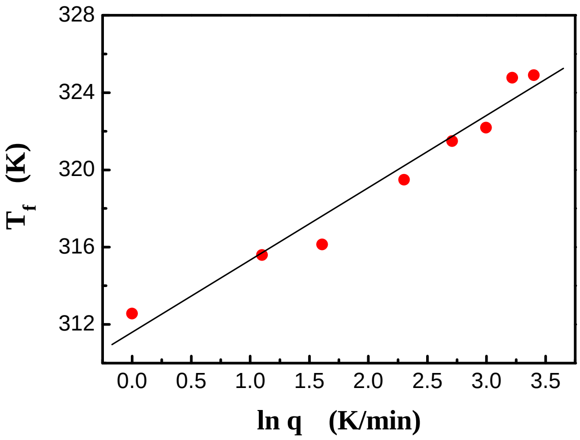

Fig. 2 Lasocka plot of the dependence of the limiting fictive temperature T_f on ln q. The solid line represents fit to Eq.3.

where B is a constant and T'_g is the value of T_f at q = 1 K/min. Fig.2 shows the variation of T_f with q. A best fit of Eq.3 is obtained with T'_g = 312 K and B = 3.7. We have also used Moynihan et al [13] method to determine T_g by heating the sample to a temperature well above the glass transition temperature to remove thermal history. The sample was kept at this rejuvenated temperature for 5 minutes. It was then cooled to around 30 °C below T_g at a cooling rate of 10 K/min. The sample is immediately heated at q = 10 K/min. The onset temperature of the endothermic peak can be used to define T_g. Using this procedure we obtain T_g = 312.7 K in agreement with the value determined using Lasocka equation.

3.2 *Non-exponentiality parameter*

The effect of physical aging on the properties of Bi_5Se_{95} glass was studied by annealing the sample at T_a = 27 °C for different aging times t_a of 0.5, 1, 2, 5, 18, 66, and 163 hrs. The extent of structural (or enthalpic) relaxation occurred when the glass held at a constant annealing temperature (T_a) can be determined by heating the sample through T_g at a particular heating rate of 10 K/min. As can be seen in Fig.3 as the aging time increases, a significant shift of the glass transition temperature T_g to higher temperatures is observed.

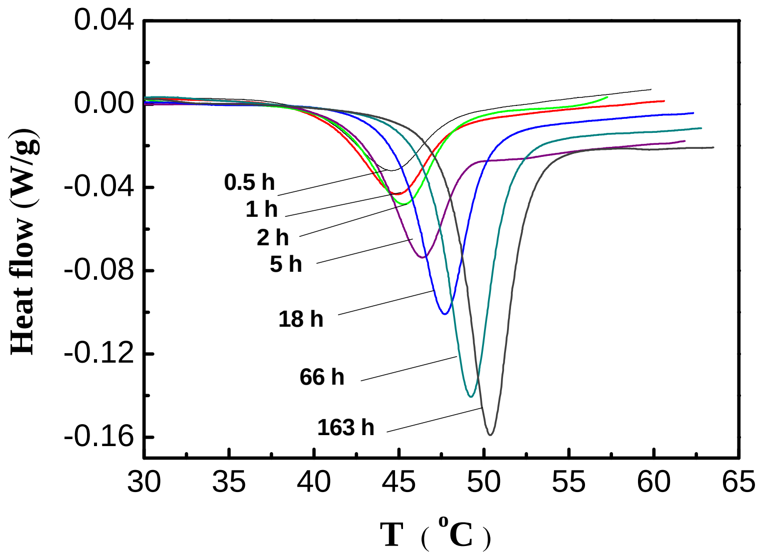

Fig. 3 Endothermic enthalpy relaxation peaks obtained at different aging times.

In addition, the area under the curve of the endothermic peak which is a measure of the enthalpy loss ΔH during aging is markedly increasing with t_a. The variation of T_g and ΔH with aging time is shown in Figs 4 and 5, respectively.

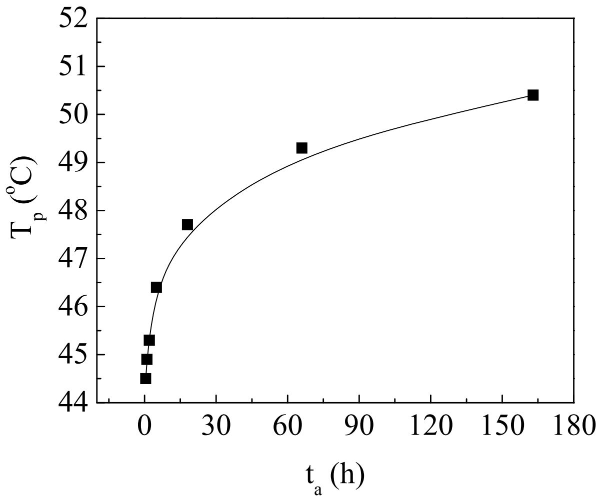

Fig. 4 The variation of peak temperature T_p with t_a for glassy Bi_5Se_{95}. The annealing temperature is 300 K. The solid line is a guide to the eye.

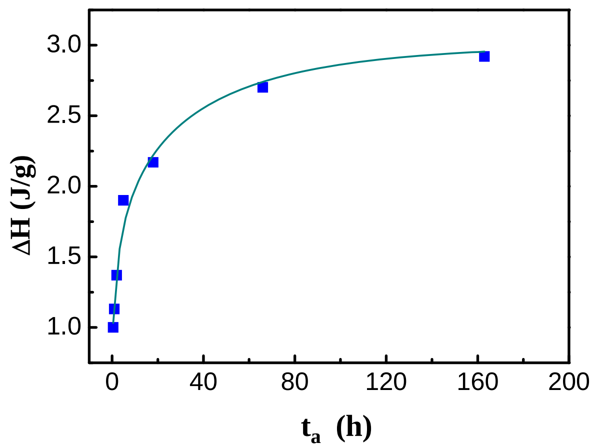

Fig. 5 ΔH versus t_a for glassy Bi_5Se_{95}. The annealing temperature is 300 K. The solid line is the theoretical fit to the Cowie-Ferguson equation.

Now, the structural relaxation can be analyzed using the Cowie-Ferguson equation [18]:

$$\Delta H(t_a) = \Delta H_\infty (1 - \phi(t_a)) \tag{4}$$

where $\varphi(t_a)$ is the KWW function given by Eq. 1 and ΔH_∞ is the value of the enthalpic loss when the t_a tends to infinity. Fitting the experimental data of Fig.5 to Eq.4 (shown as a solid line in the figure) gives $\beta = 0.23 \pm .03$ and $\Delta H_\infty = 2.92 \pm 0.13$ J/g. The obtained value of β for Bi_5Se_{95} glass is much smaller than the reported value for amorphous Se (β = 0.6 – 0.8). This indicates a remarkable change in the distribution of the relaxation times due to the introduction of Bi atoms into Se matrix. A similar observation was reported by Cortes et al [19] in Ge_xSe_{1-x} glasses.

3.3 *Nonlinearity parameter*

The nonlinearity parameter, x, can be determined by the peak shift method [20-23]. According to this method, the x value can be obtained from the variation of the endothermic peak temperature T_p with the enthalpic loss ΔH using the following equation:

$$x^{-1} - 1 = \Delta C_p \left(\frac{\partial T_p}{\partial \Delta H} \right) \quad (5)$$

where ΔC_p can be estimated from the relation $\Delta H_\infty = \Delta C_p (T_g - T_a)$.

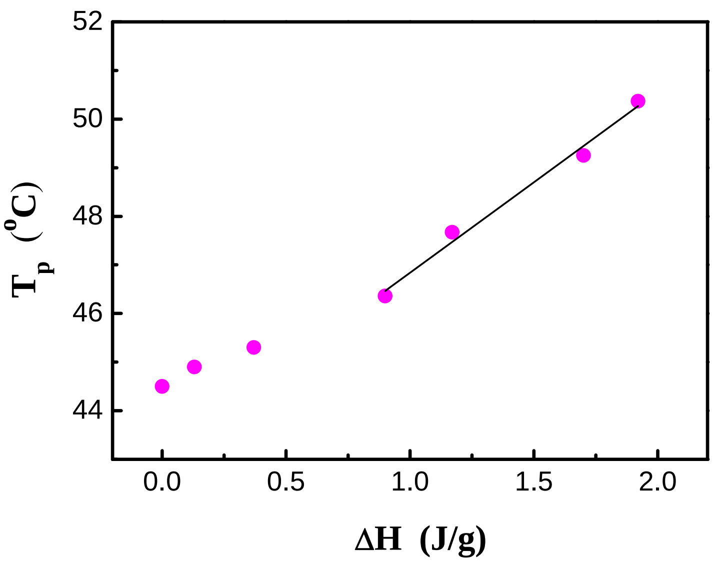

Fig. 6 Variation of the endothermic peak temperature T_p with the enthalpic loss ΔH. The full line represents a least-squares fitting to data points corresponding to higher aging times.

Eq.5 only apply to well stabilized glasses or glasses that have been annealed for a long period and show substantial non-linearity [20]. Using the value ΔC_p= 0.16 $Jg^{-1}K^{-1}$ and the value of the slope of the straight line representing the best fit to T_p vs ΔH graph of Fig. 6 (only the data points corresponding to sufficiently long aging times in Fig. 6 were used in the evaluation of the slope), x = 0.66 was obtained for the present glass. This value of x is very close to x = 0.6 for amorphous selenium. Therefore, introducing Bi into Se has insignificant effect on the nonlinearity behavior of the enthalpic relaxation associated with physical aging in Bi_5Se_{95} glass. This is also the case for Ge_8Se_{92} as reported by Cortes et al [19].

3.4 *Effect of annealing temperature on aging*

The heat flow curves for sample annealed for 1 h at sub-T_g temperatures 10 ^oC, 15 ^oC , 20 ^oC, 27 ^oC and 30 ^oC are shown in Fig. 7. From the figure, we can see that annealing the sample at T_a = 10 ^oC (i.e. $T_g - T_a \approx 30$ ^oC) shows a step-like increase of enthalpy during heating up across T_g, whereas samples annealed at higher temperatures (T_a > 10 ^oC) display endothermic peaks around T_g. It is also evident from Fig. 8 that increasing annealing temperatures increases the endothermic peak magnitude as well as shifting the peak to high temperature.

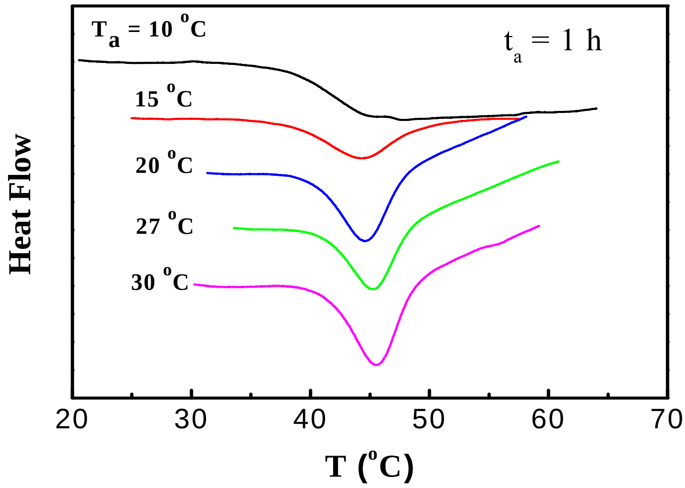

Fig. 7 DSC curves obtained for glassy Bi_5Se_{95} at aging time t_a = 1 h for various aging temperatures and for heating rate of 10 K/min.

4. Conclusions

The physical aging of Bi_5Se_{95} glass has been studied by DSC. Kinetics of relaxation in samples aged for long time was investigated at different heating rates. The enthalpic relaxation of Bi_5Se_{95} glass annealed for times up to 160 h at 27 °C has been described by the KWW and the peak-shift models. The nonexponential structural relaxation could be described by the KWW equation with nonexponentiality exponent of 0.23 indicating a broad distribution of relaxation times. The nonlinearity parameter x = 0.66 was obtained. When these values of the kinetic parameters (β ,*x*) are compared with the corresponding parameters for amorphous Se, we conclude that adding Bi into the Se matrix leads to a broader distribution of relaxation times but no significant change in the nonlinearity of the relaxation process.

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