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Structural relaxation due to sub-T_g annealing of $Se_{98}In_{1.5}Sn_{0.5}$ chalcogenide glass

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ABSTRACT

Structural relaxation during sub-T_g annealing of $Se_{98}In_{1.5}Sn_{0.5}$ chalcogenide glass below the glass transition region was investigated using differential scanning calorimeter (DSC). On annealing at 308 K, for different annealing times, the glass transition temperature T_g increases while the fictive temperature T_f decreases. The excess enthalpy ΔH has been calculated from the knowledge of the excess specific heat ΔC_p and plotted as a function of the annealing time t_a. The so obtained values of T_g, T_f and ΔH indicate that the relaxation process in $Se_{98}In_{1.5}Sn_{0.5}$ chalcogenide glass is approximately completed after 96 h of annealing at $T_a = 308 < T_g$. The structural relaxation activation energy ΔE was also calculated from the dependence of T_f on the heating rate and comes out to be 57.2 ± 3 kcal/mol for annealing at $T_a = 308$ K for $t_a = 12$ h. The obtained value of ΔE is an indication of the fact that structural relaxation occurs in $Se_{98}In_{1.5}Sn_{0.5}$ glass due to breaking and rearrangement of interchain weak bonds in the structure.

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1. Introduction

It is well known [1–3] that amorphous chalcogenide glasses synthesized from the liquid state are intrinsically in a thermodynamic non-equilibrium state. This is because the glass transition occurs when a liquid becomes highly viscous, as the temperature decreases, and cannot relax fast enough to reach the state of thermal equilibrium. At a temperature T_g, known as the glass transition temperature, or more accurately in a certain region called the glass transition region, the liquid freezes into a rigid glassy structure characterized by physical properties including enthalpy, entropy and volume that are usually larger than those of the equilibrium state. Therefore, the change in the aforementioned physical quantities with temperature and time during use, in the direction toward their equilibrium values, is usually accompanied by molecular rearrangement and is inevitable process. Such a structural relaxation process is known as physical ageing and is reported to occur in polymers [4], metallic [5–7] and chalcogenide glasses [8–11].

A survey of literature indicates that structural relaxation of amorphous Se has been studied in detail. For instance, Stephens [12] has studied thermal relaxation in melt-quenched and evaporated Se and observed that the relaxation peak occurred between 320 and 330 K, and had activation energy of ~22.5 kcal/mole. Bernatz et al. [13] performed creep and recovery measurements and found that amorphous Se is a relatively low molecular weight polymer with low concentration of rings. Volume and enthalpy relaxation of amorphous Se have been investigated by Málek et al. [8]. They concluded that the activation energy of viscous flow in the glass transition region is identical with the effective activation energy for relaxation process. The activation energy of structural relaxation for $Se_{70}Te_{30}$ glass has been calculated theoretically as well as experimentally by Svoboda et al. [10]. They have pointed out that the activation energy deduced from classic and intrinsic cycles is close to that obtained from curve-fitting. Svoboda et al. [14] have also studied the relaxation process in Ge_2Se_{98} and As_2Se_{98} glasses on the basis of Tool–Naraynaswamy–Moynihan equation. Saiter et al. [11] have shown that a very long ageing performed at low temperature, compared to T_g, leads to a reversible phase-like separation in Ge_xSe_{1-x} vitreous system. Structural relaxation of isothermally and isochronally heat treated $Se_{96}In_4$ glass in the glass transition region has been studied by Imran and co-workers [15] and the enthalpy relaxation activation energy spectra have been drawn and discussed. Physical ageing study of naturally stored $As_{10}Se_{90}$ glass as carried out by Golovchak et al. [16] indicates that the relaxation process occurs due to straightening/aligning of Se chains. Lafi and Imran [17] have studied the effect of gamma irradiation on glass transition temperature and thermal stability of $Se_{96}Sn_4$ glass. They conclude that the studied glass shows large relaxation effects after it has been irradiated at different doses of γ-ray.

Recently, semiconducting chalcogenide glasses have found a wide range of applications in several technological fields as reported by other researchers [18–22]. However, since chalco-

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genide glasses show large relaxation effects at temperatures below their glass transition, therefore if a glass is annealed isothermally at temperature $T_a < T_g$ for a certain annealing time t_a, it will lose its excess enthalpy by molecular relaxation to reach more favorable thermodynamic states of lower enthalpy [1]. As annealing time increased the enthalpy loss increased until it reached a saturated value when the relaxation is completed. Therefore, knowledge of the temperature range of utilization of glasses is necessary from industrial point of view. This is because chalcogenide glasses, generally prepared by melt quenching, are formed in a non-equilibrium thermodynamic state. Hence if a glass is used as an active component, in a certain application, in an environment where the temperature is close to or even below the glass transition temperature of that glass, then the glassy atoms will acquire thermal energy which may be large enough to change the physical properties of the glass [19,22,23].

The relaxation kinetic in sub-T_g annealing ($T_g - 100 < T_a < T_g$) exhibits [24] some characteristics, which differ from that of sub-sub-T_g annealing and also from that of annealing close to T_g. The present paper is addressed to investigate the kinetics of structural relaxation of $Se_{98}In_{1.5}Sn_{0.5}$ glass, annealed at $T_a = 308$ K below $T_g = 329$ K, using differential scanning calorimeter DSC. In this regard the enthalpy released $\Delta H(T_a,t_a)$ when the glass is annealed at T_a, during a time t_a, was evaluated from the knowledge of the specific heat difference ΔC_p between annealed and un-annealed glass. Based on the variation of T_f with the heating rate the activation energy for thermal relaxation was calculated and the structural relaxation is discussed in terms of bond interchange of the constituent elements.

2. Experimental details

The glassy sample of $Se_{98}In_{1.5}Sn_{0.5}$ was prepared by quenching technique. High purity (99.999%) of Selenium, Indium and Tin were weighed according to their atomic percentages and sealed in quartz glass ampoule (length 7 cm and internal diameter 8 mm) under the vacuum of 10^{-6} Torr. The ampoule was kept inside the furnace where temperature was raised at a rate of 3–4 K/min up to 1253 K and kept around that temperature for 12 h. The ampoule was frequently rocked to ensure the homogeneity of the sample. The molten sample was then rapidly quenched in ice cooled water. Differential scanning calorimeter DSC (PerkinElmer DSC-7) is used to measure the caloric manifestation of structural relaxation. The temperature precision of this equipment is ±0.1 K with an average standard error of about 1 K in the measured values. The DSC scans were taken at four different heating rates i.e., 5, 10, 15 and 20 K/min on accurately weighed sample taken in aluminum pan. The masses of the samples varied between 10 and 15 mg and were measured by weighing with an accuracy of about 100 μm. The DSC equipment was calibrated prior to measurements, using high purity standards Pb, Sn and In with well-known melting points. The results of temperature and enthalpy calibrations obtained for the standard materials were within 3% of the values given in literature [25]. To investigate the relaxation behavior of $Se_{98}In_{1.5}Sn_{0.5}$ glass, the sample was annealed at $T_a = 308$ K for different annealing times (i.e. 12, 18, 24, 36, 48, 72, 96, and 150 h).

3. Results and discussion

Typical DSC thermograms of as prepared $Se_{98}In_{1.5}Sn_{0.5}$ glass at four different heating rates are shown in Fig. 1. It is clear that each DSC thermogram exhibits a well-defined endothermic and exothermic peaks. The T_g values of the sample under consideration are 322, 325, 327 and 329 K at heating rates 5, 10, 15 and 20 K/min respectively. These T_g values are close to the room temperature and hence one may expect that relaxation may occur even at room temperature. The basic physical quantity for investigation of structural relaxation is the specific heat C_p. From the DSC heating data the specific heat of $Se_{98}In_{1.5}Sn_{0.5}$ glass was calculated using the procedures reported elsewhere [15]. Fig. 2 shows C_p versus temperature curves for as prepared and the glass annealed at $T_a = 308$ K for annealing time of 48 h. An abrupt jump of C_p occurs at T_g, which is an indication of glass transition [1,12,15,26,27]. The effect of annealing on $T_{g,s}$ of $Se_{98}In_{1.5}Sn_{0.5}$ for different annealing times and at annealing temperature 308 K is shown in Fig. 3. It is observed that the T_g values and the height of the specific heat change upon annealing i.e both T_g and C_p increase with increasing annealing time.

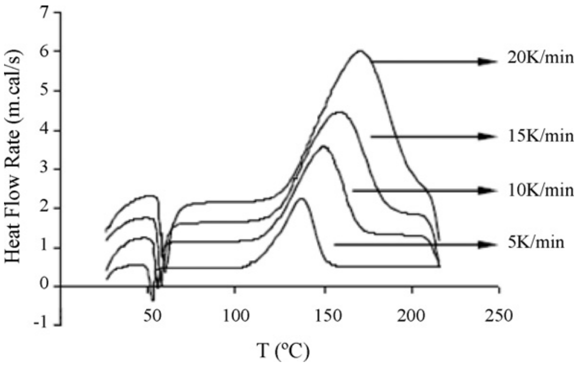

Fig. 1. DSC thermograms of $Se_{98}In_{1.5}Sn_{0.5}$ glass at four different heating rates.

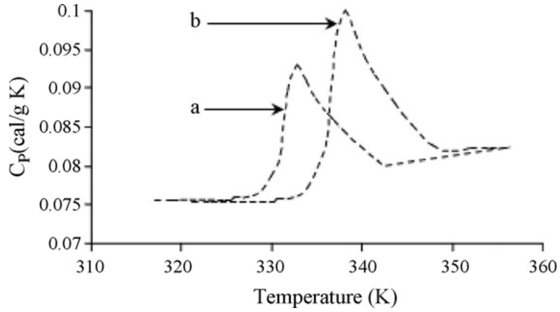

Fig. 2. A plot of specific heat C_p versus temperature for $Se_{98}In_{1.5}Sn_{0.5}$ glass annealed at $T_a = 308$ K for annealing time t_a (a) 0 h, (b) 48 h (Heating rate 20 K/min).

In our discussion of structural relaxation kinetics it is useful to use the concept of fictive temperature T_f, defined as the temperature at which a glass would be in equilibrium, to explain the structural changes in the vicinity of T_g [1]. Fig. 4 shows the DSC heating curve of $Se_{98}In_{1.5}Sn_{0.5}$ glass annealed at 308 K for 24 h and how the fictive temperature is estimated as suggested in Ref. [28]. The variation of the fictive temperature of $Se_{98}In_{1.5}Sn_{0.5}$ glass with annealing time is shown in Fig. 5. In sub-T_g annealing the decrease in fictive temperature causes a corresponding increase in T_g. The reason for that may be understood in terms of the relaxation time τ, for structural relaxation, which depends both on temperature and structure. If the structure of the sample is parameterized by the fictive temperature, the temperature/structure dependence of τ can be represented by Narayanaswamy equation [29]:

$$\tau = A \exp\left(\frac{x\Delta E}{RT} + \frac{(1-x)\Delta E}{RT_f}\right) \tag{1}$$

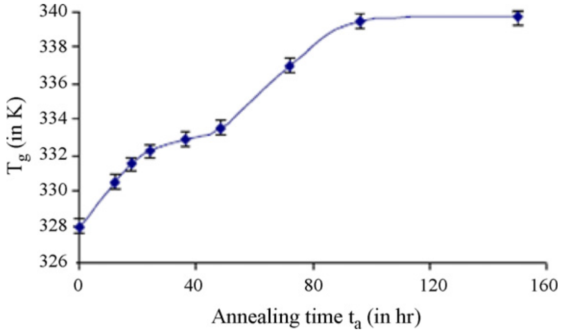

Fig. 3. Variation of the glass transition temperature T_g with annealing time at annealing temperature $T_a = 308$ K (Heating rate 20 K/min).

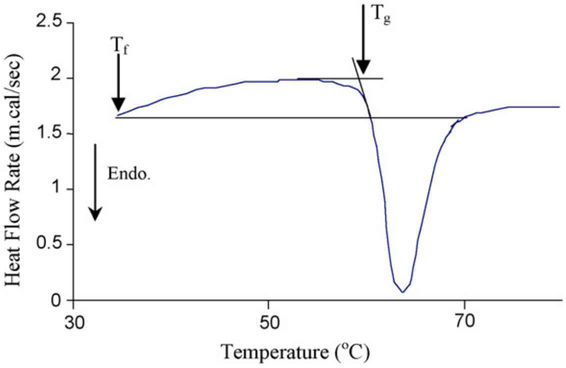

Fig. 4. DSC heating curve for $Se_{98}In_{1.5}Sn_{0.5}$ glass annealed at $T_a = 308$ K for 24 h (Heating rate 20 K/min).

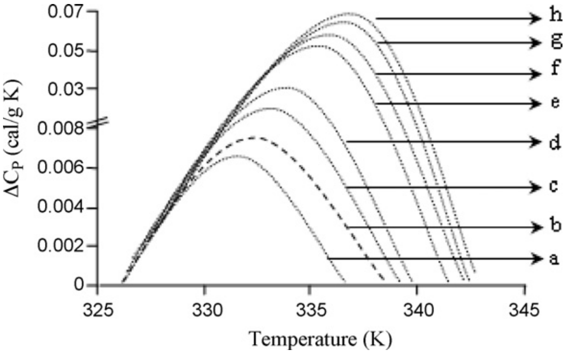

Fig. 6. Excess specific heat ΔC_p for $Se_{98}In_{1.5}Sn_{0.5}$ glass annealed at 308 K for (a)12 h, (b)18 h, (c) 24 h, (d) 36 h, (e) 48 h, (f) 72 h, (g) 96 h, (h) 150 h (Heating rate 20 K/min).

where A is constant, ΔE is the structural relaxation activation energy and x $(0 \leq x \leq 1)$ is a partition parameter. According to Narayanaswamy approximation for a given heating rate in structural relaxation study an increased specific heat will commence only at temperature $T = T_g$ at which the relaxation time τ attains a certain critical value. In the present case since T_f decreases with annealing then T_g must increase, as it is also evident from the above equation, to give the same value of τ at T_g. However, at higher annealing times, T_g is approximately constant and so does T_f reaching a temperature 301 K and one may state that the glass has relaxed and reached the equilibrium state, because both T_g and T_f attain approximately constant values at higher annealing times as evident from Figs. 3 and 5. To make sure of this earlier result we will go for further calculations of structural relaxation parameters i.e. specific heat difference between annealed and un-annealed glass ΔC_p and the excess enthalpy ΔH.

From Fig. 2 it is clear that the C_p of the annealed sample shows a behavior which follows closely the C_p curve of the un-annealed sample up to about 326 K, then exhibits an excess peak relative to the un-annealed glass before merging again at temperature above the glass transition temperature. This may be an indication of the dependence of the specific heat on thermal history at temperatures above 326 K and contains some configurational contributions besides to those arising from thermal vibrations [30,31]. For further description of the effect of low temperature annealing, the difference in specific heat between the annealed and un-annealed glass ΔC_p for different annealing times at $T_a = 308$ K was calculated and presented in Fig. 6. It is interesting to note, apart from the length of the annealing time, the excess specific heat ΔC_p curves always begin to rise at 326 K and increase with annealing time t_a in a continuous manner.

It is well known [32] that once the undercooled liquid is in equilibrium, then the enthalpy difference between each glass and the undercooled liquid give a measurement of the relaxation inherent to the formation of that particular glass. The relaxation enthalpy, however, is the thermal energy released during annealing of the glass which will again be re-absorbed during reheating process to reach undercooled liquid state and is usually calculated from knowledge of the area under the excess specific heat versus temperature curve, i.e.

$$\Delta H = \int_{T_1}^{T_2} \Delta C_p dT \qquad (2)$$

where T_1 is the temperature at which $\Delta C_p = 0$ and in the present case taken to be 326 K, whereas T_2 is taken above the glass transition temperature where the glass is in the equilibrium state. Fig. 7 shows the values of ΔH as a function of annealing time t_a at $T_a = 308$ K. It is clear that at lower annealing time ΔH vary linearly with t_a. Meanwhile, at higher annealing time the excess enthalpy levels off with a very small change in the value of ΔH indicating that the glass reached the state of equilibrium and the initial enthalpy is recovered. This is due to the fact that a glass prepared by melt quenching contains a number of liquid-like regions with un-relaxed atomic configuration, which are isolated from each other and embedded in solid like matrix [33]. As the glass is annealed at $T_a < T_g$ some liquid-like regions, with relaxation times less than the duration of annealing, will undergo local relaxation towards the local equilibrium states. Upon heating the annealed glass in the DSC furnace, each of these liquid-like regions recovers the initial structure and contributes to the excess endothermic specific heat and hence to the excess enthalpy as it is evident from Figs. 6 and 7.

For complete description of structural relaxation process in $Se_{98}In_{1.5}Sn_{0.5}$ glass we have to calculate the structural relaxation activation energy ΔE involved in Eq. (1) using a method based on

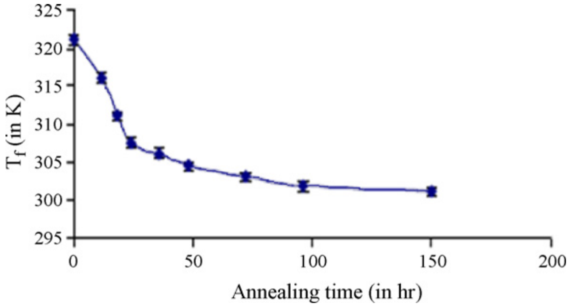

Fig. 5. Variation of the fictive temperature T_f with annealing time at annealing temperature $T_a = 308$ K (Heating rate 20 K/min).

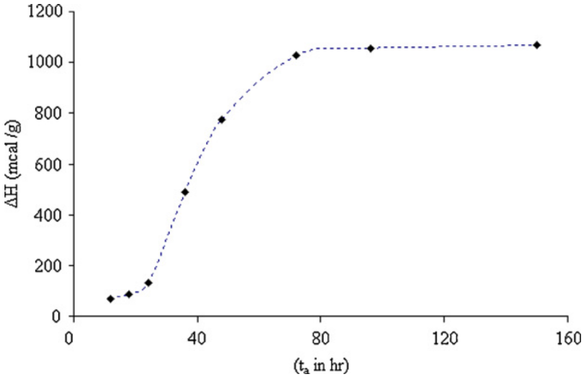

Fig. 7. Excess enthalpy ΔH for $Se_{98}In_{1.5}Sn_{0.5}$ glass as a function of annealing time t_a, for isothermal annealing at $T_a = 308$ K.

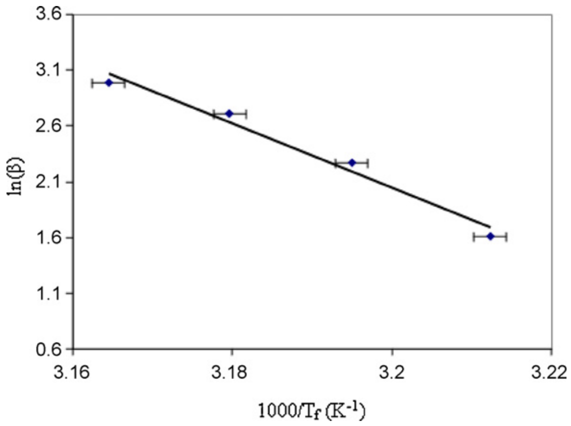

Fig. 8. A plot of ln(β) versus $1/T_f$ for determination of the structural relaxation activation energy of the sample pre-annealed at 308 K for 12 h.

the heating rate dependence of fictive temperature T_f as given by the following equation [1,15]:

$$\frac{d\ln(\beta)}{d(1/T_f)} = -\frac{\Delta E}{R} \quad (3)$$

where β is the heating rate and R is the gas constant. This equation states that the plot of ln(β) against $1/T_f$ should be a straight line the slope of which gives the value of ΔE. The structural relaxation activation energy ΔE of $Se_{98}In_{1.5}Sn_{0.5}$ glass annealed at 308 K for 12 h has been calculated from the slope of the plot shown in Fig. 8 and comes out to be 57.2 ± 3 kcal/mol. It is well known that chalcogenide glasses are characterized by a layer structure in which covalent bonding is restricted to two dimensions in the plane of the layer and with van der Waals forces in the third dimension. The calculated value of ΔE is much larger than the energies of van der Waals bonds [34] but of the order of the bond energies of some of the constituent atoms, for instance, Se–In and Sn–Sn have bond energies of 59 ± 4 and 46.7 ± 4 kcal/mol, respectively [35]. It is reasonable to state that the relaxation process in the studied glass cannot be attributed to the sliding of atomic layers but occurs due to breaking of interchain weak bonds during annealing, which will reform after the relaxation is completed.

4. Conclusions

Structural relaxation during sub-T_g annealing for different annealing times in $Se_{98}In_{1.5}Sn_{0.5}$ chalcogenide glass has been studied at annealing temperature of 308 K and the following conclusions may be drawn:

- The glass is approximately fully relaxed and reach a stable equilibrium state after annealing at T_a = 308 K for 96 h. This is because the characteristic parameters of structural relaxation i.e. T_g, T_f and ΔH attain approximately their constant values at this annealing time and any further annealing at higher times will not lead to any further relaxation.
- The structural relaxation in this particular glass is not a result of atomic layer sliding since the obtained value of the structural relaxation activation energy is much higher than the van der Waals bond energies. It is most likely that the relaxation process is due to breaking of interchain weak bonds during relaxation which will reform after relaxation is completed.

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