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Internal friction in Se–Sb glasses

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The internal friction, Q^{-1}, as a function of temperature has been investigated for $Se_{100-x}Sb_x$ systems, where $x = 7.5$, 12.5 and 17.5 at% , using the magnetostrictive pulse-echo method in the range of vibrational frequencies 50–100 kHz. Two well-defined peaks appeared, characterizing this glass. The first peak covers the temperature range 320–330 K, where the peak position has been shifted to the higher temperature as Sb content increases. This peak indicates the glass transition temperature, T_g, of the tested glassy samples. The second peak was detected in the temperature range 360–378 K. The position of this peak has been shifted to a lower temperature as Sb content increases. This peak is attributed to the crystallization temperature, T_c, of each glassy sample tested. The peak height of both of the above peaks decreased as the Sb content increased. Also, the appearance of these two peaks was affected by annealing.

1. Introduction

It is known that selenium, Se, is an inorganic polymer. This amorphous metal contains two types of molecules, monomeric rings and polymeric chains. It crystallizes to a trigonal structure when the composing rings and chains are broken and their constituent atoms become rearranged [1].

The study of amorphous Se is important for several reasons. (1) It can provide a better insight into the complicated internal friction spectrum (i.e. all mechanisms by which a material is capable of dissipating energy or damping it internally) of most amorphous polymers. This is because of its simple structure which has no side groups and the monomer reduces to a single atom, and (2) most polymers exhibit internal friction peaks associated with various kinds of thermally activated processes [2–4], but a single peak located around 30 K at a vibrational frequency of 160 MHz has been reported in Se [5]. This peak is observed below its glass transition temperature and the microscopic processes involved seem to be an intrinsic feature of the amorphous polymeric structure [6].

The ability and ease of glass-forming region of the Ge–Sb–Se system has been studied [7] and it has been found that the tendency to form glass, even upon slow cooling, is only possible when the bonding arrangement of the atoms in the melt coincide with that of cooled glass. The structure of glasses which are formed from the above system can be pictured to be made up of cross-linked three-dimensional structural units of the tetrahedral $GeSe_2$ and trigonal Sb_2Se_3 which are distributed among other constituents in the glass [8].

The study of internal friction of the binary system Se–Ge is interesting because the atoms of germanium cross-link the polymeric chains of amorphous–Se (a–Se). Previous measurements [5] on Se–Ge or S–Ge glasses in the 100 kHz range have shown that the internal friction properties at low temperature (lower than 200 K) are very sensitive to concentration of germanium. Clearly the classical methods for structural studies are usually diffraction experiments. Those techniques are not always, sufficiently sensitive to discuss the short-range order or even defect [9] in amorphous metals. Indirect methods which deal with the measurements of structure-sensitive properties, such as internal friction, thermal coefficient of expansion, specific heat, etc., are therefore of great importance.

The internal friction and the dynamic modulus are the most basic of all mechanical properties, and their importance in any end-use application is well-known. Either internal friction or modulus of a given material is sensitive, not only to many kinds of molecular motion, but also to various transitions, relaxation processes, structural heterogeneities and the morphology of multiphase systems [10]. Therefore, interpretations of the dynamic mechanical properties at the molecular level are of great scientific and practical importance in understanding the mechanical behaviour of polymers.

In the present work the variation of internal friction with temperature was investigated for the $Se_{100-x}Sb_x$ systems where $x = 7.5$, 12.5 and 17.5 at %. The effect of annealing the specimen under different conditions was also investigated.

2. Experimental procedure

2.1. Glass preparation

Glassy samples of the system $Se_{100-x}Sb_x$ where $x = 7.5$, 12.5 and 17.5 at % were prepared by the usual melt-quench technique [11]. Batches of Se and Sb (purity 99.99 %) were weighed and sealed in an evacuated silica glass tube which was then inserted in an electric furnace maintained at 850 °C for 8 h. The tube was frequently agitated in order to intermix the consti-

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tuents, to ensure homogeneity of the melt. The melt was then quenched in ice–water. Specimens were cut and prepared as cylindrical rods of nearly constant cross-sectional area with 1 cm diameter and lengths ranging from 0.5–1 cm. However, samples of nearly equal lengths and different compositions were used to facilitate comparison of the results.

2.2. Internal friction measurements

The magnetostrictive pulse-echo system described previously in detail [12, 13] is used here for internal friction investigations. In this system a generated burst of mechanical oscillations is used to excite the tested glass specimen, along its main length at either the natural frequency or one of the harmonic frequencies of the specimen. The resultant signal echo which is recorded by the system is shown schematically in Fig. 1. The formation of the echo pattern has been investigated by Bell [14] and the establishment of this echo has been described in more detail by Chaplain [15]. It is a combination of two parts; (1) the echo signal from the resonator specimen and the background signal from the interface between the specimen and the transmission wire-line. These two signals are in reverse phase to each other; consequently, they form a cross-over at a stage when they have the same amplitude. This cross-over confirms the adhesion of the specimen and the coupled line by the cementing agent (Araldite) and it indicates, also, that the frequency of the transmitted signal is equal to either the natural frequency, or one of the higher mode frequencies of the specimen; and (2) the echo decrement which is the exponential radiation of the stored energy due to the resonator and follows the echo-signal. The parameters shown in Fig. 1 are used to calculate, absolutely, the internal friction, Q^{-1}, according to the following equations [12, 13]

$$\frac{Q_c}{Q_m} = \frac{A_0 + A_\infty}{A_0 - A_\infty} = y \qquad (1)$$

$$\frac{\pi N}{Q_c} = \frac{\ln[2/(1 - y)]}{1 + y} \qquad (2)$$

where Q_c and Q_m are the coupling and the material Q-factors respectively, A_0, A_∞ are the initial and steady state amplitudes of the echo-signal and N is the number of oscillations to cross-over.

In all measurements of internal friction carried out in the present work, the temperature of the tested specimen was raised in steps of 5 °C from room temperature to 450 K with the temperature maintained constant for about 5 min to ensure that the distribution of heat was constant inside the specimen. The readings of A_0, A_∞ and N were recorded and the corresponding internal friction values were calculated. The measurements were performed on three samples for each studied system and the results obtained for internal friction were reproducible with a standard deviation ± 0.0019 over the studied range of temperature. Also, the resonance frequency of the worked specimen was noted to within an accuracy of ± 3 Hz at each selected temperature.

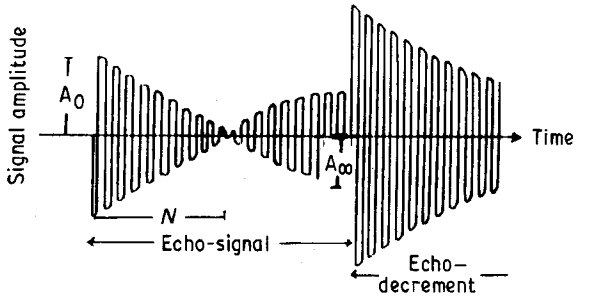

Figure 1 Schematic diagram of the resultant echo-pattern displayed in the magnetostrictive delay-line system.

3. Results and discussion

3.1. Internal friction and glass transition temperature of Se–Sb systems

The change of internal friction and resonance frequency with temperature have been investigated in the $Se_{100-x}Sb_x$ glasses. Fig. 2 shows the average results obtained for tested systems, where $x = 7.5$, 12.5 and 17.5 at % respectively. In general, the results obtained for the studied glasses revealed two well-defined peaks in the internal friction spectra. Also, a deep trough was observed in the resonance frequency plots which shifts to lower temperature as the Sb content increases.

The Se–Sb systems can be pictured [8] to be made up of cross-linked three-dimensional structural units of the trigonal Se_3Sb_2 phase distributed among other constituent phases of the polymeric Se chains and the minor Sb phase. Accordingly, the first internal friction peak detected for all specimens is attributed to the glass transition of the studied glasses, which agrees

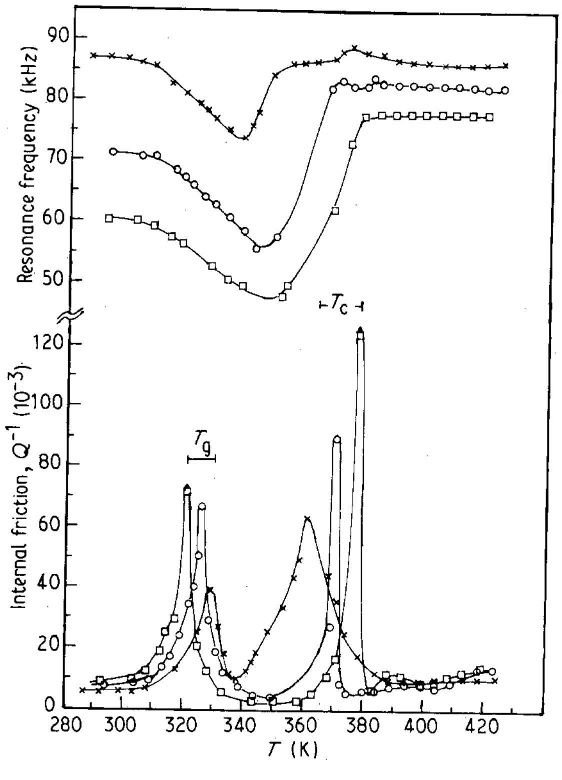

Figure 2 Variation of internal friction and resonance frequency with temperature for different ($Se_{100-x}Sb_x$) systems: x = (□) 7.5, (○) 12.5, (×) 17.5.

well with data [16] obtained by DTA investigations on some $Se_{100-x}Sb_x$ glasses where $x = 5$, 10 and 15 at %. This transition is so conspicuous that it is called the primary dispersion (the α-peak) [10]. The appearance of such a peak in the present work is attributed to the initiation of micro-Brownian motion of the amorphous selenium chains leading to best orientation. Some of the molecular Se chain segments are free to move, while others are not. A frozen-in segment can store much more energy, as absorbed, from applied ultrasonic waves for a given deformation than can a free-to-move segment. Thus, every time a stressed frozen-in segment becomes free to move, its excess energy is dissipated as heat.

In the glass transition region, the dynamic modulus of the glassy state decreases to a great extent as indicated by the considerable decrease in the resonance frequency with increase in temperature as shown in Fig. 2. This reveals the softening of the glass of the non-crystalline regions of Se under the structural restraint of the neighbouring molecular chains in the cross-linked crystalline Se_3Sb_2 regions. For this reason there is a tendency for the peak to shift to higher temperatures as structural restraint of the crystalline Se_3Sb_2 region increases with the Sb content (Fig. 2). On the other hand, the observed decrease in the height of the α-peak during the transition region is interpreted as being due to the cross-linking effect of Sb atoms to Se chains as the Sb content increases in the sample, which reduces the mean length of the polymeric chains between cross-links.

3.2. Internal friction and crystallization temperature of Se–Sb systems

In addition to the glass transition or the α-peak, Fig. 2 also shows another peak which has been detected at higher temperatures. It is known that semi-crystalline polymers exhibit another dispersion peak between the glass transition peak and the melting temperature. This relaxation is called α_c or the α′-dispersion. Takayanagi [17], attributed this peak to molecular motion within the crystalline phase. He concluded that this crystalline dispersion is due to the frictional viscosity among specific crystalline planes or molecules inside the crystals. Therefore, the second peak observed by our internal friction measurements is interpreted as being due to the transformation of the sample to a crystalline state. These results are also in good agreement with the previous data obtained by DTA measurements on Se–Sb systems [16].

The loss tangent, tan δ, is called internal friction, Q^{-1}, or damping [10] and it is the ratio of energy dissipated per cycle to the maximum potential energy stored during a cycle. This loss tangent has been given [18] by the following equation

$$\tan\delta = W_c(\tan\delta)_c + (1 - W_c)(\tan\delta)_a \quad (3)$$

where W_c is the degree of crystallinity, and the subscripts a and c refer to the contributions of the amorphous and pure crystalline phases, respectively. Because the damping, in general, is mostly due to the amorphous phase, Equation 3 for tan δ simplifies to

$$\tan\delta = (1 - W_c)(\tan\delta)_a \quad (4)$$

which shows that the intensity of the damping peak decreases with increasing degree of crystallinity. From Fig. 2 it is clear that crystallization peak has been affected by the increasing Sb content which, in turn, increases the degree of crystallinity through the formation of a Se_3Sb_2 crystalline phase at the expense of the amorphous matrix. This leads to a corresponding decrease in the peak height as implied by Equation 4. The observed shift in the peak position to lower temperatures and its broadening as Sb content increased were consequences of the inhibiting effect of crystalline Se_3Sb_2 regions on the molecular motion in the amorphous regions.

3.3. Effect of annealing

In the preceding investigations of this work, the first-run data during heating were considered. The effect of annealing on both the glass and the crystallization transitions was investigated by repeating the measurements on the system $Se_{82.5}Sb_{17.5}$ several times under different annealing conditions. This specimen was chosen for this experiment because it showed two considerable α and α_c peaks. The first run was conducted as mentioned in Section 2.2, but at the end of the experiment the specimen was removed from the unevacuated furnace to be cooled in air. On the next day the second run was performed up to 450 K which is less than the melting temperatures of these glasses (~ 500–505 K) [16]. Then the specimen was left inside the furnace to be annealed and the third run was carried out on the third day. The results obtained are shown in Figs 3 and 4. From Fig. 3, it is observed that the second day run is characterized by the absence of the glass-transition peak and only the crystallization peak appeared with its height decreased by 34% compared to that of the corresponding first-run peak. In addition, its position has shifted about 10 K to a lower temperature. A small hump is observed in the

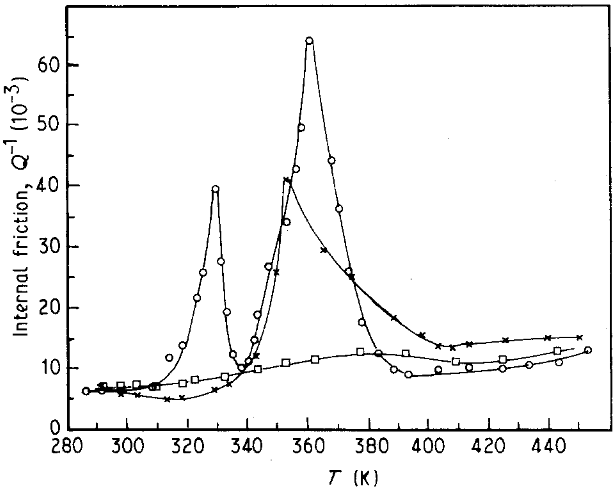

Figure 3 Effect of annealing on both the glass transition and the crystallization peaks observed in the glass ($Se_{82.5}Sb_{17.5}$) system. Run: (○) first, (×) second, (□) third.

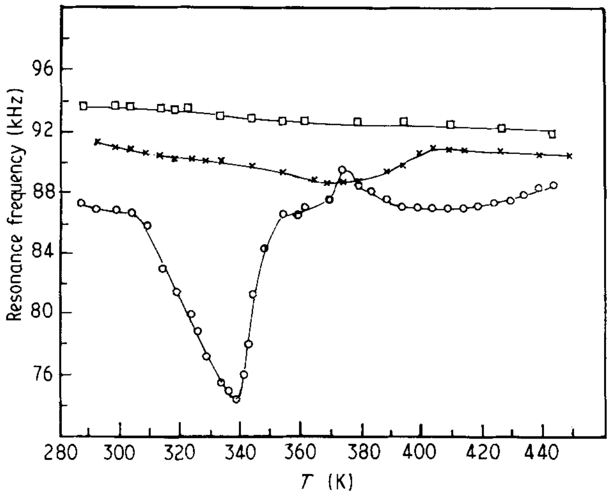

Figure 4 Effect of annealing on the variation of resonance frequency with temperature in the glass ($Se_{82.5}Sb_{17.5}$) system. Run: (○) first, (×) second, (□) third.

curve representing the third run in the region of the crystallization peak. Hence the appearance of both the observed peaks has been shown to be dependent on the annealing conditions of the specimen. However, the observed behaviour indicates that the degree of crystallinity in the worked glass is more greatly affected by the annealing in the furnace than that in the air, i.e. in the case of air annealing, crystallization is produced by the formation of new crystallites rather than a crystal growth process which is dominant during annealing of the specimen in the furnace.

Fig. 4 also illustrates the variation of resonance frequency with temperature under different annealing conditions. However, this figure confirms the absence of the glass-transition peak on the second-run plot by the disappearance of the deep trough which was observed on the first-run plot. Therefore, when the glass has become crystallized by annealing it inside the furnace for a long time, neither damping peaks are observed in the spectra of internal friction nor troughs in the resonance frequency plots in the studied temperature range from room temperature to 450 K.

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