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Physical ageing in Se–Te–Sb glasses

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ABSTRACT

Bulk $Se_{60-x}Te_{40}Sb_x$ glasses in the composition range $0 \le x \le 14$ were prepared by the melt quenching method. Differential Scanning Calorimetric (DSC) and thermal crystallization studies were performed to understand the thermodynamic property like glass transition and structural transformations. These glasses exhibit sharp endothermic peak at the glass transition (T_g). Disappearance of the endothermic peak at T_g in the rejuvenated samples clearly indicates the ageing effect in these glasses. Addition of Sb to Se–Te increases the connectivity of the structural network which is evidenced from the increase in T_g. A distinct change in the slope of the T_g at $x=6$, indicates a major change in the way the network is connected. The glass forming ability and the thermal stability also exhibit a maximum at $x=6$. T_g increases with the ageing time and the corresponding fictive temperature (T_f) calculated from the specific heat curves shows a decreasing trend. The molecular movements along the polymeric Se chains might cause the structural relaxation and the physical ageing. The physical ageing effect has been understood on the basis of the Bond Free Solid Angle (BFSA) model proposed by Kastner. Thermally crystallized samples show the formation of rhombohedral Sb_2Te_3, rhombohedral Sb_2Se_3 and hexagonal Te phases.

1. Introduction

Tellurium based chalcogenide glasses find wide range of applications in many fields like thermal imaging, ultra-high density phase change storage and memory, integrated fiber optics, infrared photo detectors and photo voltaic and bio sensors [1–9]. For example, Ge–Ga–Te glasses transmit infrared light even up to 25 μm [10]. Ge–Sb–Te is known for its phase change and memory applications [11,12]. Ge–As–Te glasses are found to have good sensitivity for toxic gasses at room temperature [13]. *a*-Se is well known for its application in xerography and recently it has been used as X-ray image detectors in medical imaging [14]. The chemical durability and corrosion resistance of Te can be increased to a larger extent by the addition of Se [15,16]. Tellurium polymerizes the Se network by entering into the Se chains. Te also opens up the Se_8 rings and forms mixed rings of Se and Te (rings of Se_2Te_6) [17]. The increase of Te increases the number of chains linearly and reduces the length of the chains logarithmically in Se network. When the length of the chains becomes very less, the glass formation becomes very difficult. Thus the glass formation in systems with higher Te content is difficult [17–19]. To improve the glass forming ability and alter the properties of a binary glass, a third element can be added or the cooling rate has to be increased [20,21]. For example, the addition of Group V element Sb to binary Se–Te modifies the structural and electrical properties considerably [22–24]. The increase of Sb in Se–Te increases the electrical conductivity by decreasing the conductivity activation energy. Even with the addition of the third element Sb to $Se_{60}Te_{40}$, the glass formation is found to be difficult in this work as the Te content is high. Hence, obtaining glasses with higher Te and Sb is a difficult task.

Though, chalcogenide glasses find applications in many fields, their performance can be affected by the ageing effect since the glasses are not in thermodynamic equilibrium state [25,26]. It means the properties can vary over a period of time which can result in the poor performance of the device made out these glasses. Since the glasses are generally prepared by the melt quenching method, they deviate from their metastable equilibrium state. Hence, they have excess enthalpy, excess free volume and excess configurational entropy compared to their crystalline counterparts and extrapolated equilibrium states of the supercooled liquid at a fixed temperature [25,26]. Exposure of the chalcogenide glasses to light can accelerate the ageing process [27–29]. When a glass is heated in a Differential Scanning Calorimeter (DSC), it undergoes an endothermic reaction at the glass transition region. This can be observed as an endothermic step (base line shift) in the DSC scan if the sample is not aged and as an endothermic peak in an aged glass. Reheating (rejuvenation)

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the sample through its glass transition region removes the ageing effect. Particularly, glasses with low coordination undergo physical ageing easily and are suitable for studying the ageing effect [30]. The $Se_{60-x}Te_{40}Sb_x$ ($0 \le x \le 14$) glasses studied in this present work are low coordinated glasses with the coordination varies between 2.0 and 2.14.

In this work we have attempted to prepare $Se_{60-x}Te_{40}Sb_x$ glasses with a maximum of 14 at% of Sb. DSC and thermal crystallization studies have been carried out to understand the effect of the addition of Sb to Se–Te glasses on the glass transition, crystallization, glass forming ability, thermal stability and physical ageing.

2. Materials and methods

Glasses in $Se_{60-x}Te_{40}Sb_x$ ($0 \le x \le 14$) were prepared by the conventional melt quenching method. Appropriate amounts of high-purity elements (99.999%) were sealed in a quartz ampoule under a vacuum of better than 10^{-5} Torr and heated in a resistive furnace. The sealed ampoules were heated to 850 °C in a horizontal resistive furnace for 48 h. The ampoules containing the melt were continuously rotated to ensure the homogeneity. The melt was quenched in a mixture of ice+water+NaOH solution. The resulting samples were subjected to X-ray Diffraction (XRD) to confirm its amorphous nature, shown in Fig. 1.

DSC studies were performed on the $Se_{60-x}Te_{40}Sb_x$ samples in MDSC 2920 (TA Instruments Inc., USA) in the normal DSC mode under dry N_2 atmosphere at a heating rate of 10 °C/min. About 20 mg of sample was weighed into Al crimped pans and then sealed. An empty Al pan was taken as reference. Fig. 2 shows the DSC thermo grams of $Se_{60-x}Te_{40}Sb_x$ samples for representative samples $x=2$, 6 and 12. The heat capacity measurements were carried out in the modulated mode at a heating rate of 5 °C/min with the modulation amplitude of ±1 °C and the modulation period of 60 s. The samples were stored at room temperature in darkness to avoid the effect of light on the structural relaxation.

$Se_{60-x}Te_{40}Sb_x$ glasses were sealed in quartz ampoules at a vacuum of 10^{-4} Torr and annealed at their respective crystallization temperatures for 2 h in a resistive furnace and cooled back to room temperature. All the annealed samples were subjected to XRD to identify the crystallized phases.

3. Results and discussions

3.1. Thermal studies

It can be seen from Fig. 2 that $Se_{60-x}Te_{40}Sb_x$ ($0 \le x \le 14$) glasses show single glass transition temperature (T_g), followed by an intense first crystallization peak, T_{c1}. The compositions with $2 \le x \le 12$ show

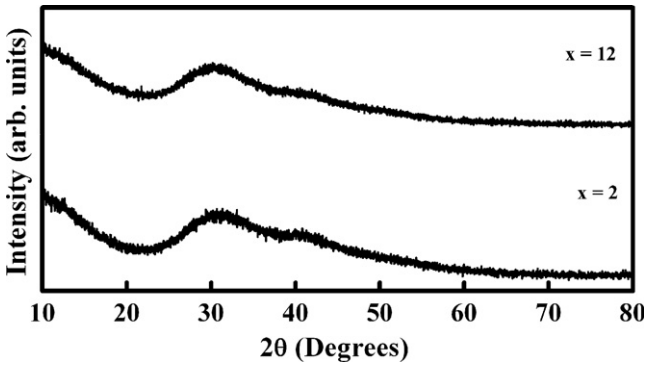

Fig. 1. XRD patterns of the representative samples ($x=2$ and 12) showing the amorphous nature of the prepared samples.

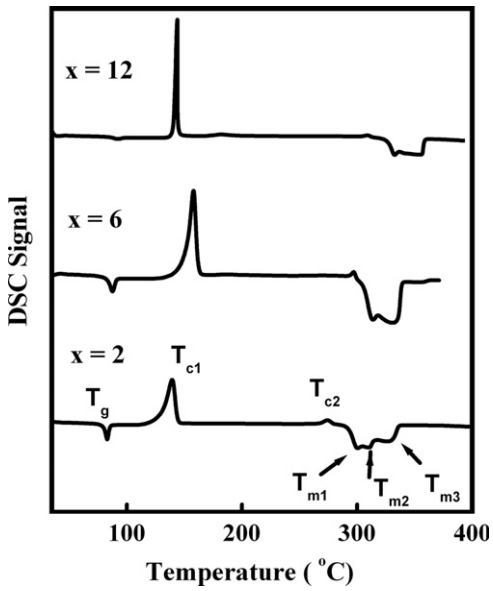

Fig. 2. DSC thermograms of the $Se_{60-x}Te_{40}Sb_x$ glasses recorded at a heating rate of 10 ° C/min for representative compositions ($x=2$, 6, and 12).

a low intense second crystallization peak at T_{c2}. These glasses also exhibit a broad melting transition with three depressions for $x=0$, 2 and 14 and two depressions for $4 \le x \le 12$. It is also worth to mention that $Se_{55-x}Te_{45}Sb_x$ ($0 \le x \le 9$) glasses show a single T_g and single T_c whereas $(Se_{65}Te_{35})_{100-x}Sb_x$ ($0 \le x \le 9$) glasses show a single T_g and double T_c [22,31]. The broad melting observed in the present studies may be due to the formation of a complex three-phase stage (liquid+Se–Te solid+Sb_2Se_3) before complete melting.

Glasses are frozen states and their free energy is higher than the systems which are in equilibrium state. The properties of an equilibrium sate depend on the external variables whereas the properties of the frozen state depend also on thermal history. The systems with higher free energy and thermal history tend to equilibrate at a finite rate by relaxation process/ageing. Generally, in a DSC spectrum T_g is seen as a baseline shift [25,26]. Ageing which is seen as an endothermic peak, shifts the glass transition to higher temperatures. In this study, the $Se_{60-x}Te_{40}Sb_x$ glasses exhibit a sharp endothermic peak at T_g for $x \le 6$. For $x > 6$, the endothermic peak disappears and T_g is exhibited as a baseline shift. The sharp endothermic peak at T_g is due to the ageing effect of the glasses as discussed above. It should also be mentioned that the DSC spectra shown in Fig. 2 were recorded for the samples which are 1 month old (30 days after the preparation of the samples). The observation of the sharp endothermic peak, made us to prepare all the compositions again in the $Se_{60-x}Te_{40}Sb_x$ glasses to understand the ageing effect. The freshly prepared samples were transferred to the DSC pans immediately after opening the ampoules. Even these freshly prepared samples also exhibit the ageing effect as shown in Figs. 3 and 4 for $x \le 6$. This aspect will be discussed later in this section.

The glass forming ability and thermal stability can be evaluated by the Hruby criterion (H_R) [32] and Saad and Poulain's criterion (S_p) [33] respectively from the following equations:

$$H_R = \frac{(T_{c0}-T_g)}{(T_m-T_{c0})} \quad (1)$$

$$S_p = \frac{(T_{c0}-T_g)(T_{c1}-T_{c0})}{T_g} \quad (2)$$

where T_g is the glass transition temperature, T_{c0} is the onset of crystallization temperature, T_c is the peak temperature of crystallization, and T_m is the onset melting temperature. Higher values