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Glass transition, thermal stability and glass-forming tendency of $Se_{90-x}Te_5Sn_5In_x$ multi-component chalcogenide glasses

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ABSTRACT

Glass transition kinetics of glassy $Se_{90-x}Te_5Sn_5In_x$ ($x = 0$, 3, 6 and 9) alloys have been investigated using differential scanning calorimetric (DSC) technique under non-isothermal conditions at different heating rates 5, 10, 15 and 20 K/min. It is observed that in these glasses, the glass transition temperature (T_g) is found to be dependent on composition and heating rates. The activation energy of glass transition (E_g), fragility index (F) and stability parameter (S) are evaluated for glassy Se–Te–Sn–In alloys. The glass transition activation energy (E_g) and fragility index (F) were found to be minimum at 9 at.% of In, as well as thermal stability parameter (S) was found to be maximum at same glassy composition due to maximum crosslinking structures. Results indicate that thermal stability increases on the addition of In to ternary $Se_{90}Te_5Sn_5$ glass. Hence $Se_{81}Te_5Sn_5In_9$ glass is the better thermally stable glass in this system.

1. Introduction

Chalcogenide semiconductors truly emerged as multipurpose materials and have been used to fabricate technologically important devices [1–3]. In contrast to amorphous silicon and other group IV tetrahedral bonded semiconductors, the chalcogenide glasses have attracted much attention due to their interesting thermal, optical, electrical and mechanical properties, which can be controlled by changing their chemical composition.

Amorphous Se rich semiconducting alloys are of particular interest due to their current uses as photoconductors in high definition TV pick up tubes and particularly in digital X-ray imaging. Recent studies indicate that the structure of a-Se having twofold coordination consists of randomly mixed long polymeric Se_n chains in which various portions of a chain have ring fragments [4–6]. Addition of tellurium (Te) brings about changes in Van der Waals bonds, or interchain secondary bonds because the Te atom is larger than the Se atom and has more electrons in its orbital. One can therefore argue an increase in secondary bonding between chains due to Te addition. Te addition will also increase the valence alteration pair (VAP) type defects, connecting neighboring chains and limiting molecular mobility. Amorphous Se–Te alloys have greater hardness, higher photosensitivity and smaller aging effects than pure Se [7]. As these glasses have poor thermomechanical properties, in order to enlarge their domain of applications, it is necessary to increase their softening temperature and mechanical strength. The addition of an indium (In) which has a large electro-negativity difference with Se and Te, expands the glass forming area and also creates compositional and configurational disorder in the system, and also is found to modify the structure and thus the electrical and thermal properties of the Se–Te system [8–13]. The effect of addition of third elements (In Sn, Sb) into Se–Te glasses has been carried out many research groups [14–23]. The addition of impurities like Sn is particularly of much interest as it has produced a remarkable change in the optical, electrical and thermal properties of chalcogenide glasses. The lattice perfection and the optical gap of the material play a major role in the preparation of the device which can be modified by the addition of the dopant (Sn). Various new quaternary glassy alloys have been prepared and the study of their different properties is in fashion in current time [24–30]. Recently, we have reported the effect of indium additive on crystallization and thermal stability on Se–Te–Sn multi-component chalcogenide glasses [31]. In the present work, the glass transition, thermal stability and glass forming tendency have investigated for a new glassy $Se_{90-x}Te_5Sn_5In_x$ ($x = 0$, 3, 6 and 9) multi-component system.

2. Experimental techniques

High purity (99.999%) Se, Te, and Sn and In elements were weighed in appropriate atomic weight percent proportions using an electronic balance. The materials were evacuated in quartz ampoules (length 8 cm and internal diameter 12 mm). The ampoules were sealed under a vacuum of 10^{-5} Torr to remove possibility of any reaction of alloys with oxygen at high temperature.

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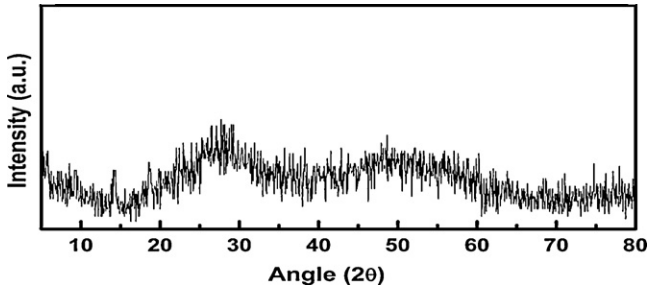

Fig. 1. XRD pattern of $Se_{84}Te_5Sn_5In_6$ chalcogenide glass.

The ampoules were heated in an electronic furnace at the rate of 3–4 K/min up to 1098 K for 12 h. They were frequently rocked to ensure homogeneity of the samples. The molten samples were then rapidly quenched in ice-cooled water to obtain the alloys in their glassy state. The X-ray diffraction pattern of as-prepared samples was recorded using Philips PW-1700 powder diffractometer (operating at 20 keV) with Cu Kα (λ = 1.54056 Å) radiation to confirm the glassy nature of alloys. The XRD pattern of $Se_{84}Te_5Sn_5In_6$ glass is shown in Fig. 1. The thermal behavior of each sample was investigated using a DSC instrument (Model: Shimadzu DSC-60). The DSC equipment was calibrated prior to measurements, using high purity standards, Pb, Sn and In with well known melting points. The instrument constant was deduced by measuring the total area of the complete melting endotherms of the above mentioned standard materials using the well known melting enthalpy of these standards. The results of temperature and enthalpy calibrations obtained for the standard materials were within 3% of the values given in the literature [32] and the instrument constant is obtained and comes out to be 1.5. The operation of a differential scanning calorimeter is based on measurement of the thermal response of an unknown specimen as compared with a standard when the two are heated uniformly. A typical DSC consists of two sealed pans: a sample pan and a reference pan (which is generally an empty sample pan). These pans are often covered by lids that act as a radiation shield. The two pans are heated, or cooled, uniformly while the heat flow difference between the two is monitored. This can be done at a constant temperature (isothermally), but is more commonly done by changing the temperature at a constant rate (non-isothermally) as reported in the present work. Typically, 10 mg of the sample in powder form was used in standard aluminum pans and heated at four different rates ranging from 5 to 20 K/min. The accuracy of the heat flow was ±0.01 mW and the temperature precision as determined by the microprocessor of the thermal analyzer was ±0.1 K.

3. Results and discussion

A typical DSC thermogram showing the endothermic effects obtained at heating rate 15 K/min of glassy $Se_{90-x}Te_5Sn_5In_x$ (x = 0, 3, 6 and 9) alloys is shown in Fig. 2. The heating rate dependences of glassy $Se_{81}Te_5Sn_5In_9$ alloy are shown in Fig. 3. It is clear from these figures that well defined peaks are observed at glass transition temperatures (T_g). The characteristic phenomena (endothermic and exothermic peaks) are evident in the DSC thermograms in the temperature range of investigation. From the analysis point of view, the DSC thermogram is divided into two parts: the first one corresponds to the glass transition region represented by an endothermic event and the other part is related to the crystallization process indicated by exothermic part of DSC curve. The glass transition temperature, T_g, is identified from the endothermic peak in the DSC signal. Calorimetric studies were made under non-isothermal conditions at different heating rates. T_g was taken as the temperature corresponding to the intersection of the two linear portions adjoining

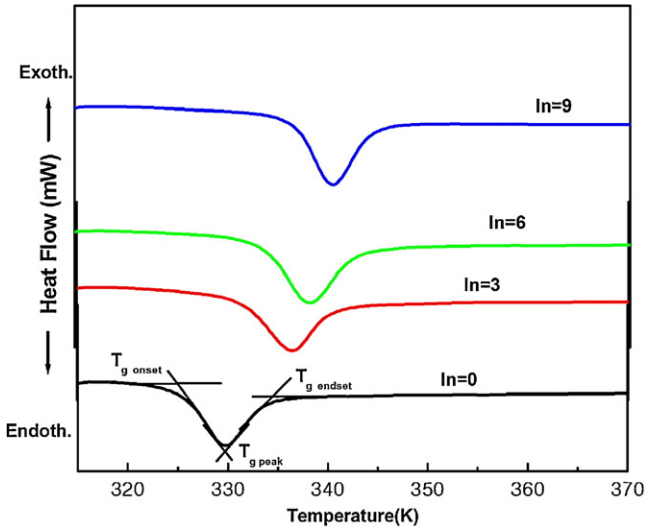

Fig. 2. DSC thermograms of the $Se_{90-x}Te_5Sn_5In_x$ (x = 0, 3, 6, and 9) chalcogenide glasses at 15 K/min heating rate for glass transition region.

the transition elbow in the DSC traces of endothermic peak (see Fig. 2). It is evident from Fig. 2 that T_g shifts to higher temperatures with increasing heating rate. The pronounced variation of T_g with heating rate is a manifestation of the kinetic nature of the glass transition. The relatively large endothermic peaks observed in the present work are most likely due to aging effect. The samples used in this study were stored at room temperature for a considerable period of time. As the output of the DSC during heating is proportional to the heat capacity, it is a straightforward and convenient method of detecting the glass transition and investigating its kinetics.

3.1. Variation of glass transition temperature

The variation of T_g with average coordination number for $Se_{90-x}Te_5Sn_5In_x$ (x = 0, 3, 6, 9) alloys is shown in Fig. 4. It is clear

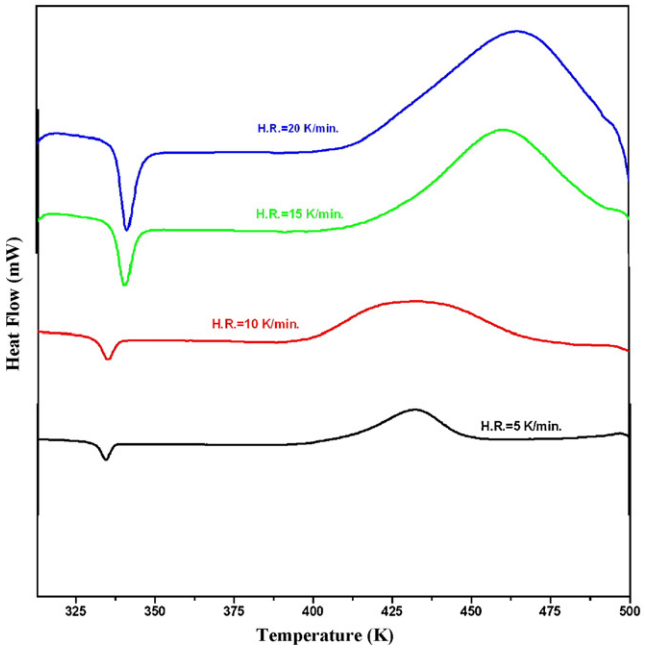

Fig. 3. DSC thermogram of the $Se_{81}Te_5Sn_5In_9$ chalcogenide glass at heating rates 5, 10, 15 and 20 K/min.