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Effect of antimony addition on thermal stability and crystallization kinetics of germanium–selenium alloys

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ABSTRACT

Chalcogenide glasses are promising materials for threshold and memory switching. Alloys of $Ge_{19}Se_{81-x}Sb_x$ ($x = 0, 4, 8, 12, 16, 17.2, 20$) have been prepared by melt quench technique. Differential thermal analysis has been used to characterize samples at different heating rates ($\alpha = 5, 10, 15, 20$ K/min). Glass transition temperatures, crystallization temperature, melting temperature, activation energy for glass transition and crystallization have been determined. Thermal stability of alloys has been analyzed in terms of ease by which atomic rearrangements take place and the resistance to devitrification. The correlation between thermal stability and glass forming ability has also been studied.

1. Introduction

Chalcogenide glasses have drawn a great attention due to their electrical, optical and thermal properties [1–5]. These properties of chalcogenide glasses are found to vary with composition, heat treatment, irradiation and glass forming method, etc. [6]. These characteristics are used in various applications like optical data storage devices, infrared detectors, optical fibers, etc. [7]. Glasses exhibiting no crystallization reaction above the glass transition (T_g) show threshold switching [8,9]. On the other hand, glasses exhibiting crystallization reaction above T_g exhibit memory switching. Memory switches are formed at the boundaries of glass-forming regions where glasses are stable and have tendency to crystallize when heated or cooled slowly [8].

In chalcogenides, each atom needs two neighbors to satisfy the valence requirements. Amorphous *Se* in its pure form consists of mixture of two structural species i.e. long helical chains and eight member rings held to each other by weak Van der Waals forces [10]. However, glassy *Se* has some shortcomings such as short lifetime and thermal instability. To overcome these difficulties *Ge* is added to *Se*, which strengthens the network by cross-linking the *Se* chain structure [11]. The addition of third element causes compositional and structural disorder leading to an increase in glass forming region [12,13]. *Sb* added *Ge–Se* system has shown interesting physical and optical properties [11,14]. This motivates to study thermal stability and crystallization kinetics for *Ge–Se–Sb* system.

Differential thermal analysis (DTA) has been performed on $Ge_{19}Se_{81-x}Sb_x$ to study the glass transition temperature (T_g), crystallization temperature (T_c) and melting temperature (T_m), thermal stability and ease of glass formation at different heating rates ($\alpha = 5, 10, 15, 20$ K/min). Dependence of T_g on the heating rate has been investigated. Activation energy for glass transition and crystallization has also been calculated using various methods [15–20]. For DTA study, non-isothermal method has been used due to its applicability on a wide range of temperature and quick analysis in shorter time period [21].

2. Experimental details

Melt quench technique has been used for alloy preparation of $Ge_{19}Se_{81-x}Sb_x$ ($x = 0, 4, 8, 12, 16, 17.2, 20$) samples. Detailed sample preparation procedure is given elsewhere [14]. X-ray diffraction spectra of bulk samples were obtained from an X-ray diffractometer [X'Pert Pro]. The analysis of spectra reveals that the bulk samples were amorphous in nature as no distinguishable peaks were observed. The freshly prepared materials were ground to fine powder and were taken in the alumina pan for the DTA studies (EXSTAR TG/DTA 6300). For each DTA scan, 10 mg of powder was used with different heating rates, 5, 10, 15 and 20 K/min. The melting temperature and melting enthalpy of high purity indium, zinc and lead were used to calibrate the instrument and the measurements were carried out in nitrogen atmosphere at a flow rate of 200 ml/min. All the measurements were made under non-isothermal conditions.

3. Results and discussion

3.1. Glass transition temperature, crystallization temperature and melting temperature

Figs. 1 and 2 show DTA thermograms of $Ge_{19}Se_{81-x}Sb_x$ alloys, having well defined endothermic step at glass transition temperature (T_g) and exothermic at crystallization temperature (T_c) for $x = 0$ and

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17.2 at the heating rate of 5, 10, 15, and 20 K/min (as reference). T_g represents the strength and rigidity of glass structure. An exothermic peak (originated from the amorphous-crystalline phase) gives the value of crystallization temperature. Third peak, which is endothermic, indicates the melting temperature (T_m). Values of T_g, T_c and T_m (Table 1) are found to increase up to $x = 17.2$ and thereafter decrease with *Sb* addition. T_c, T_g and T_m increase with increase in heating rate. T_g shows maximum at $Ge_{19}Se_{63.8}Sb_{17.2}$ glasses, the polymeric chains get reduced and system becomes cross linked. For $x = 17.2$, *Se* chains are completely cross linked and structural units of tetrahedral $Ge(Se_{1/2})_4$ and trigonal Sb_2Se_3 are formed [11]. Hence system changes from two dimensional to three dimensional network. The maximum value of T_g at $x = 17.2$ may also be explained on account of the presence of stable heteropolar bonds only. This makes the $x = 17.2$ composition most stable.

3.2. Glass forming ability and reduced glass transition temperature

The glass forming ability (K_{gl}) is calculated from Hruby's parameter [22]

$$K_{gl} = \frac{T_c - T_g}{T_m - T_c} \tag{1}$$

where $T_c - T_g$ represents the nucleation process and $T_m - T_c$ indicates the growth process.

Reduced glass transition temperature (T_{rg}) can be calculated as [23]

$$T_{rg} = \frac{T_g}{T_m}. \tag{2}$$

It has been observed that the obtained values (Table 2) obey the two third rule which is given as; $T_g/T_m = 2/3$. T_{rg} values indicate the ease of glass formation in all samples. The value of K_{gl} (Table 2) increases with the addition of *Sb* content till $x = 17.2$ and with further *Sb* addition K_{gl} decreases. The kinetic resistance to crystallization is higher for larger differences between T_c and T_g. There is an increase in difference between T_c and T_g up to $x = 17.2$ due to delay in nucleation process (slow crystallization). This leads to enhanced thermal stability and hence increases the glass forming ability. The decreased nucleation rate leads to increase in viscosity [24], implying that the glass forming ability increases up to $x = 17.2$ of *Sb*. With further addition of *Sb*, $x = 20$, difference between the two temperatures decreases causing rapid crystallization. On the basis of conductivity, *Sb* is a semi-metal with higher conductivity. This decreases the difference between crystalline and glassy states and makes the glass less stable.

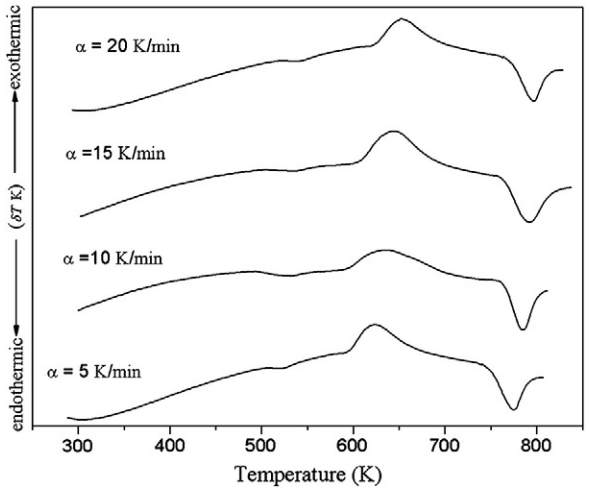

Fig. 1. DTA thermograms for $Ge_{19}Se_{81}$ alloys at heating rate of 5, 10, 15 and 20 K/min.

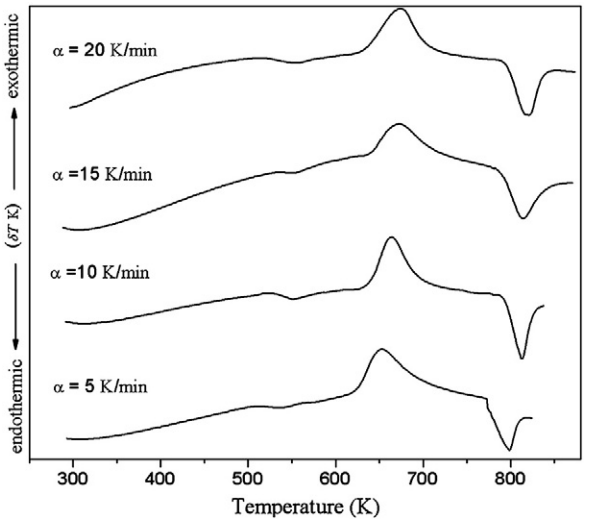

Fig. 2. DTA thermograms for $Ge_{19}Se_{63.8}Sb_{17.2}$ alloys at heating rate of 5, 10, 15 and 20 K/min.

3.3. Dependence of glass transition temperature on the heating rate and the activation energy for glass transition temperature

The dependence of glass transition temperature (T_g) on heating rate has been analyzed using empirical relation [25];

$$T_g = A + B\ln(\alpha) \tag{3}$$

where *A*, and *B* are constants and α is the heating rate for the given glass compositions. The values of *A* and *B* have been obtained from the intercept and slope in Fig. 3. The value of *A* indicates the glass

Table 1
Values of glass transition temperature (T_g), crystallization temperature (T_c) and melting temperature (T_m) for $Ge_{19}Se_{81-x}Sb_x$ ($x = 0, 4, 8, 12, 16, 17.2, 20$) glassy alloys at different heating rates α.

Sample	α (K/min)	T_g (K)	T_c (K)	T_m (K)
$x = 0$	5	520.00	622.00	775.00
	10	530.00	636.00	784.00
	15	536.00	645.48	792.00
	20	540.00	654.34	799.00
$x = 4$	5	524.00	627.00	780.00
	10	533.00	642.00	790.00
	15	540.00	651.00	796.00
	20	543.27	659.00	802.00
$x = 8$	5	529.00	634.00	784.00
	10	537.00	647.00	795.00
	15	544.35	657.00	801.00
	20	548.00	665.00	806.00
$x = 12$	5	531.00	640.00	789.00
	10	540.00	653.5	801.00
	15	546.59	662.00	806.00
	20	549.67	671.00	811.00
$x = 16$	5	534.00	645.00	792.00
	10	543.00	657.61	806.00
	15	549.70	668.00	810.00
	20	552.00	675.00	817.00
$x = 17.2$	5	537.00	649.00	798.00
	10	546.00	663.72	812.00
	15	551.81	672.25	815.00
	20	555.44	679.18	821.00
$x = 20$	5	535.00	646.76	797.00
	10	544.00	659.93	810.00
	15	550.47	670.00	813.00
	20	553.00	676.82	819.00