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Crystallisation kinetics and thermal stability analysis of $Se_{82-x}Te_{15}Sn_3Sb_x$ $(0 \leq x \leq 6)$ glassy alloys

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ABSTRACT

This paper reports the results of study of crystallization kinetics and thermal stability in $Se_{82-x}Te_{15}Sn_3Sb_x$ $(0 \leq x \leq 6)$ glassy alloys. The alloys were analysed using DTA (differential thermal analysis) technique under non-isothermal conditions at heating rates of 5, 10, 15, 20 K/min, Activation energy of glass transition has been evaluated using Kissinger and Moynihan methods while Matusita, Kissinger and Augis and Bennett approaches has been employed to study the crystallization mechanism. Thermal stability and glass forming ability for all compositions has been analysed in terms of reduced glass transition temperature and Hruby's parameter.

1. Introduction

Chalcogenide glasses find numerous application in modern electronic devices, memory switching, optoelectronics and xerography etc. due to their special properties such as higher transparency in IR region and low optical losses [1–5]. These glasses offer the additional advantage of wide range tuning of their properties by varying the composition. Chalcogen elements S, Se and Te can be alloyed with elements from other groups to form binary, ternary or quaternary systems with tailor made properties and use in specific applications. Addition of a new element to a glass system introduces the configurational disorder in the system and changes its various physical properties such as thermal, optical and electrical [6]. This aspect of chalcogenide glasses has been extensively exploited by scientific community to form new glass systems with improved properties for specific applications [7–13]. Researchers have shown particular interest in glass systems containing heavy elements such as Sn and Sb for their advantage of better transmittance in IR region. Thermal and optical properties of Sn—Sb—Se—Te have been reported by Chander and Thangaraj [14]. Chen et al. reported the physical and thermal properties of Ge—Sb—Se—Sn glasses [16]. Addition of Sn to Se—Te matrix is known to improve its crystallization ability and affects the dimensionality of growth [17]. Nidhi and co-workers have reported the effect of Sb substitution on thermal properties of Te—Se—Ge glass system [15]. They concluded that incorporation of Sb in Te—Se—Ge network introduces strain in the system due to large size of Sb atoms and weakens the glass system. This leads to enhancement in the suitability of this system for phase change applications. This observation prompted the authors to study the effect of Sb addition in Se—Te—Sn glass system. All glasses have a tendency to crystallize and crystallization is a thermally activated process. Understanding of crystallization mechanism and glass transition of a system is very important for determining its suitability for memory and switching applications [18]. In the present work we have studied the crystallization kinetics of $Se_{82-x}Te_{15}Sn_3Sb_x$ $(0 \leq x \leq 6)$ glass system using differential thermal analysis and computed the crystallization parameters for these compositions using different models. Composition dependence of crystallization parameters have been discussed.

2. Experimental techniques

Glass samples of $Se_{82-x}Te_{15}Sn_3Sb_x$ $(0 \leq x \leq 6)$ were prepared using melt quenching technique. The constituent elements of 99.999% purity were weighed as per atomic percentages and sealed in evacuated quartz ampoules. The ampoules were heated in rocking furnace to 900 °C at a heating rate of 2–3 °C per minute. The ampoules were rocked at a constant rate to ensure homogeneity of the mixture. The samples were maintained at 900 °C for 24 h and then quenched in ice cold water. The amorphous nature of bulk samples prepared was confirmed using x-ray diffraction (XRD) technique. The XRD scans for prepared samples are shown in Fig. 1.

The samples in powder form were analysed for thermal studies using differential thermal analysis (DTA) technique in nitrogen atmosphere under non-isothermal conditions. DTA scans were obtained from room temperature to about 600 K at heating rates of 5, 10, 15 and 20 K/

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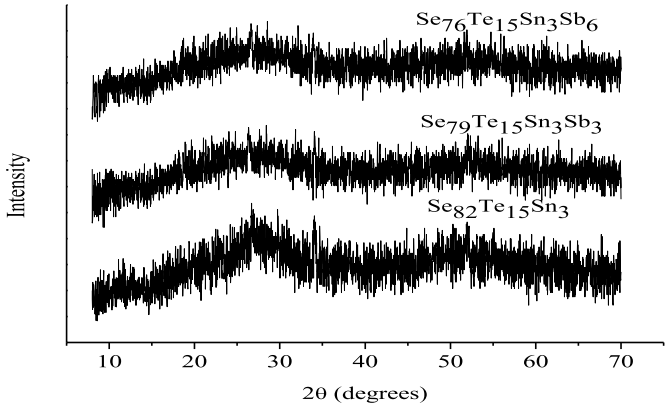

Fig. 1. XRD scans for $Se_{82-x}Te_{15}Sn_3Sb_x$ (x = 0, 3, 6).

min for all the samples.

3. Results and discussion

DTA scans for $Se_{76}Te_{15}Sn_3Sb_6$ for different heating rates are shown in Fig. 2. Similar scans were obtained for other compositions. All the scans showed well defined endothermic and exothermic peaks corresponding to glass transition temperature and crystallization respectively. Glass transition temperature was taken as the temperature corresponding to the intersection of two linear portions of transition elbow in endothermic direction in DTA scans. Glass transition temperature (T_g), peak crystallization temperature (T_p) and melting points calculated from the thermograms are summarized in Table 1.

3.1. Glass transition and activation energy

The glass transition temperature (T_g) has been found to be increasing with increasing Sb concentration. This can be explained on the basis of chemical bond approach, according to which heteropolar bonds are preferred over homopolar bonds and bonds are formed in decreasing order of energy [19]. With the introduction of Sb in Se—Te—Sn system, number of weaker homopolar Se—Se bonds (bond energy 44 kcal/mol) decrease and relative number of stronger Se—Te (44.19 kcal/mol) and Se—Sn (49.23 kcal/mol) bonds increase leading to increase in glass transition temperature with increasing Sb concentration. The variation of T_g with Sb content is shown in Fig. 3. It is observed that T_g and T_p shifts towards higher side with increasing heating rate.

The variation of T_g with heating rate has been analysed using the empirical relation by Lasocka [20].

$$T_g = A + Bln(\alpha)$$

where α is the heating rate and A and B are constants for a glass

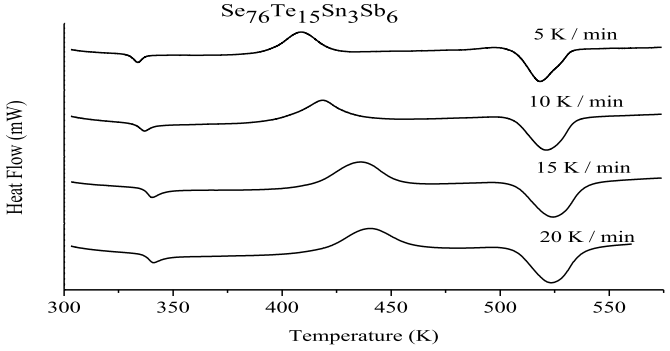

Fig. 2. DTA scan for $Se_{76}Te_{15}Sn_3Sb_6$ at heating rates of 5, 10, 15 and 20 K/min.

Table 1
Values of Glass transition temperature (T_g), Peak crystallization temperature (T_p), Melting point (T_m), Hurby's parameter (H_r) and Reduced glass transition temperature (T_{rg}) for $Se_{82-x}Te_{15}Sn_3Sb_x$ ($0 \le x \le 6$) at different heating rates.

Heating rate		x = 0	x = 3	x = 6
5 K/min	T_g	44.8	50.2	56.1
	T_p	112.3	109.5	134.6
	T_m	243.0	241.1	245.5
	H_r	0.52	0.45	0.71
	T_{rg}	0.62	0.63	0.63
10 K/min	T_g	47.4	52.5	59.1
	T_p	123.3	122.6	145.2
	T_m	244.6	249.5	248.4
	H_r	0.63	0.55	0.83
	T_{rg}	0.62	0.62	0.64
15 K/min	T_g	49.3	55.6	62.8
	T_p	130.1	128.3	161.8
	T_m	246.2	251.3	251.6
	H_r	0.70	0.59	1.10
	T_{rg}	0.62	0.63	0.64
20 K/min	T_g	50.2	56.1	63.0
	T_p	134.4	133.4	165.9
	T_m	247.1	249.5	250.8
	H_r	0.75	0.67	1.21
	T_{rg}	0.62	0.63	0.64

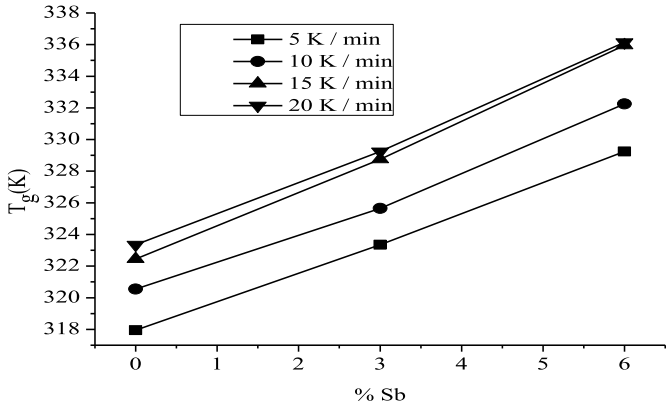

Fig. 3. Variation of glass transition temperature (T_g) with Sb concentration at different heating rates.

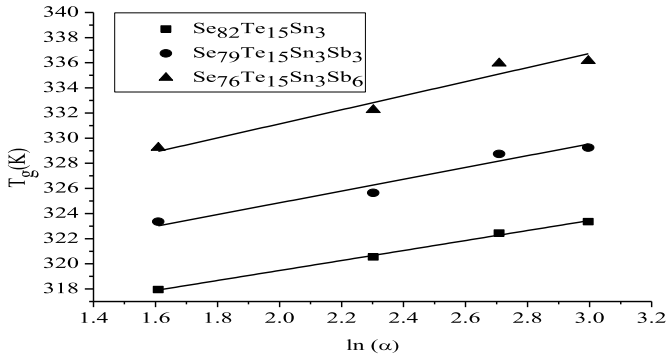

Fig. 4. Plot of glass transition temperature (T_g) with ln α.

composition. While A represents the glass transition temperature for 1 K/min, B indicates the structural changes in the system and depends on the quenching rate. The plot of Tg with ln (α) is shown in Fig. 4.

The calculate values of B for various glass compositions are summarized in Table 2. The values of B vary from 3.97 to 5.36 indicating structural changes in the glass with change in composition.

The apparent glass transition activation energy has been evaluated using the Kissinger equation [21].