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Glass transition and crystallization kinetics analysis of Sb–Se–Ge chalcogenide glasses

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Abstract Differential thermal analysis (DTA) has been employed to investigate the effect of Ge addition on the glass transition behavior and crystallization kinetics of $Sb_{10}Se_{90-x}Ge_x$ ($x = 0, 19, 21, 23, 25, 27$) alloys. The three characteristic temperatures viz. glass transition (T_g), crystallization (T_c), and melting (T_m) have been determined and found to vary with the heating rates and Ge content. Thermal stability and glass forming tendency have been evaluated in terms of ΔT ($= T_c - T_g$) and reduced glass transition temperature. The activation energies for glass transition and crystallization have been used to analyze the nucleation and growth process. The activation energy analysis also determines the suitability of alloys to be used in switching applications. Results have been interpreted in terms of bond energies and structural transformations in the investigated alloys.

Keywords Non-isothermal kinetics · Glass transition kinetics · Activation energy · Cohesive energy

Introduction

The thermal stability of chalcogenide glasses is related to the nucleation and growth processes which in turn depend on glass transition and crystallization kinetics [1]. The two processes glass transition and crystallization, limit the applications of inorganic glassy materials. Chalcogenide glasses can be potentially used in threshold and memory switching devices [2, 3]. Glassy alloys must be stable in the amorphous state at low temperature and should have a short crystallization time to be used as an optical recording media [4]. The switching properties depend upon crystallization temperature (T_c) and hence, the thermal stability of the glasses. These characteristics rely on the composition of the system. Higher the value of T_c for a particular composition more will be the thermal stability of the glass [5] and therefore, better will be its suitability for applications.

Amorphous Se deteriorates in xerographic properties near glass transformation region [6]. Adding Sb to Se leads to greater hardness, higher sensitivity, conductivity and smaller ageing effects in comparison to pure a–Se [7]. The a–SbSe glass has potential applications in photoconductive elements [8]. But, these properties are restricted by the rapid crystallization of stoichiometric composition Sb_2Se_3 [9]. Sb–Se glasses can be stabilized by adding Ge, as the physical and optical properties change, when it substitutes Se atoms and hence may increase the stability [10, 11]. In $Sb_{10}Se_{90-x}Ge_x$ system, $x = 25$ shows highest optical band gap, and structure stability [10–12]. So, the thermal study of $Sb_{10}Se_{90-x}Ge_x$ system may present an insight into the configurational and conformal changes.

The paper deals with the study of glass-crystal transformation of $Sb_{10}Se_{90-x}Ge_x$ ($x = 0, 19, 21, 23, 25, 27$) alloys. Differential thermal analysis has been used to determine the glass transition (T_g), crystallization (T_c), and melting (T_m) temperature of alloys. Non-isothermal technique is used instead of isothermal technique as it can be performed rapidly and the temperature range of measurements can be

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extended. The thermal stability and glass forming tendency have been studied in terms of ΔT (= $T_c - T_g$) and reduced glass transition temperature (T_{rg}). Heating rate dependence of T_g has been evaluated. The activation energy of glass transition has been determined by Moynihan's method and Kissinger's method. The activation energy of crystallization has been calculated using Mahadevan's method and Augis-Benett method. The results using different methods have been analyzed and compared.

Experimental

Bulk samples of $Sb_{10}Se_{90-x}Ge_x$ (x = 0, 19, 21, 23, 25, 27) were prepared using melt quench technique. The detailed experimental procedure for sample preparation is given elsewhere [11]. The composition of the bulk samples was analyzed using a scanning electron microscope (SEM) (Zeiss EVO 40 EP with EDAX attachment operated at 20 kV). The amorphous state of the alloys was confirmed by the absence of sharp peaks in the X-ray diffraction peaks (X'Pert PRO) [11]. The thermal behavior of the samples was investigated using DTA (EXSTAR TG/DTA 6300). DTA runs were taken at four different heating rates 5, 10, 15, and 20 K min^{-1}. For each run, approximately 10 mg of the sample was taken in alumina pans in an atmosphere of dry nitrogen at a flow rate of 200 mL min^{-1} under non-isothermal conditions. The analyzer was calibrated prior to the measurements using the known latent heats of high purity elements zinc, indium and lead. The temperature precision of microprocessor of thermal analyzer was ±0.1 K.

Results and discussion

EDAX indicates that the atomic mass percentages of the constituent elements are close to their starting elements (Table 1).

In the studied temperature range for DTA, three characteristic peaks are observed. The first endothermic peak corresponds to T_g, second exothermic peak to T_c and third endothermic peak to melting T_m. T_g represents the rigidity of the system. Hence, it provides valuable information about the thermal stability of the glass. Crystallization process is a heating rate dependent phenomenon because nucleation is a thermally activated process whereas T_g depends on heating rate (α) due to relaxation processes [1]. Figures 1, 2 and 3 shows the three characteristic temperatures for $Sb_{10}Se_{90-x}Ge_x$ (x = 0, 19, 21, 23, 25, 27) samples at different heating rates. The difference between T_g and T_c increases with an increase in *Ge* alloying concentration, pointing toward the stability of the system. The three parameters, T_g, T_c, and T_m increase with increase in heating rate for all the samples. T_g attains maximum value for $Sb_{10}Se_{65}Ge_{25}$ because Ge on entering the polymeric structure of $Sb_{10}Se_{90}$ forms tetrahedral $Ge(Se_{1/2})_4$ units, in addition to trigonal Sb_2Se_3 units, replacing the Se–Se bonds [12]. At x = 25, the system becomes heavily cross linked with the formation of Sb_2Se_3 and $Ge(Se_{1/2})_4$ units only and becomes completely rigid. On further increase of Ge content, at x = 27, the system contains homopolar Ge–Ge bonds in addition to Sb_2Se_3 and $Ge(Se_{1/2})_4$ structural units, thereby decreasing T_g [12].

The thermal stability factor, ΔT [13], indicates thermal stability of the glass. The ease of glass formation can also be determined by evaluating T_{rg} (= T_g/T_m) values which obey two-third rule [14]. The T_{rg} values are found to be of the order of 2/3 (Table 2) indicating a good glass forming

Table 1 Elemental composition of bulk glasses

Composition	Sb	Se	Ge
$Sb_{10}Se_{90}$	10.83	89.17	0
$Sb_{10}Se_{71}Ge_{19}$	9.86	71.56	18.58
$Sb_{10}Se_{69}Ge_{21}$	9.96	69.84	20.20
$Sb_{10}Se_{67}Ge_{23}$	10.10	67.73	22.17
$Sb_{10}Se_{65}Ge_{25}$	10.37	64.13	25.50
$Sb_{10}Se_{63}Ge_{27}$	10.41	61.85	27.74

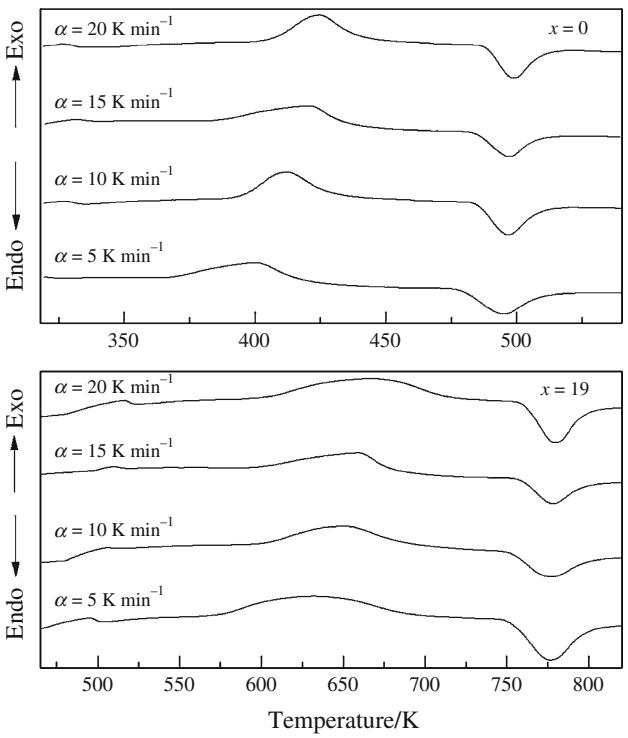

Fig. 1 DTA traces of $Sb_{10}Se_{90}$ and $Sb_{10}Se_{71}Ge_{19}$ glassy alloys at heating rates 5, 10, 15 and 20 K min^{-1}

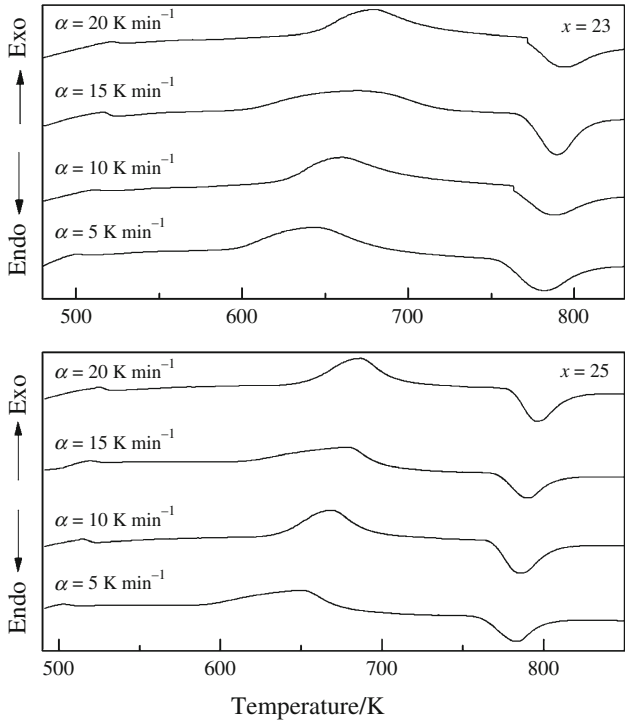

Fig. 2 DTA thermograms for $Sb_{10}Se_{69}Ge_{21}$ and $Sb_{10}Se_{67}Ge_{23}$ glassy alloys at heating rates 5, 10, 15 and 20 K min^{-1}

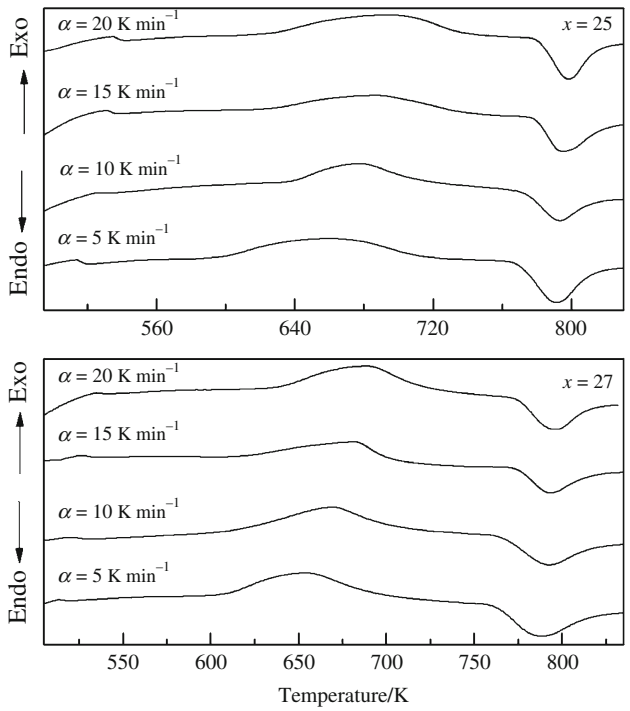

Fig. 3 DTA scans of $Sb_{10}Se_{65}Ge_{25}$ and $Sb_{10}Se_{63}Ge_{27}$ glassy alloy at heating rates 5, 10, 15 and 20 K min^{-1}

tendency of the material. The values of ΔT increase with increase in Ge content showing maximum at 25 at.% Ge and then decreases for 27 at.% (Table 2). The kinetic

Table 2 Values of glass transition (T_g), crystallization (T_c), melting (T_m) temperatures, thermal stability parameter (ΔT) and reduced glass transition temperature (T_{rg}) at 10 K/min for $Sb_{10}Se_{90-x}Ge_x$ ($x = 0$, 19, 21, 23, 25, 27) glassy alloys

Sample	T_g/K	T_c/K	T_m/K	ΔT/K	T_{rg}
$x = 0$	335.45	412.48	496.59	77.03	0.6755
$x = 19$	512.71	650.91	777.04	138.20	0.6598
$x = 21$	518.45	660.61	788.37	142.16	0.6576
$x = 23$	523.36	669.37	786.17	146.01	0.6657
$x = 25$	531.47	678.74	793.71	147.27	0.6696
$x = 27$	530.28	670.30	792.71	140.02	0.6689

resistance to crystallization increases with increase in the ΔT values. This leads to a slowdown of nucleation rate due to the increase in viscosity of the system [15]. Thus, $Sb_{10}Se_{65}Ge_{25}$ shows maximum thermal stability and lower crystallizing ability.

The heating rate dependence of T_g can be evaluated using the empirical relation [16],

$$T_g = A + B \ln \alpha, \tag{1}$$

where A indicates T_g at a heating rate of 1 K min^{-1} and B is related to the cooling rate of the melt. The values of A and B (Table 3) have been determined from the intercept and slope respectively, in Fig. 4. A shows variation similar to that of T_g, obtained from the DTA thermograms. B corresponds to the time response of configurational changes within the glass transition region to the heating rate. The values of activation energy of glass transition (E_g) have been calculated from heating rate dependence of T_g using two methods [17, 18].

In the first method, the heating rate dependence of T_g in terms of thermal relaxation phenomenon is given by Moynihan et al. [17] as,

$$\mathrm{d}(\ln \alpha)/\mathrm{d}\left(1/T_g\right) = -E_g/R, \tag{2}$$

where E_g is activation energy of glass transition and R is gas constant. The slope of $ln\ \alpha$ versus $1{,}000/T_g$ graph in Fig. 5a gives the activation energy involved in molecular motions and rearrangements around T_g. The slope increases with rise in the Ge content to maximum at 25 at.% Ge alloying and decreases with further Ge addition. Activation energy values obtained depend on the thermal history of the sample as the thermal relaxation depends on the temperature as well as structure.

The dependence of T_g on heating rate can also be found using Kissinger's equation [18], suggested for crystallization processes with spherical nuclei and having less dependence on thermal history of the sample, as,

$$\ln\left(\alpha/T_g^2\right) = -E_g/RT_g + \text{constant}, \tag{3}$$

Table 3 Values of A, B, activation energies for $Sb_{10}Se_{90-x}Ge_x$ ($x = 0$, 19, 21, 23, 25, 27) glassy alloys

Sample	A/K	B	E_g/kJ mol^{-1} [17]	E_g/kJ mol^{-1} [18]	E_c/kJ mol^{-1} [20]	E_c/kJ mol-1 [21]
$x = 0$	308.76	11.74	79.62	73.97	79.21	75.80
$x = 19$	479.01	14.89	146.76	138.20	137.78	132.37
$x = 21$	483.84	14.98	148.84	140.19	142.11	136.61
$x = 23$	489.15	15.06	151.26	142.60	144.77	139.19
$x = 25$	496.68	15.32	153.34	144.52	147.85	142.19
$x = 27$	494.93	15.29	152.51	143.69	146.52	140.94

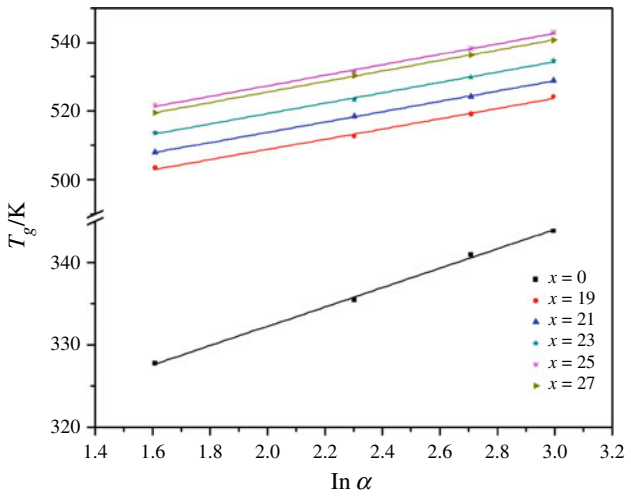

Fig. 4 Dependence of glass transition temperature (T_g) on heating rate (α) for $Sb_{10}Se_{90-x}Ge_x$ ($x = 0$, 19, 21, 23, 25, 27) glassy alloys

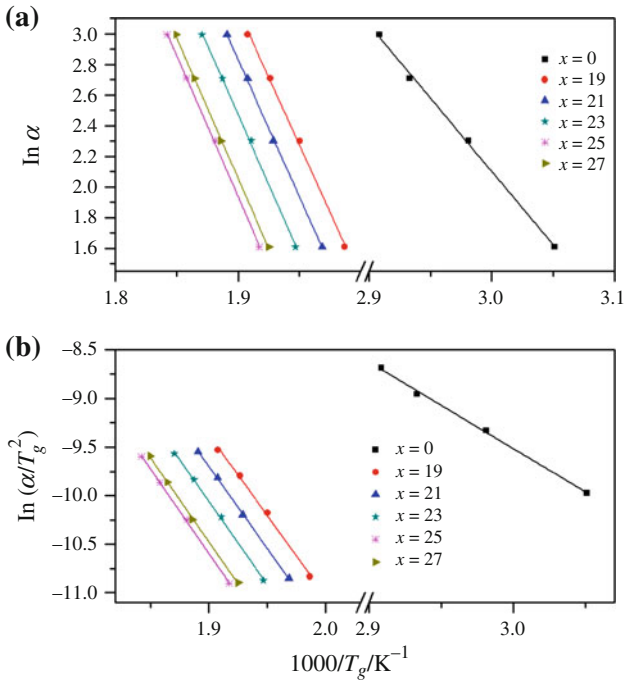

Fig. 5 Plot of **a** ln α versus 1,000/T_g, **b** ln (α/T_g^2) versus 1,000/T_g for $Sb_{10}Se_{90-x}Ge_x$ ($x = 0$, 19, 21, 23, 25, 27) glassy alloys

where R is gas constant. The activation energy values obtained from Fig. 5b are in good agreement with those obtained using Moynihan's method, with a maximum in E_g at $x = 25$.

Variation in values of activation energy calculated (Table 3) by different methods is due to dissimilar approximations used in the models. On heating the sample in DTA furnace, atoms undergo transitions between the local potential minima having different characteristic structures in the configuration space and energy barriers. The internal energy associated with the most stable local minimum is lowest and hence, corresponds to the most stable structure. The atoms can jump more easily to these metastable states [19].

The crystallization involves three types of activation energies *i.e.,* nucleation, growth and whole crystallization process. The activation energy for growth may be taken equal to the crystallization process, provided it is evaluated using thermal analysis. Activation energy of crystallization (E_c) has been evaluated using different approaches given by [20, 21].

Firstly, Mahadevan et al. [20] have proposed an approximation for the calculation of E_c using,

$$\ln \alpha = -E_c/RT_c + \text{constant} \tag{4}$$

The activation energy is evaluated from the slopes in Fig. 6a and found to be maximum for $x = 25$ at.%.

In second approach, Augis and Benett [21] also suggested a method for the evaluation of crystallization activation energy using relation,

$$\ln\left(\alpha/T_c\right) = -E_c/RT_c + \ln K_0, \tag{5}$$

where K_0 is the frequency factor. This method is preferred over other methods as the values of kinetic parameter K_0 in addition to E_c can be obtained. The slope in this relation gives the value of E_c. The value of E_c increases to maximum as Ge is added to $Sb_{10}Se_{90}$ till 25 at.% alloying and then decreases as shown in Fig. 6b.

The values of E_c calculated using different methods are found to be in good agreement with each other (Table 3).

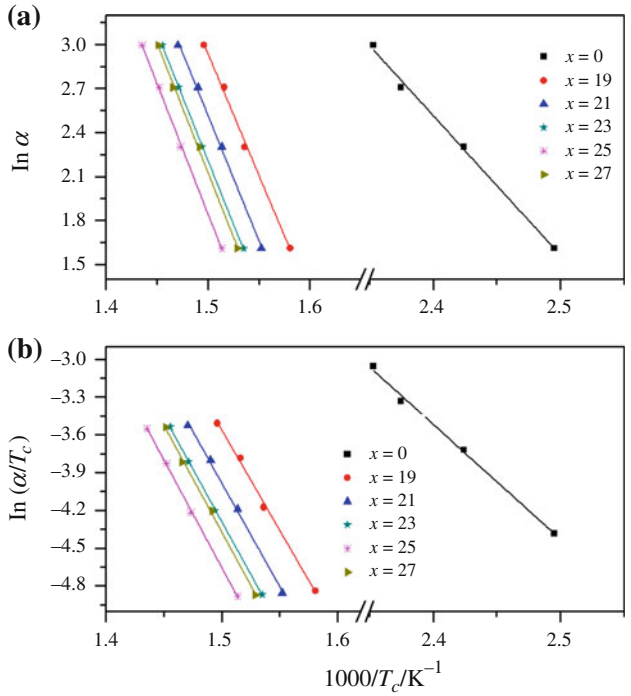

Fig. 6 Variation of **a** ln α with 1,000/T_c, **b** ln (α/T_c) with 1,000/T_c for $Sb_{10}Se_{90-x}Ge_x$ ($x = 0$, 19, 21, 23, 25, 27) glassy alloys

The variation in E_c values may be interpreted in terms of bond energies of the system. The bond energy of the heteropolar bond is [22],

$$E_{A-B} = (E_{A-A} \times E_{B-B})^{0.5} + 30(\chi_A - \chi_B)^2, \quad (6)$$

where E_{A-A} and E_{B-B} are the homopolar bond energies and χ_A and χ_B are corresponding electronegativities. According to chemical bond approach [23], atoms combine more favorably with the atoms of different kind than with the same kind. Bonds are formed in order of decreasing bond energies thereby favoring chemical order. The base binary system contains Sb–Se and Se–Se bonds with energies 43.96 and 44 kcal mol^{-1}, respectively [10]. On addition of Ge, additional Ge–Se bonds, having energy 49.92 kcal mol^{-1}, start replacing Se–Se bonds resulting in an increase of cohesive energy, $CE = \sum_i C_i E_i$, where C_i is the distribution of chemical bonds and E_i is the energy associated with bonds. At $x = 25$, the system emerges as a 3D structure with maximum cohesive energy containing only Ge–Se and Sb–Se heteropolar bonds [10]. The increase in the cohesive energy enhances the bonding strength, therefore, increasing T_c and hence E_c up to $x = 25$ [24]. The maximum value of E_c for $Sb_{10}Se_{65}Ge_{25}$ indicates that atoms in its glassy state require more energy to jump to the crystalline phase. Therefore, $Sb_{10}Se_{65}Ge_{25}$ is observed to be the most stable composition among investigated compositions. For $x = 27$, homopolar Ge–Ge bonds with energy 37.60 kcal mol^{-1} are also formed leading to a decrease in the cohesive energy [10]. The decrease in cohesive energy of the system reduces T_c and hence, E_c. Therefore, the atoms require less energy to overcome the barrier, decreasing the stability.

The evaluated parameters suggest that the investigated glasses are thermally stable and offer a wide temperature range for various applications like in threshold switching [25, 26].

Conclusions

Thermal studies have been carried out on $Sb_{10}Se_{90-x}Ge_x$ ($x = 0$, 19, 21, 23, 25, 27) under non-isothermal conditions using DTA. The three characteristic temperatures, glass transition (T_g), crystallization (T_c), and melting (T_m) increase to maximum for $x = 25$ and then decrease for $x = 27$ at.% Ge. This signifies an increase in the rigidity and resistance to devitrification of the glassy system. At $x = 25$, $T_c - T_g$ and activation energy of crystallization (E_c) show maximum which indicates that this composition is thermally stable with a complete three dimensional network and is less prone to phase separation. These properties suggest that the composition with $x = 25$ may be explored for threshold switching applications.

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