J Therm Anal Calorim (2011) 103:903–909
DOI 10.1007/s10973-010-1181-2

Effect of some chemical modifiers on the glass/crystal transformation in binary $Se_{90}In_{10}$ alloy

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Received: 4 September 2010 / Accepted: 9 November 2010 / Published online: 14 December 2010

Abstract This work reports the effect of Ge, Sb, Sn additives on the thermally activated glass to crystal phase transition in binary $Se_{90}In_{10}$ alloy. Differential scanning calorimetry (DSC) technique is used for this purpose. Different kinetic parameters of glass/crystal transformation have been calculated. The results are explained using the chemical bond approach for the covalent network of such glasses.

Keywords Recrystallization · Crystallization kinetics · Differential scanning calorimeter · Glasses · Chalcogenide glass · Semiconducting II–VI materials

Introduction

Glassy Selenium (g-Se) is very useful material from application point of view due to its current use as photoreceptors in TV vidicon pick-up tubes [1] and particularly in conventional xerographic machines and digital X-ray imaging [2, 3]. Recently, it has been pointed out that Se–In alloys have more advantages than g-Se from the technological point of view due to their greater hardness, higher crystallization temperature, higher photosensitivity and smaller ageing effects [2–9]. The energy band gap of glassy Se–In alloys is about 1.3 eV at 300 K [4]. This value is close to the theoretical optimum for solar energy conversion, and hence several attempts have been made to utilize glassy Se–In alloys in solar cells [5, 6]. Therefore, glassy Se–In alloys are used to extend the utility of g-Se.

In Se-In system, In_4Se_3, InSe, and In_2Se_3 were proved to be of particular interest because of their applicability in semiconductor technology, electrochemical and photovoltaic cells and switching devices [7–9]. Ternary systems combining In, Se and a metallic element as chemical modifier might present phases showing new interesting properties. The continued scientific interest in Se-In binary system is due to potential use of chalcogenides in phase change optical (PCO) recording, sensors and infrared fibre-optics [10–15].

In PCO recording, the recording of information is based on writing and erasing of amorphous marks in a crystalline layer of a phase change material with the help of a laser beam. In PCO technology, the laser pulse duration used to erase the recorded marks is usually several hundred nanoseconds. Hence, the amorphous to crystalline phase transformation in PCO recording layer material should be very fast so that erasing is possible in such a time scale. For this reason, the study of glass/crystal transformation is very important for the development of some new chalcogenide glasses as better PCO recording materials.

The structural modification method for controlling properties of glass chalcogenides by changing the material structure during its preparation was proposed by Ovshinsky [16]. Properties of chalcogenide glasses are usually affected by the addition of impurities as a third element. Most of these additives, especially when added to the melt, play the role of chemical modifier and occupy the lowest-energy configuration (i.e. satisfy the $(8 - N)$ rule where N is the valency of an atom).

A remarkable property of certain glass-forming liquids is that a fast mode of crystal growth is activated near the

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glass transition temperature T_g and continues in the glassy state. The kinetic parameters of glass transition in glassy Se–In system are, therefore, studied by various workers by changing the composition of a particular binary alloy using a third element as chemical modifier [17–19]. However, no serious attempt has been made to study the effect of changing the chemical modifier on glass transition kinetics and glass/crystal transformation of a Se–In alloy for particular composition, which is an interesting problem from both research and technological points of view. In this paper, we have studied the effect of some additives (Ge, Sb, Sn) on the glass/crystal transformation in a binary $Se_{90}In_{10}$ glass using differential scanning calorimetry (DSC) technique.

Theoretical basis

DSC technique is widely used for study of the kinetics of glass/crystal transformation. This method offers unique advantages: it is quite sensitive, not demanding with regard to sample preparation, and relatively independent of the sample geometry [20]. DSC measures a volume fraction transformed as a function of time (isothermal DSC) or temperature (non-isothermal) by measuring the heat released or absorbed during a phase change. In recent years, especially non-isothermal DSC measurements have become very attractive for the study of phase transformations. Non-isothermal experiments can be performed more rapidly than isothermal ones, and they can also be used to extend the temperature range of measurements beyond that accessible in isothermal experiments. Industrial processes often depend on the kinetic behavior of system undergoing phase transformations under non-isothermal conditions [21, 22]. In this respect, a definite measurement of non-isothermal transformations kinetics is desirable.

In DSC unit, the difference in heat flow to the sample and reference materials at the same temperature is recorded as a function of temperature. The heat flow and the heating rate can be expressed as:

$$\frac{\text{Heat}}{\text{Time}} = \frac{q}{t} = \text{Heat Flow} \quad (1)$$

$$\frac{\text{Temperaure increase}}{\text{Time}} = \frac{\Delta T}{t} = \text{Heating rate} \quad (2)$$

Dividing Eq. (1) by (2), we obtain the expression for heat capacity:

$$\frac{\left(\frac{q}{t}\right)}{\left(\frac{\Delta T}{t}\right)} = \frac{q}{\Delta T} = C_p = \text{Heat capacity} \quad (3)$$

In DSC technique, the reference material is an inert material such as alumina, or just an empty aluminium pan. The temperatures of both the sample and reference materials are increased at a constant rate. Since the DSC thermogram is recorded at constant pressure, heat flow is equivalent to enthalpy changes:

$$\frac{dQ}{dt} = \frac{dH}{dt} \quad (4)$$

Here (dH/dt) is the heat flow measured in mcal s^{-1}. The heat flow difference between the sample and reference materials is:

$$\Delta\left(\frac{dH}{dt}\right) = \left(\frac{dH}{dt}\right)_{\text{sample}} - \left(\frac{dH}{dt}\right)_{\text{reference}} \quad (5)$$

In an endothermic process, such as glass transition phenomenon and melting, heat is absorbed and, therefore, heat flow to the sample material is higher than that to reference material. Hence $\Delta(dH/dt)$ is positive for endothermic processes. In an exothermic process, such as crystallization phenomenon, heat is released and, therefore, the opposite is true, i.e., heat flow to the reference material is higher than that to sample material. Hence $\Delta(dH/dt)$ is negative for exothermic processes.

Experimental

Binary $Se_{90}In_{10}$ alloy and ternary $Se_{90}In_6M_4$ (M = Ge, Sb, Sn) alloys were prepared by a melt quenching technique. The exact proportions of high purity (99.999%) elements, in accordance with their atomic percentages, were weighed out using an electronic balance (LIBROR, AEG-120) with a sensitivity of 10^{-4} g. The materials were then sealed in evacuated ($\sim 10^{-5}$ Torr) quartz ampoules (length ~5 cm and internal diameter ~8 mm). Each ampoule was kept inside the furnace at a temperature of 1000°C (where the temperature was raised at a rate of 3–4°C/min.). During heating, all the ampoules were constantly rocked by rotating a ceramic rod to which the ampoules were attached in the furnace. This was done to obtain homogeneous glassy alloys.

After rocking for about 12 h, the obtained melts were cooled rapidly by removing the ampoules from the furnace and dropping rapidly into ice-cooled water. The ingots were then taken out by breaking the quartz ampoules. The size of the samples was ~3 cm in length and ~8 mm in diameter. The glassy nature of the alloys was ascertained by X-ray diffraction. The patterns were run in a normal 2θ scan, with Cu as target at 30 kV and 20 mA and with scanning speed 3°/min. The XRD pattern of glassy $Se_{90}In_6Ge_4$ alloy is shown in Fig. 1. It is clear that no sharp Bragg reflections were observed in the diffraction pattern. This confirms the glassy nature of $Se_{90}In_6Ge_4$ alloy.

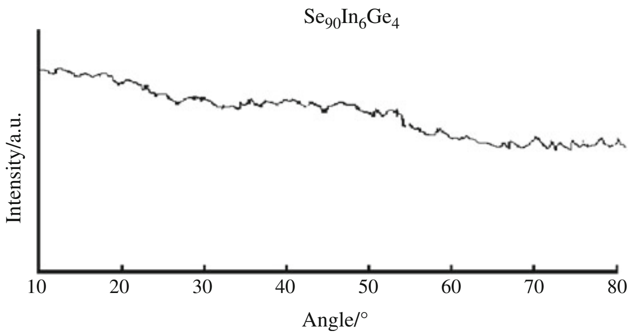


Fig. 1 XRD pattern of glassy $Se_{90}Ge_4In_6$ alloy

Similar XRD patterns are obtained for the other glassy alloys, confirming their amorphous nature.

The glasses, thus prepared, were ground to make fine powder for DSC studies. 10 to 20 mg of the powder was heated at constant heating rate, and the changes in heat flow with respect to an empty reference pan were measured. A Pyris Diamond DSC (Perkin Elmer instrument, USA) was used at four different heating rates (5, 10, 15, and 20 K/min).

Results and discussion

Thermal stability

Figure 2 shows the typical DSC thermograms for present glassy alloys for heating rate of 20 K/min. This figure shows the well-defined endothermic peaks at the glass transition temperature (T_g) and melting temperature (T_m), and exothermic peak at crystallization temperature (T_c) for binary $Se_{90}In_{10}$ alloy and ternary $Se_{90}In_6Sb_4$ and $Se_{90}In_6Sn_4$ alloys. However, the exothermic peak between T_g and T_m could not be observed in the ternary $Se_{90}In_6Ge_4$ alloy. Similar behaviour has been observed in the thermograms of other heating rates. The absence of an exothermic peak in the DSC thermograms of ternary $Se_{90}In_6Ge_4$ alloy may be due to very slow rate of glass/crystal transformation over the large range of temperature between T_g and T_m. Similar results have been found by Acharya et al. [23] in case of Se–Ge–Te system and Rabinal et al. [24] in case of Se–Ge–In. This absence confirms the higher thermal stability of ternary $Se_{90}In_6Ge_4$ alloy against divitrification after the incorporation of Ge in binary $Se_{90}In_{10}$ alloy.

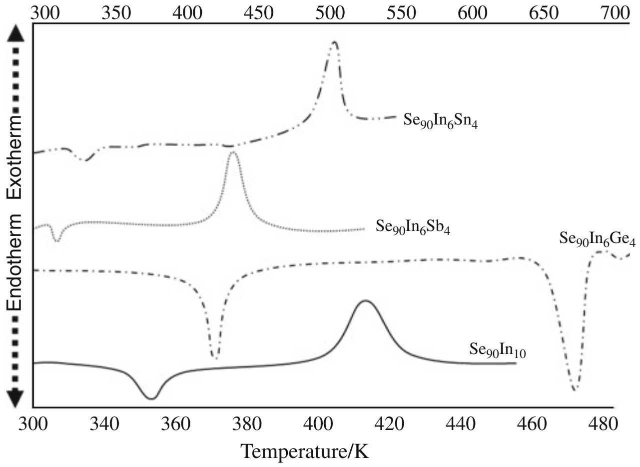


Fig. 2 DSC scans of glassy $Se_{90}In_{10}$ and $Se_{90}In_6M_4$ (M = Ge, Sb, Sn) alloys at heating rate of 20 K/min. Lower *x*-axis indicates temperature for $Se_{90}In_{10}$ and $Se_{90}In_6Ge_4$ alloys and upper *x*-axis indicates temperature for $Se_{90}In_6Sb_4$ and $Se_{90}In_6Sn_4$ alloys

Heating rate dependence of T_g

The glass transition temperature T_g represents the strength or rigidity of the glassy structure of the alloys. It is well known that T_g of glassy alloys varies with the heating rate β [25]. The empirical relation used to analyze the dependence of T_g on β is of the form:

$$T_g = A + B \log \beta \tag{6}$$

Here A and B are constants. The plots of T_g versus log β for glassy $Se_{90}In_{10}$ and $Se_{90}In_6M_4$ (M = Ge, Sb, Sn) alloys are shown in Fig. 3. The value of A indicates the glass transition temperature for the heating rate of 1/K min^{-1}. It has been found by various workers that the slope B in the Eq. 6 is related to the cooling rate of the melt: the lower the cooling rate of melt, the lower the value of *B*. The physical significance of *B* seems to be related to the response of configurational changes occurring within the glass transformation region. The values of *B* for glassy $Se_{90}In_{10}$ and $Se_{90}In_6M_4$ (M = Ge, Sb, Sn) alloys are found different, indicating that these glassy alloys undergo

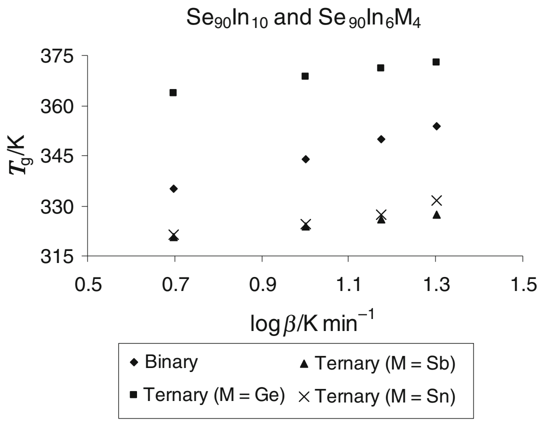


Fig. 3 Plots of T_g versus log β for glassy $Se_{90}In_{10}$ and $Se_{90}In_6M_4$ (M = Ge, Sb, Sn) alloys, where β = 5, 10, 15, 20 K/min

Table 1 Kinetic parameters of glass transition kinetics of glassy $Se_{90}In_{10}$ and $Se_{90}In_6M_4$ (M = Ge, Sb, Sn) alloys

Sample	A/K	B/min^{-1}	ΔE/kJ mol^{-1}	
			From Eq. 9	From Eq. 10
$Se_{90}In_{10}$	31.6	312.7	71.5	65.6
$Se_{90}In_6Ge_4$	15.1	353.2	171.2	165.4
$Se_{90}In_6Sb_4$	11	313.1	182.8	177.8
$Se_{90}In_6Sn_4$	16.2	309.2	107.2	113.0

different structural changes. The values of A and B are given in Table 1.

Evaluation of activation energy of glass transition (ΔE_t)

The kinetics of glass transitions can be studied using the theory of glass transition kinetics and structural relaxation developed by Moynihan et al. [26] from the heating rate dependence of glass transition temperature. Using such a theory, one can calculate the activation energy of molecular motion and rearrangement near the glass transition temperature.

The heating rate dependence of the glass transition temperature in chalcogenide glasses is interpreted in terms of a thermal relaxation phenomenon. In this kinetic interpretation, the enthalpy at a particular temperature and time $H(T, t)$ of the glassy system, after an instantaneous isobaric change in temperature, relaxes isothermally towards a new equilibrium value $H_e(T)$. The relaxation equation can be written in the following form [26]:

$$\left(\frac{\delta H}{\delta t}\right)_T = -\frac{(H - H_e)}{\tau} \tag{7}$$

where τ is a temperature dependent structural relaxation time and is given by the following relation:

$$\tau = \tau_0 \exp\left(\frac{-\Delta E_t}{RT_g}\right) \exp[-c\,(H - H_e)] \tag{8}$$

where$\tau_0$and c are constants, and ΔE_t is the activation energy of relaxation time. Using the above equations, it can be shown [27, 28] that:

$$\frac{d(\ln \beta)}{d(1/T_g)} = \frac{-\Delta E_t}{R} \tag{9}$$

Equation 9 states that ln β versus $1/T_g$ plot should be a straight line and the activation energy involved in the molecular motions and rearrangements around T_g can be calculated from the slope of this plot. The plots of ln β versus $10^3/T_g$ are shown in Fig. 4 for various glassy alloys.

The values of ΔE_t are also evaluated from the slopes of plots of ln (β/T_g^2) against $10^3/T_g$ using Kissinger's relation [27]:

$$\ln\left(\frac{\beta}{T_g^2}\right) = \frac{-\Delta E_t}{RT_g} + \text{constant} \tag{10}$$

The plots of ln (β/T_g^2) versus $1000/T_g$ are also shown in Fig. 5.

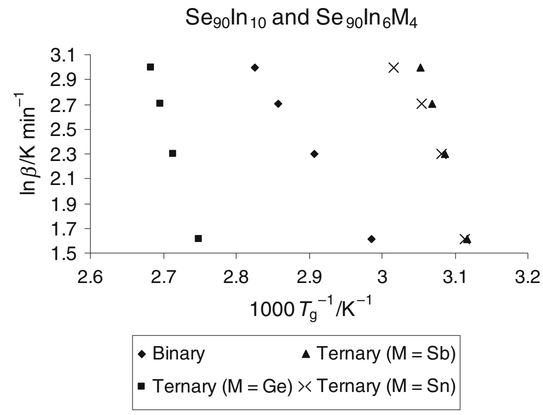


Fig. 4 Plots of ln (β) versus $1000/T_g$ for glassy $Se_{90}In_{10}$ and $Se_{90}In_6M_4$ (M = Ge, Sb, Sn) alloys, where β = 5, 10, 15, 20 K/min

The values of activation energy of glass transition are given in Table 1. From Table 1, it is clear that the value of ΔE_t is increased after the incorporation of Ge, Sb, and Sn chemical modifiers. The increasing sequence of ΔE_t is $(\Delta E_t)_{Binary} < (\Delta E_t)_{Sn} < (\Delta E_t)_{Ge} < (\Delta E_t)_{Sb}$.

Fragility index (F)

Structural relaxation is a general phenomenon occurring when a glass is maintained at a temperature below its glass transition temperature (T_g). Glass forming liquids that exhibit an approximately Arrhenius temperature dependence of the viscosity are defined as strong glass formers and those, which exhibit a non-Arrhenius behaviour are declared fragile glass former [28–35]. Fragile glasses are usually substances with non-directional interatomic/

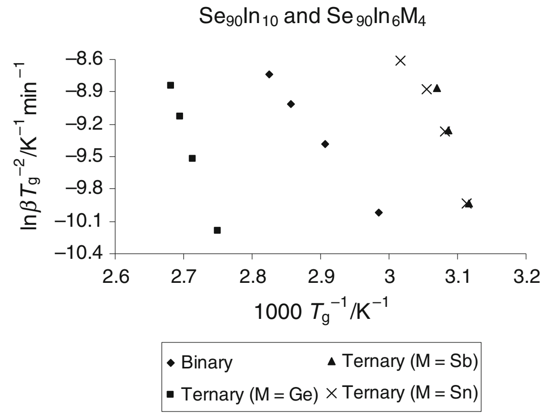


Fig. 5 Plots of ln (β/T_g^2) vs. $1000/T_g$ for glassy $Se_{90}In_{10}$ and $Se_{90}In_6M_4$ (M = Ge, Sb, Sn) alloys, where β = 5, 10, 15, 20 K/min

intermolecular bonds. Strong glasses are those which show resistance to structural degradation in the liquid state.

The fragility index can be calculated using the following relation [29]:

$$F = \frac{\Delta E_t}{T_g \ln 10} \tag{11}$$

Generally, the limit for kinetically strong-glass-forming (KS) liquids is reached for a low value of F ($F \approx 16$) [30], while the limit for kinetically fragile-glass-forming (KF) liquids is characterized by a high value of F ($F \approx 200$) [31]. The values of F for glassy $Se_{90}In_{10}$ and $Se_{90}In_6M_4$ (M = Ge, Sb, Sn) alloys are calculated at different heating rates (see Table 2) and their variation with heating rates content is shown in Fig. 6. It is interesting to note that the values of F for ternary $Se_{90}In_6M_4$ (M = Ge, Sb, Sn) alloys are near to KF limit, whereas the values of F are near to KS limit for binary $Se_{96}In_4$ alloy (see Fig. 6). This indicates that the glassy structure of binary $Se_{96}In_4$ alloy is transformed kinetically strong-glass-forming type to kinetically fragile-glass-forming type after the incorporation of Ge, Sb and Sn chemical modifiers. The incorporated elements modify the molecular mobility of the structure in such a way that the relaxation processes associated with linear polymeric Se are restored for the networks of the ternary alloys.

Table 2 Fragility index for glassy $Se_{90}In_{10}$ and $Se_{90}In_6M_4$ (M = Ge, Sb, Sn) alloys at different heating rates

β/K/min	Sample			
	$Se_{90}In_{10}$	$Se_{90}In_6Ge_4$	$Se_{90}In_6Sb_4$	$Se_{90}In_6Sn_4$
5	92.7	204.5	247.5	145
10	90.3	201.8	245.1	143.5
15	88.7	200.5	243.7	142.2
20	87.7	199.5	242.5	140.5

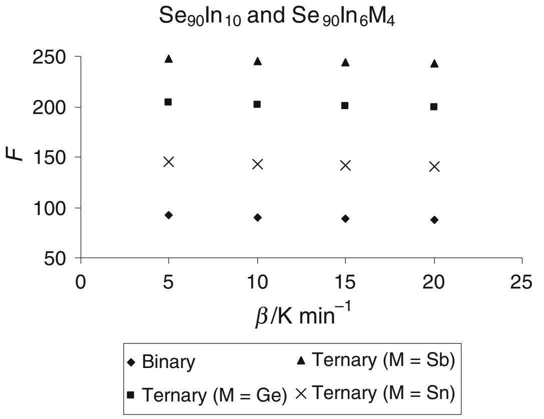


Fig. 6 Heating rate dependence of fragility index F

The observed effect of chemical modifiers on the kinetic parameters can be explained in terms of overall mean bond energy $\langle E \rangle$. The estimation of $\langle E \rangle$ was proposed by Tichy and Ticha by developing a theory based on the chemical bond approach [36]. This approach is applicable to glasses in which the bonding is predominantly covalent. Within the model, the following assumptions are made.

(1) Each element in the covalent structure has a preferred coordination number. For the elements from the VIB, VB, and IVB groups of the periodical system the preferred coordination numbers are 2, 3, and 4, respectively. These values satisfy the '$8 - N$' rule, where N corresponds to the number of s, p-valence electrons. Applying the $8 - N$ rule to the elements from the groups IB–IIIB would result in coordination numbers larger than 4. This is not possible in a covalently bonded structure. To solve this problem, Liu and Taylor [37] proposed to assume that for the elements from group IB–IIIB formal charge transfer takes place from the chalcogen elements or, when not available, the group VB elements. This then leads to tetrahedral coordination for the group IB–IIIB elements and increased coordination for the group VIB or VB elements. The elements then satisfy the generalized '$8 - n$' rule where n is the number of valence electrons formally assigned to the elements [37]. The average coordination number $\langle Z \rangle$ can be calculated from the generalized $8 - n$ rule as follows:

$$\langle Z \rangle = 8 - \langle n \rangle = 8 - \langle N \rangle \tag{12}$$

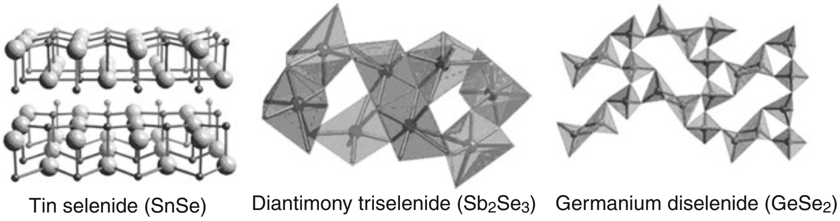
Here $\langle n \rangle$ is the averaged number of formal valence electrons per atom in the glass composition. $\langle n \rangle$ equals the average number of valence electrons per atom $\langle n \rangle$ in the glass composition.

(2) Heteronuclear bonds are preferred to homonuclear bonds. This can be explained to some extent with the help of Chemical Order Network Model (CONM). According to CONM, the formation of heteropolar bonds is favored over homopolar bonds in glassy alloys. In Se–In–M system, the various bonds involved are Se–Se, In–In, Se–In, M–Se, M–In etc. The strength of Se–Se bond is greater than that of In–In bonds [38]. The electronegativity of Se is also greater than that of In. Thus according to Pauling [39, 40], M–Se bonds are found stronger than M–Te bonds. Hence,

Table 3 Overall mean bond energy for glassy $Se_{90}In_{10}$ and $Se_{90}In_6M_4$ (M = Ge, Sb, Sn) alloys

Sample	$\langle E \rangle$/kJ mol^{-1}
$Se_{90}In_{10}$	232.9
$Se_{90}In_6Ge_4$	432.1
$Se_{90}In_6Sb_4$	411.7
$Se_{90}In_6Sn_4$	402.2

Fig. 7 Possible crystalline phases of chemical modifiers for thermally activated crystal growth after their incorporation in glassy $Se_{90}In_{10}$ alloy



the metallic additives (Ge, Sb, Sn) are expected to combine preferably with Se.

(3) Bonds are formed in the sequence of decreasing bond enthalpy (bond enthalpies are defined positive) until all available formal valences of the atoms are saturated and the total number of bonds divided by the number of atoms corresponds to $\langle Z\rangle = 2$.

Values of the overall mean bond energy ($\langle E\rangle$) for any glassy alloys, which were found to depend on $\langle Z\rangle$, the degree of cross-linking per atom (P_p), the type of bonds and the bond energy forming a network can be evaluated as described by Tichy and Ticha [37].

The average coordination number $\langle Z\rangle$ of the studied glasses were evaluated using the standard procedure described by Tanaka [41], using coordination numbers (CN) of 4, 4 and 2 for M (M = Cd, In, Pb), Ge and Se respectively. Thus, for the glassy system $Se_aIn_cM_c$ (a + b + c = 1), the values of $\langle Z\rangle$ could be given by the following relation:

$$\langle Z\rangle = \frac{(aZ_{Se} + bZ_{In} + cZ_M)}{(a+b+c)} \tag{13}$$

Here Z_{Se}, Z_{In}, and Z_M are the co-ordination numbers of Se, In and additive M (M = Ge, Sb, Sn), respectively, in $Se_{94}In_6M_4$ system.

The bond energies (E_{AB}) of hetropolar A–B bonds can be, in first approximation, estimated using Pauling's relation [39, 40]:

$$E_{AB} = 0.5(E_{AA} + E_{BB}) + 23(\chi_A - \chi_B)^2 \tag{14}$$

Here $E_{A\text{–}A}$ and $E_{B\text{–}B}$, and χ_A and χ_B are, respectively, homopolar bond energies and electro-negativity for A and B atoms. The homopolar bond energies and electronegativity are obtained from [23].The degree of cross-linking per atom for chalcogen-rich region, as in the present case, can be expressed as:

$$P_R = \frac{(bZ_{In} + cZ_M)}{(a+b+c)} \tag{15}$$

The mean bond energy of average cross-linking per atom (E_{cl}) is given by

$$E_{cl} = P_R \cdot E_{hb} \tag{16}$$

where the average hetropolar bond energy is given by

$$E_{hb} = \frac{(bZ_{In}E_{Se-In} + cZ_M E_{Se-M})}{(bZ_{In} + cZ_M)} \tag{17}$$

Here, $E_{Se\text{–}In}$ and $E_{Se\text{–}M}$ are the heteropolar bond energies of Se–In and Se–M heteropolar bonds. The average bond energy per atom of the 'remaining matrix', E_{rm} is defined as:

$$E_{rm} = \frac{2\,(0.5\langle Z\rangle - P_R)E_{Se-Se}}{\langle Z\rangle} \tag{18}$$

Finally, the overall mean bond energy is given by

$$\langle E\rangle = E_{cl} + E_{rm} \tag{19}$$

The values of the overall mean bond energy for the present glassy alloys are given in Table 3. From Table 3, it is clear that value of $\langle E\rangle$ is higher in ternary alloys as compared to binary alloy. The maximum value of $\langle E\rangle$ is found for ternary $Se_{90}In_6Ge_4$ alloy.

g-Se contains long polymeric chains and eight members rings in various proportions as its structural units, which are dissociated by the addition of In in g-Se. The addition of In forms the cross-linked structure in terms of In_2Se_3 phase. The most probable structural units of chemical modifiers Ge, Sb, and Sn in Se-rich glasses are $GeSe_{4/2}$, Se_2Sb_3, and SeSn, respectively [42]. The structures of these phases are shown in Fig. 7. The tetrahedral structural unit $GeSe_{4/2}$ is more rigid as compared to Se_2Sb_3 and SeSn structural units. It is well known that the rate of crystallization is associated with the nucleation and growth process that dominates the devitrification of most glassy solids. The lower flexibility of $GeSe_{4/2}$ phase as compared to Se_2Sb_3 and SeSn phases may be also responsible for the higher thermal stability of glassy $Se_{90}In_6Ge_4$ alloy.

Conclusions

The effect of some chemical modifiers on the glass/crystal transformation of binary $Se_{90}In_{10}$ alloy is studied using DSC technique. The major conclusions are:

(i) The absence of exothermic (crystallization) peaks in DSC scans of ternary $Se_{90}In_6Ge_4$ alloy indicates that Ge additive element enhances the thermal stability of binary $Se_{90}In_{10}$ alloy.

(ii) The activation energy of glass transition of binary $Se_{90}In_{10}$ alloy is increased after incorporation of Ge, Sb, and Sn. The maximum change is observed for Sb additive.

(iii) The glassy structure of binary $Se_{96}In_4$ alloy is transformed kinetically strong-glass-forming type to kinetically fragile-glass-forming type after the incorporation of Ge, Sb, and Sn

(iv) The overall mean bond energy significantly increases after the incorporation of Ge, Sb, and Sn.

Acknowledgements The authors are thankful to Prof. S. C. Agarawal, Physics Department, I.I.T., Kanpur for providing his research facilities.

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