SeXSb (X = In, Zn) thermal stability and sample composition comparative study

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In this paper, are compared the non-isothermal crystallization kinetics of two investigated rich selenium glasses SeXSb (X=In, Zn). We found that the systems exhibit high glass transition and crystallization temperatures T_g and T_c values indicating that they don't crystallize easily and both glassy systems become less fragile with increasing Sb contents. It's also seen that the heat of atomization of these systems increases while their activation energy of glass transition decreases with average coordination number. In the other hand, according to Dietzel and Hrubý criteria, the glassy system SeZnSb becomes more stable with high Sb contents, corresponding to high activation energy of crystallization, making it suitable candidate for PC-RAM devices, while SeInSb exhibits the opposite behaviour.

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Keywords: Chalcogenide glasses, DSC, SeInSb, SeZnSb, glass transition, crystallization process, coordination number.

1. Introduction

Chalcogenide glasses are interesting materials for reversible phase change recording devices [1-3]. They have been used in infrared optical fibres [4] and in fabrication of inexpensive solar cells [5]. In addition, they found applications in xerography [6] and photolithography [7]. Se-In and Se-Zn alloys are widely used regarding their higher photosensitivity, higher crystallization temperature and greater hardness [8, 9], in addition to their small ageing effects [10] and present band energy of about 1.3 eV at 300 ° K [11]. The properties of these systems can be varied by adding a third element from Group IV or V of the periodic table for required purpose. Structural and electrical measurement of selenium rich SeZnCd and SeTeSb have been widely investigated by Vibhav K. Saraswat et al. and V. K. Saraswat respectively [12, 13] and A. S. Maan et al. and A.M. Abd Elnaeim suited the crystallization kinetics of SeInTe system [14, 15]. Doped binaries with antimony SeInSb and SeZnSb have been experimentally studied by our team [16, 17] and important parameters are obtained based on several methods using Differential Scanning Calorimetry (DSC) thermograms. In addition, we investigated important physical properties of SeInSb glassy system [18]. Both In and Zn elements have lower electronegativity (1.78 and 1.65 respectively) compared to Se (2.4) and Sb (2.04). Their presence in the glassy alloy will create positively lower atomic radius than that of In but is characterized by a high melting point. Indium is known to form reduced bond energies and thus to favour nucleation, in the other hand incorporation of Sb atoms leads to a rapid crystallization [19].

The purpose of this review is to make a comparison between the important properties of the two investigated systems SeInSb and SeZnSb and conclude the possible best candidate for the PC-RAM application.

2. Experimental setup

The glassy samples were prepared by the well-known melt quenching technique. The appropriate amounts of constituent elements of 99.999% purity were weighed and sealed in a quartz ampoule under a vacuum of 10^{-5} Pa. The ampoules were placed in a horizontally rotating oven and annealed at 1000 °C for 3 h. Then, each ampoule was quenched into ice-cold water to obtain glassy samples.

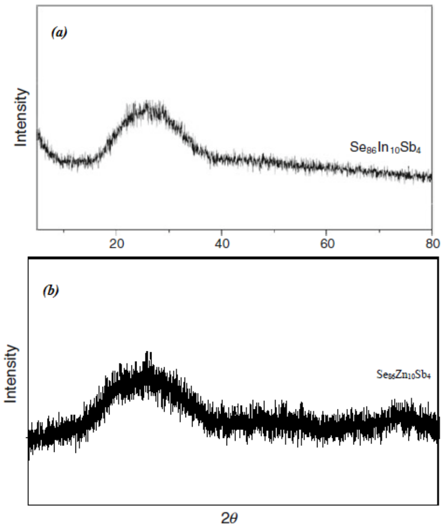

Fig.1. XRD pattern of (a) $Se_{86}In_{10}Sb_4$ [16] and (b) $Se_{90}Zn_{10}Sb_4$ [17] glassy alloys

The amorphous nature of the alloys was verified by X-Ray diffraction (XRD) technique. Fig. 1 (*a* and *b*) show

XRD patterns of $Se_{86}In_{10}Sb_4$ and $Se_{86}Zn_{10}Sb_4$ respectively as examples [16, 17].

3. Results and discussion

Fig. 2 shows DSC thermograms of $Se_{86}In_{10}Sb_4$ and $Se_{86}Zn_{10}Sb_6$ glassy alloys under non-isothermal condition at 10 °C/min. Well-defined endothermic peaks are observed at glass transition temperature (T_g), crystallization temperature (T_c) and melting temperature (T_m). Similar DSC thermograms were observed at other heating rates and for different compositions (not shown). The characteristic temperatures are listed in Table 1. The experimental results of the thermal studies are more detailed in the previous papers [16, 17].

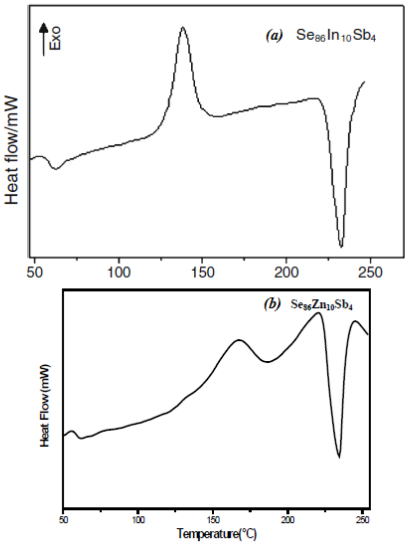

Fig.2. DSC thermogram of (a) $Se_{86}In_{10}Sb_4$ [16] and (b) $Se_{90}Zn_{10}Sb_4$ [17] glassy alloys at 10 °C/min

Table 1. Average coordination number, number of zero-frequency modes per atom, fragility and heat of atomization of the investigated systems

System / Composition	Average coordination number $\bar{r}$	f	F	H_S (KJ/mol)
$Se_{90}In_{10}$	2.10	0.250	172.3	228.06
$Se_{89}In_{10}Sb_1$	2.11	0.242	156.6	228.42
$Se_{88}In_{10}Sb_2$	2.12	0.233	134.6	228.77
$Se_{86}In_{10}Sb_4$	2.14	0.217	122.1	229.49
$Se_{85}In_{10}Sb_5$	2.15	0.208	112.9	229.84
$Se_{90}Zn_{10}$	2.20	0.167	96.80	216.95
$Se_{88}Zn_{10}Sb_2$	2.22	0.150	92.80	217.66
$Se_{86}Zn_{10}Sb_4$	2.24	0.133	91.40	218.37
$Se_{84}Zn_{10}Sb_6$	2.26	0.117	88.30	219.09

3.1. Theoretical basis

The thermal analysis such as DSC and DTA methods are widely used for analysing the crystallization processes in amorphous materials. The crystallization kinetics under non-isothermal conditions deduced from these methods is usually interpreted according to nucleation and growth models introduced by Johnson-Mehl-Avrami [20, 21].

$$x(t) = 1 - \exp\left(-Kt^n\right) \tag{1}$$

where $x(t)$ is the fraction of the initial material transformed at time t, n is the Avrami exponent and K is the reaction rate constant which is related to temperature as:

$$K = K_0 \exp\left(-\frac{E_a}{kT}\right) \tag{2}$$

where K_0 is the frequency factor, E_a denotes the activation energy for the crystallization process, k is Boltzmann constant and T is the isothermal temperature.

There are different theoretical bases for interpreting the DSC results:

- Kissinger [22] method using the highest rate of the process at maximum peak, especially for determining the activation energy, is:

$$\ln\left(\frac{\alpha}{T_p^2}\right) = -\frac{E_a}{kT_p} + cst \tag{3}$$

where T_p is temperature at maximum peak, $\alpha = \frac{dT}{dt}$ is the heating rate and E_a is the activation energy.

- Ozawa [23] method used to calculate the activation energy of crystallization E_c at maximum peak T_p:

$$\ln(\alpha) = -\frac{E_c}{kT_p} + cst \tag{4}$$

- Matusita [24] method to calculate the Avrami index n and the integer m:

$$\ln\left(-\ln(1-x)\right) = -n\ln\alpha - 1.052m\frac{E_c}{RT} + cst \tag{5}$$

3.2. Average coordination numbers

Knowing the coordination of the three elements, the average coordination number of the $Se_xIn_ySb_z$ glassy system has been evaluated [12, 25]:

$$\bar{r} = \frac{xN_{Se}+yN_{In}+zN_{Sb}}{x+y+z} \tag{6}$$

where x, y and z are atomic fractions of Se, In and Sb respectively and N_{Se}, N_{In} and N_{Sb} are their respective coordination numbers. The calculated values of the average coordination number are given in Table 1, where it is seen that $\bar{r}$ increases for both systems with increasing Sb content.

The number of zero-frequency modes per atom is given by:

$$f = 2 - \frac{5}{6}\bar{r} \tag{7}$$

Thorpe [26], by counting this number, showed that undercoordinated networks would possess a finite fraction of zero-frequency modes in the absence of the weaker longer range forces. This number approaches zero as $\bar{r}$ approaches the critical value of 2.4, where there is a phase transition from underconstraints floppy network to overconstrainted rigid network having maximum stability. From the values of this number listed in Table 1, we consider then that the Phillips'-Thorpe threshold is realized for both investigated systems.

3.3. Fragility

The fragility parameter F characterizes and quantifies the anomalous non-Arrhenius transport behaviour of glassy materials near the ergodicity breaking glass transition region [27-29]. Fragile glasses are materials with non-directional interatomic/intermolecular bonds. Strong glasses are those which show resistance to structural degradation and usually associated with a small ΔCp. Fragility is calculated using the relation:

$$F = \frac{E_g}{T_g \ln 10} \tag{8}$$

Both T_g and E_g (activation energy of glass transition) are taken from our previous papers [16, 17]. The values of F, for both systems, are found to decrease with increasing average coordination number $\bar{r}$ as seen in Table 1. This indicates that both studied glassy systems become less fragile when adding more Sb atoms and their tendency to structural rearrangement decreases with increasing non-directional interatomic bonds. The system SeZnSb is more affected than SeInSb.

The bond energies for heteropolar bonds can be calculated using Pauling [30] empirical relation:

$$D_{A-B} = \left[D_{A-A} \times D_{B-B}\right]^{1/2} + 30\left[\chi_A - \chi_B\right]^2 \tag{9}$$

where *D(A-A)* and *D(B-B)* are the energies of homopolar bonds and χ_A and χ_B are the electro negativity values of involved atoms. The bonds in SeInSb system are stronger than those in SeZnSb system ($D_{Se\text{-}In}$ = *54.01 kcal/mol* and $D_{Se\text{-}Zn}$ = *40.79 kcal/mol*).

The heat of atomization has also been calculated for the glassy systems using the relation [31]:

$$H_S = \frac{xH_S^{Se}+xH_S^{In}+xH_S^{Sb}}{x+y+z} \tag{10}$$

and the corresponding values, listed in Table 1, are found to be increasing with increasing Sb contents for both systems.

3.4. Glass transition region

Kinetics of glass transition processes has great importance in the study of glassy alloys. There is no generalized quantitative equation describing T_g as a function of the heating rate for all materials or for any single material within a wide range of heating rate.

Glasses which don't exhibit exothermic crystallization peak above the glass transition temperature are known to show a threshold switching while those showing crystallization above T_g exhibit memory switching.

Glass transition temperature T_g is the temperature at which the relaxation time for the segmental motion in the main chain is of the same order of magnitude as the time scale of experiment. Theory is concerned with describing the rate at which system approaches the equilibrium.

The glass transition temperature is known to depend on several independent parameters such as band gap, bond energy, effective molecular weight, type and fraction of various structural units formed, cohesive energy, the average heats of atomization and the average coordination number.

It's observed from the previous works [16, 17] and Table 2, that T_g values are closer for both investigated systems, and increase with increasing heating rate while with increasing Sb content, T_g increases for SeInSb and decreases for SeZnSb systems. This is related to the connectivity which takes place in SeInSb in opposite of SeZnSb in agreement with Saiter et al. [32].

Table 2. Average coordination number, experimental transition glass and crystallization temperatures at 5°/min and 12°/min and activation energies of glass transition [16, 17], Dietzel, Hruby and β parameters and calculated T_g as per "Gibbs-DiMarzio" equation of the investigated systems

System / Composition	$\bar{r}$	T_g (K) (5°/min)	T_g (K) (12°/min)	T_c (K) (5°/min)	T_c (K) (12°/min)	E_g (kJ/mol)	ΔT (K)	K_H	β	Calculated T_g (K)
$Se_{90}In_{10}$	2.10	319	328	394	407	130.00	79	0.67	0.28	360.12
$Se_{89}In_{10}Sb_1$	2.11	324	330	391	406	118.85	76	0.57		365.45
$Se_{88}In_{10}Sb_2$	2.12	325	331	389	404	102.48	73	0.54		370.72
$Se_{86}In_{10}Sb_4$	2.14	327	333	388	402	93.50	69	0.51		381.74
$Se_{85}In_{10}Sb_5$	2.15	330	336	387	400	87.25	64	0.47		387.49
$Se_{90}Zn_{10}$	2.20	325	332	374	385	73.92	53	0.36	0.43	355.86
$Se_{88}Zn_{10}Sb_2$	2.22	323	331	388	405	70.65	74	0.56		358.11
$Se_{86}Zn_{10}Sb_4$	2.24	321	328	391	412	68.98	84	0.60		360.40
$Se_{84}Zn_{10}Sb_6$	2.26	319	327	397	431	66.44	104	0.73		362.72

When analysing this region using the empirical relation proposed by Lasocka, we deduced the constants A and B, where A is the glass transition temperature at heating rate of 1°C/min. It was suggested that B value depends on the cooling rate during the preparation of the glass [33] and it decreases with decreasing cooling rate of the melt. According to our results, the response of configurational changes within the glass transition region for SeInSb system on the heating rate is expected to differ due to the observed variation of B values, but it doesn't for SeZnSb system.

The glass transition activation energy E_g was then evaluated using Kissinger equation [22]. We found that E_g values decrease with increasing Sb content, and are greater for SeInSb than for SeZnSb system. Therefore, the rigidity of both systems decreases with increasing Sb content.

The analysis of this region can also be treated using Gibbs-DiMarzio equation which predicts the glass transition temperature of a glassy alloy [34]:

$$T_g = T_0 / \left(1 - \beta\left(\bar{r} - 2\right)\right) \tag{11}$$

where T_0 is glass transition temperature of the chain like glass (for Selenium T_0 = 316 K), $\bar{r}$ is the average coordination number [35] and β is a system dependant parameter given by:

$$\frac{1}{\beta} = \sum \left(r_i - 2\right) \ln\left(\frac{r_i}{2}\right) \tag{12}$$

Eq. 12 computes β parameter value when the coordination numbers r_i of the involved atoms are known. The calculated values are listed in Table 2, where it's also seen that the predicted T_g is not in agreement with experiment and for the system SeZnSb the difference is less but it increases with increasing Sb content.

3.5. Crystallization

In Table 2, we reported values of the crystallization temperature corresponding to two different heating rates (5 and 12 °/min) for comparison. It's seen that T_c increases with increasing heating rate α and shows low values for both systems. This can be explained by the fact that for high values of α, the crystallization process needs much time to be achieved *i.e.* much time to break atomic bonds which leads to an increase in crystallization temperature in order to complete the crystallization process.

From the application of Matusita equation, it can be seen a linear dependence of Avrami index with temperature which explains a perturbation in the crystallization process. The values of *n* and *m* (4 and 3 respectively) lead to a three-dimensional growth. Knowing that for PC-RAM $n = a + m$, it can be concluded that $a = 1$, which means that the process is achieved with a constant nucleation rate. The value of *a* increases along the crystallization progression near T_c.

Crystallization rate is a critical parameter for the PC-RAM in the way that it fixes the threshold of the data transfer rate. The material is chosen with crystallization duration necessarily lower than the amorphous one and thus, with high glass stability.

The glass stability (GS) represents the resistance of a glass system towards devitrification upon reheating. Dietzel [36] criterion ($\Delta T = T_c - T_g$) and Hrubý [37] parameter ($K_H = \frac{T_c - T_g}{T_m - T_c}$) are used to estimate this characteristic. The larger is ΔT or K_H, the greater is the glass stability of a glassy alloy against devitrification due to structural units with small crystallization tendency.

According to Table 2 and Fig. 3, the glass stability of the SeInSb system decreases with increasing Sb content while the SeZnSb glassy system is much stable with high Sb concentration. In these terms, the SeZnSb, compared to SeInSb, it represents a good candidate for PC-RAM devices, in addition to its phase transition occurring at high temperature which is an interesting property.

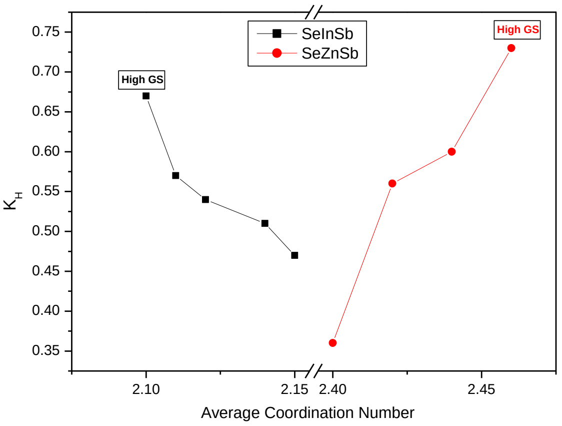

Fig. 3. Hrubý parameter variation versus average coordination number for SeInSb and SeZnSb systems

The activation energy of crystallization calculated from Kissinger and Ozawa methods showed different behaviour for the tow systems. With increasing Sb content, it increases for SeZnSb while it decreases for SeInSb. The maximum value of E_c for the first system is higher than for the second one, and thus, with more Sb atoms, SeInSb crystallizes easier than SeZnSb.

4. Conclusion

The non-isothermal crystallization kinetics and important physical properties of selenium based glasses SeXSb (X=In, Zn) are compared in this research paper. The results show that the systems exhibit high T_g and T_c values indicating their difficult crystallization. We also found that with increasing Sb content, the heat of atomization of both systems increases while the activation energy of glass transition decreases and the investigated systems become less fragile. In order to investigate the glass stability of the systems, Dietzel and Hruby criteria were used and we found that the glassy system SeZnSb becomes more stable when adding more Sb atoms, corresponding to high activation energy of crystallization E_c, which is an important feature of PC-RAM materials, in opposite of SeInSb.

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