

THERMAL PROPERTIES OF SELENIUM-BISMUTH GLASSY ALLOYS

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The crystallization kinetics of $\text{Se}_{100-x}\text{Bi}_x$ ($x = 0, 0.5, 2.5, 5$ and 10) glassy alloys at different heating rates (5, 10, 15 and 20 K/min) have been studied by using Differential Scanning Calorimeter. The glass transition temperature at different heating rates and structural changes during glass transition have been determined from an empirical relation. The glass transition temperature (T_g), the crystallization temperature (T_c), the order parameter (n), the activation energy of crystallization (ΔE_c) and the enthalpy released (ΔH_c) have been calculated and their compositional dependence has been discussed in terms of the structure of Se-Bi system. The results of crystallization have been discussed on the basis of Kissinger's approach and Matsusita's modified expression for non-isothermal crystallization.

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1. Introduction

Chalcogenide glasses have attracted much attention because of their potential application in various solid state devices. Impurity effects in chalcogenide glasses have importance in the fabrication of glassy semiconductors. Several workers [1-5] have reported the impurity effects in various chalcogenide glasses. Moreover, they are interesting as core materials for optical fibers used for transmission especially when short length and flexibility are required [6-8]. Since the advent of electrophotography, amorphous selenium became a material of commercial importance. Selenium exhibits the unique property of reversible phase transformation [9]. Its various device applications like rectifiers, photocells, vidicons, xerography, switching and memory etc. have made it attractive, but pure selenium has disadvantages like short lifetime and low photosensitivity. This problem can be overcome by alloying Se with some impurity atoms (Bi, Te, Ge, Ga, Sb, As etc) which gives higher photosensitivity, higher crystallization temperature and smaller ageing effects [10-12]. Here we have chosen Bi as an additive because it readily alloys with most of the metals and modify their physical properties.

Kinetic investigations of the crystallization of chalcogenide glasses are of interest for understanding the nature of processes involved. One of the common and perhaps the least cumbersome experimental method of obtaining the kinetics parameters is through the use of Differential Scanning Calorimetry (DSC) [17]. The physical properties of materials depend very much on their atomic structure. Metallic glasses do not retain their atomic structure on production; and the change is dependent on the conditions under which a sample is stored [18, 19]. Moreover, it is suggested in many studies that the stability of metallic glasses is influenced by the production process and composition, which lead to different initial structural and energy states [18, 20]. In the crystallization phenomena of glasses, the activation energy is related to nucleation and growth processes that are responsible for most of the devitrification of glassy solids. In general, the

activation energy is composed of two activation energies; the activation energy of nucleation (E_n) and that of growth (E_g) [19]. Crystallization studies were made under non-isothermal conditions in which the samples were heated at uniform heating rates.

In the present work, the thermal properties of $\text{Se}_{100-x}\text{Bi}_x$ glassy alloys (where $x = 0, 0.5, 2.5, 5$ and 10) have been studied. Our aim is to throw light on glass transition region, crystallization and thermal stability in the given system.

2. Experimental

Glassy alloys of $\text{Se}_{100-x}\text{Bi}_x$ (where $x = 0, 0.5, 2.5, 5$ and 10) were prepared by quenching technique. Highly pure materials (99.999%) having the desired compositional ratio of elements were sealed in quartz ampoules (length ~ 10 cm, internal diameter ~ 0.8 cm) in a vacuum of 10^{-3} Pa. The sealed ampoules were kept inside a programmable furnace where the temperature was raised to 1100 K at a rate of 4K/min for 10 hours with frequent rocking to ensure the homogenization of the melt. The quenching was done in ice water. Amorphous nature of the samples has been confirmed by X-ray diffractograms.

For thermal studies, we have taken 5 mg of each sample of $\text{Se}_{100-x}\text{Bi}_x$ glassy alloys in powder form in separate aluminium pans. Each of these samples were heated at different rates, that remain constant for every heating process (5, 10, 15 and 20 K/min) and their thermograms were recorded by Differential Scanning Calorimetry (DSC plus, Rhemetric Scientific, UK). The measurements were made under the same experimental conditions for all the samples.

3. Results and discussion

Fig. 1 shows the thermograms of $\text{Se}_{95}\text{Bi}_5$ glassy alloys at different heating rates (5, 10, 15 and 20 K/min). It is clear from this figure that well-defined exothermic and endothermic peaks were obtained at all heating rates. Two characteristic phenomena are evident in the DSC thermograms. The first one corresponds to the glass transition (T_g) and the other to the crystallization temperature (T_c). Similar trends in thermograms were obtained with other samples at different heating rates (figures not shown here). It is observed that both T_g and T_c shift to higher temperature region as the heating rate is increased from 5 to 20 K/min and are given in Table 1. It depicts the variation of T_g with Bi content at different heating rates for all samples of $\text{Se}_{100-x}\text{Bi}_x$ glassy alloys. Since T_g represents the rigidity of the glass network, it can be expected to scale with the average coordination number and the binding energy. The composition dependence of T_g can be explained on the basis of Chemically Ordered Network Model [17]. It has been indicated [18] that in glass containing Se, there is a tendency to form a polymerized network and a homopolar bond is qualitatively suppressed. The structure of Se-Bi system prepared by melt quenching is regarded as a mixture of Se rings, Se-Bi mixed rings and Se-Bi chains. A strong covalent bond [19] exists between the atoms in the ring, whereas in between the chains only the Vander Waals forces are dominant. The addition of a small amount of Bi in a-Se leads to its entry into the cross linked chains [20] and hence increasing T_g of the system. The addition of bismuth atoms bind the selenium chains and hence make the structure more rigid. Therefore, the T_g must increase with the bismuth content. The heating rate dependence of T_g is an experimentally observed fact [21]. In the present study, T_g increases with increasing heating rate. Theoretically, T_g is defined as the temperature at which the relaxation time τ becomes equal to the time of observation τ_{obs} . At the same time, T_g varies inversely with the relaxation time [22]. With increasing heating rate, τ_{obs} decreases and hence T_g increases. Tab. 1 also exhibits the variation of T_c with Bi content at different heating rates for all the samples of $\text{Se}_{100-x}\text{Bi}_x$ glassy alloys. The crystallization temperature increases as the heating rate is increased. It is found that T_c decreases on adding Bi content in the Se-Bi system. The presence of cross linked chains determine the decrease of the crystallization temperatures. Hence it is logical to observe a decrease of $(T_c - T_g)$ with x . The thermal stability of glass forming system against crystallization is often reported in terms of difference between T_c and T_g detected during heating of glassy sample at a steady heating rate. The higher the value of $(T_c - T_g)$, the greater is the thermal stability, and easier is the glass formation

[23]. The values of $(T_c - T_g)$ for different compositions at 15 K/min heating rate are given in Table 2.

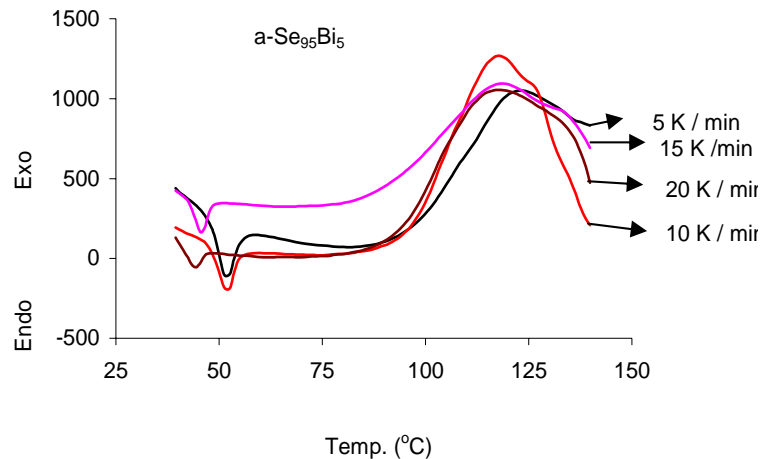


Fig. 1. DSC thermogram for $\text{Se}_{95}\text{Bi}_5$ glass at heating rates (5, 10, 15, 20 K/min).

Table 1. Heating rate dependence of T_g and T_c in $\text{Se}_{100-x}\text{Bi}_x$ glassy alloys.

Samples	5 K/min		10 K/min		15 K/min		20 K/min	
	T_g (K)	T_c (K)	T_g (K)	T_c (K)	T_g (K)	T_c (K)	T_g (K)	T_c (K)
a-Se	314.7	374.6	315.3	385.2	316.5	390.1	317.7	396.2
a- $\text{Se}_{99.5}\text{Bi}_{0.5}$	315.2	373.1	316.8	381.7	317.9	385.6	318.4	393.5
a- $\text{Se}_{97.5}\text{Bi}_{2.5}$	315.9	372.4	317.3	379.6	318.3	383.4	319.9	390.8
a- $\text{Se}_{95}\text{Bi}_5$	316.3	372.9	318.5	377.8	320.1	381.7	321.2	388.1
a- $\text{Se}_{90}\text{Bi}_{10}$	318.4	371.5	319.9	376.3	322.6	380.3	322.5	386.7

Non-isothermal measurements of crystallization are easier to conduct than isothermal one, which are based on Avrami's equation. In a non-isothermal DSC experiment, the temperature changed linearly with time at a known scan rate β ($= dT / dt$). We may write

$$T = T_o + \beta t \quad (1)$$

where T_o is starting temperature and T is temperature after time t .

As temperature changes linearly with time, the reaction rate constant K is no longer a constant but varies with time as

$$\alpha(t) = 1 - \exp[-\{K(T - T_o) / \beta\}^n] \quad (2)$$

where α is the degree of crystallization and n is the order parameter.

After rearranging and taking double logarithms of equation (2), Ozawa [24] obtained

$$\ln[-\ln(1-\alpha)] = n \ln K(T - T_o) - n \ln \beta \quad (3)$$

According to equation (3), a plot of $\ln[-\ln(1-\alpha)]$ versus $\ln \beta$ yield a straight line having slope equal to n . Fig. 2 shows the variation of $\ln[-\ln(1-\alpha)]$ against $\ln \beta$ at different temperatures for $\text{Se}_{100-x}\text{Bi}_x$ glassy alloys. The values of n are calculated from the slope of these curves and are given in Table 2. The value of n increases on increasing bismuth content in $\text{Se}_{100-x}\text{Bi}_x$ glassy alloys. Such an increase in order parameter (n) means that the crystallization is faster in Bi rich alloys. The degree of crystallization (α) is calculated after dividing the partial area by the total area of the exothermic peak [25].

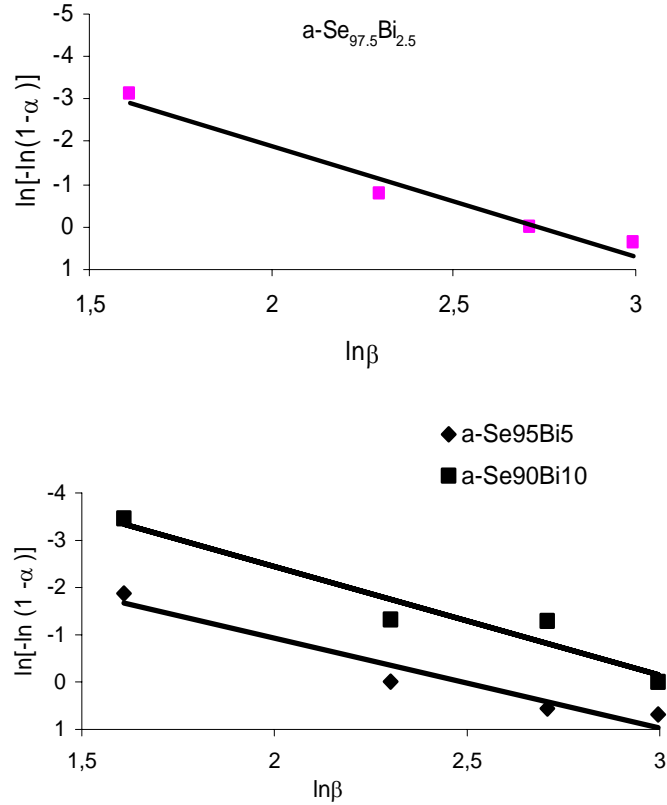


Fig. 2. $\ln[-\ln(1-\alpha)]$ as a function of $\ln\beta$ at different temperatures for $\text{Se}_{100-x}\text{Bi}_x$ glassy alloys.

Table 2. Thermal parameters in $\text{Se}_{100-x}\text{Bi}_x$ glassy alloys (at heating rate of 15 K/min).

Samples	ΔE_c (kJ/mol)	ΔE_t (kJ/mol)	n	15 K/min T_c-T_g	15 K/min ΔH_c (joule/g)
a-Se	257.81	93.54	1.60	73.6	488.63
a- $\text{Se}_{99.5}\text{Bi}_{0.5}$	231.06	106.23	1.62	67.7	507.45
a- $\text{Se}_{97.5}\text{Bi}_{2.5}$	197.28	117.67	1.67	65.1	526.32
a- $\text{Se}_{95}\text{Bi}_5$	161.72	129.80	1.73	61.6	604.56
a- $\text{Se}_{90}\text{Bi}_{10}$	152.43	141.48	2.41	57.7	617.24

The activation energy of crystallization ΔE_c can be obtained from the variation of the onset crystallization temperature T_c with the heating rate β by using Ozawa's relation [26] as,

$$\ln \beta = -\Delta E_c / RT_c + \text{constant} \quad (4)$$

Fig. 3 shows $\ln \beta$ versus $1000/T_c$ curves which come out to be linear for the entire heating process. The values of ΔE_c are calculated from the slope of these curves for all the samples. The composition dependence of ΔE_c in $\text{Se}_{100-x}\text{Bi}_x$ glassy alloys is given in Table 2.

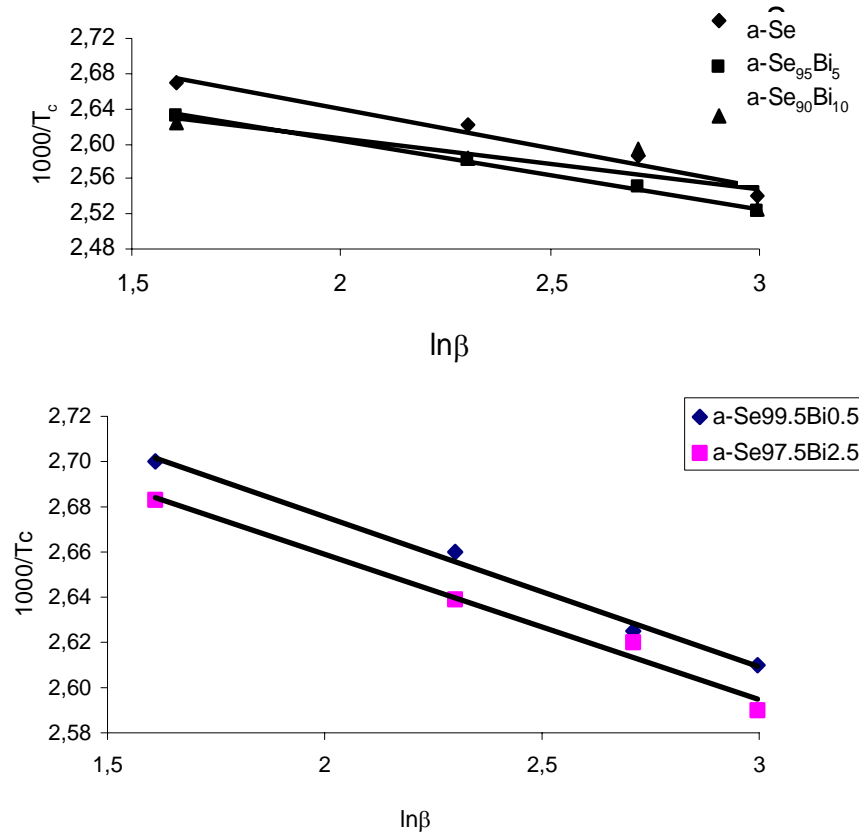


Fig. 3. $\ln \beta$ as a function of $1000/T_c$ for $\text{Se}_{100-x}\text{Bi}_x$ glassy alloys.

The variation of glass transition temperature T_g with the heating rate β in chalcogenide glasses may be interpreted in terms of thermal relaxation phenomena. It has been shown by Moynihan et. al. [27] that the activation energy of structural relaxation ΔE_t can be related to T_g and β by,

$$d \ln \beta / d(1/T_g) = -\Delta E_t / R \quad (5)$$

It is evident from this equation that a plot of $\ln \beta$ against $1/T_g$ should be a straight line and its slope provides the activation energy involved in the molecular motion and rearrangement around T_g . Fig. 4 shows the variation of $\ln \beta$ against $1000/T_g$, which comes to be a straight line for all the samples. The values of ΔE_t for different compositions are calculated from the slope of these lines. The composition dependence of ΔE_t in $\text{Se}_{100-x}\text{Bi}_x$ glassy alloys is given in Table 2. It is found that ΔE_t increases on increasing bismuth content in $\text{Se}_{100-x}\text{Bi}_x$ glassy alloys.

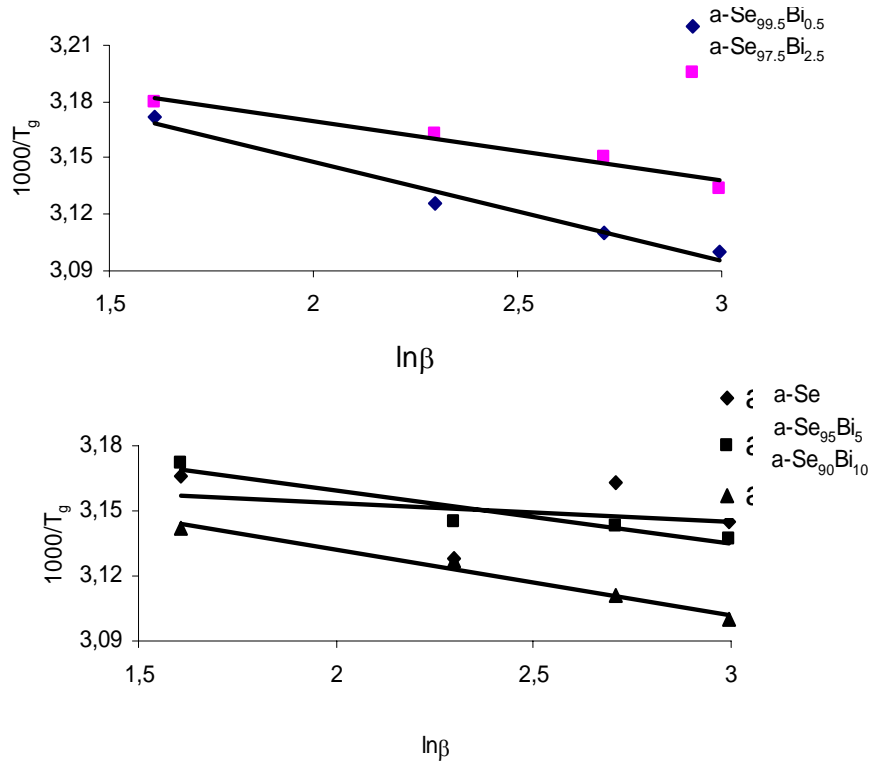


Fig. 4. $\ln \beta$ as a function of $1000/T_g$ for $\text{Se}_{100-x}\text{Bi}_x$ glassy alloys.

Schottmiller et. al. [28] has studied the effect of the addition of group V elements (As, Sb, Bi) on the structure of Se by infrared and Raman spectroscopy. According to them, in glassy Se about 40% of the atoms have a ring structure and 60% of the atoms are bonded as polymeric chains. An introduction of Bi increases the Se ring concentration favoring Se-Bi mixed rings. A slight increase in the polymeric chain of Se is also observed. Due to increase in Se-Bi mixed rings, the tendency of crystallization becomes faster in Se-Bi system and the decrease in the value of activation energy of crystallization (ΔE_c) with bismuth content ensures it.

The enthalpy of crystallization (ΔH_c) can be evaluated for all compositions of the system using the relation

$$\Delta H_c = K A / M \quad (6)$$

where A is the area of the crystallization peak, M is the mass of the sample and K is the instrument constant which is found to be 1.5. The values of ΔH_c for different samples of $\text{Se}_{100-x}\text{Bi}_x$ glassy alloys at the heating rate of 15 K/min are given in Table 2. The enthalpy of crystallization increases with increase in bismuth content of $\text{Se}_{100-x}\text{Bi}_x$ glassy alloys. The enthalpy released is closely associated with the metastability of glasses. The least stable glass with minimum ($T_c - T_g$) is supposed to have maximum enthalpy released (ΔH_c) [29, 30].

4. Conclusion

It may be concluded from thermal studies that glass transition and crystallization temperatures depend on heating rate as well as on composition. T_g and T_c both increases with increase in heating rate; while T_g increases and T_c decreases with increase in bismuth content in $\text{Se}_{100-x}\text{Bi}_x$ glassy alloys. The activation energies for crystallization and for structural relaxation are useful in the understanding of thermal relaxation phenomena in these glasses. The values of ΔH_c ,

ΔE_c and n increases with increase in Bi content in $Se_{100-x}Bi_x$ glassy alloys indicating that the crystallization increases as the Bi content increases.

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