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THERMAL INVESTIGATIONS IN BULK $Se_{80-x}Te_{20}Bi_x$ CHALCOGENIDE GLASS

Nikhil Suri[a], K.S. Bindra[a], P. Kumar[a], M.S.Kamboj[b], R. Thangaraj[a*]

[a] Semiconductors Laboratory, Department of Applied Physics,
Guru Nanak Dev University, Amritsar, 143005, India.
[b] Department of Electrical Computer Engineering, Ryerson University
350 Victoria Street Toronto Ontario M5B 2k3, Canada

Crystallization studies using differential scanning calorimetry under non-isothermal conditions with the samples heated at different rates (5,10,15 and 20 K/min) have been reported and discussed. The effect of Bi addition to the Se-Te matrix on the mechanism of crystal growth has been investigated. The glass transition temperature is found to increase with increase in heating rate as well as with the addition of bismuth. The activation energy for glass transition and that for crystallization have been determined using the Kissinger equation and the Matusita equation. Thermal stability and glass-forming tendency have also been studied. Theoretical calculations of the viscosity have been done using data of heating rate dependence of glass transition temperature and the peak crystallization temperature.

Keywords: Amorphous semiconductors, Chalcogenide glasses, Differential Scanning Calorimetry, Glass transition, Activation energy, Thermal stability.

1. Introduction

Amorphous chalcogenide glasses have been given great attention recently due to their wide range of applications in technological and scientific fields. They have many applications in optics and optoelectronics such as optical imaging, photo lithography and phase change optical recording [1-6]. The concept of phase change optical recording is, that some physical property of microscopic area of recording layer on disc surface is altered [1]. In this technique, spots of a crystalline material are melted momentarily by short laser pulses for recording and the recorded marks are erased through annealing process during which long laser pulses heat the amorphous spot to return it to crystalline phase. Se-Te-Bi system is one of the most characteristic chalcogenide glasses because the addition of a third element likes Sb, Sn, In, Pb etc. in Se-Te has been found to improve the reversibility and increase the glass transition and crystallization temperatures [7]. Further, the addition of Bi to the Se-Te matrix changes the conduction from p- to n-type [8]. In the present work, the crystallization kinetics of $Se_{80-x}Te_{20}Bi_x$ (x = 0, 0.2, 0.5, 1.0, 1.5) has been studied under non-isothermal conditions at different heating rates viz., 5, 10, 15 and 20 K/min. From the heating rate dependence of glass transition temperature (T_g) and peak crystallization temperature (T_p) the apparent activation energy for glass transition and the activation energy for crystallization have been investigated. The thermal stability factor and the glass-forming tendency of the samples have been investigated. The viscosity values have been calculated using Vogel-Tamman-Fulcher equation using data of heating rate (α) dependence of T_g and the peak crystallization temperature (T_p).

2. Experimental

Bulk samples of $Se_{80-x}Te_{20}Bi_x$ (x=0, 0.2, 0.5, 1.0, 1.5) were prepared by conventional melt quenching technique. Materials of 99.999% purity were sealed in a cleaned and evacuated quartz ampoule in a vacuum of 10^{-5} mbar. The ampoule was kept inside a vertical furnace and the temperature was raised up to 1123K slowly (3-4 K/min) and kept for 48 h. The ampoule was inverted at regular intervals of time to ensure homogeneous mixing of the constituents. The ampoule was then quenched in ice-cold water .The bulk material was separated from the quartz ampoule by

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[*] Corresponding author: rthangaraj@rediffmail.com

dissolving the ampoule in $HF+H_2O_2$ solution for approx.48 h. The amorphous nature of the bulk samples was confirmed by the absence of peaks in the X-ray diffractogram. The thermal behaviour of the samples was investigated using Mettler Toledo Star^e DSC System. In each study approximately 25 mg of the bulk material was used. DSC runs were taken for four different heating rates i.e., 5, 10, 15 and 20 K/min for each of the composition so as to get glass transition, peak crystallization and melting temperature. The glass transition temperature is defined as the temperature corresponding to the intersection of two linear portions adjoining the transition elbow of DSC trace of first endothermic peak. The onset crystallization temperature T_c, has been defined as the temperature corresponding to the intersection of the two linear portions adjoining the transition elbow of the DSC trace in the exothermic direction. The fraction X crystallized at any temperature T was calculated using the relation $X = \frac{A_T}{A}$, where A is the total area of the exotherm between T_c and the temperature at which crystallization is completed, A_T is the area of exotherm between T_c and T [9].

3. Results and discussion

DSC thermograms for $Se_{80-x}Te_{20}Bi_x$ (x=1.0) are shown in Fig 1. It can be seen from the figure that T_g and T_p shift towards higher temperature with increase in the heating rate. Samples with other x values also show similar behaviour. The variation of T_g in $Se_{80-x}Te_{20}Bi_x$ system with Bi concentration at different heating rates is shown in Fig 2. In the system under study the glass transition temperature was found to increase with the increase in heating rate as well as with the addition of bismuth content. This increase in the value of T_g with bismuth content can be explained with the help of chemically ordered network (CON) model according to which the heteropolar bond is favoured over the homopolar bond. The various types of bonds involved in the present system are Se-Se, Te-Te, Se-Te, Bi-Se, Bi-Te etc. When the percentage of Bi is increased, Bi is expected to form bond with Se rather than with Te, as the bond energy of Bi-Se (170.4KJ/mol) is larger than the bond energy of Bi-Te (125.6 KJ/mol) [10]. This explains the increase in T_g with increase in Bi content. A plot of glass transition temperature (T_g) versus the heating rate (α) is shown in Fig 3. In all samples T_g obeys the empirical relation

$$T_g = A + B\log(\alpha) \tag{1}$$

where A and B are constants. The value of B is calculated from the slope of T_g versus log (α) plots.

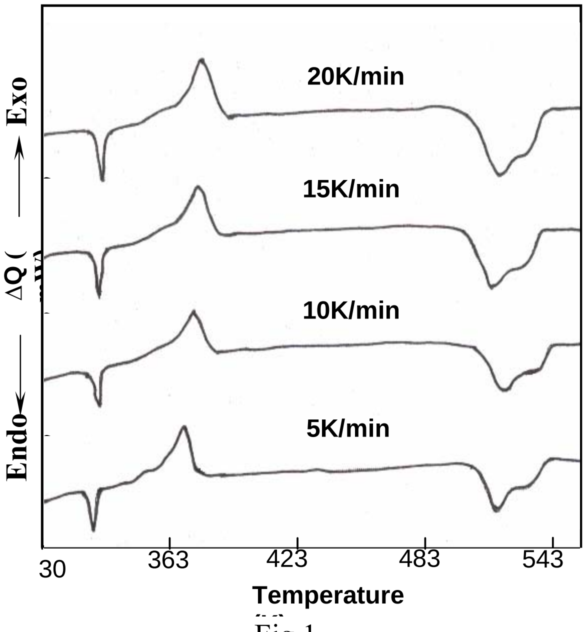

Fig.1.

Fig. 1. DSC thermograms for $Se_{80-x}Te_{20}Bi_x$ (x=1.0) at different heating rates

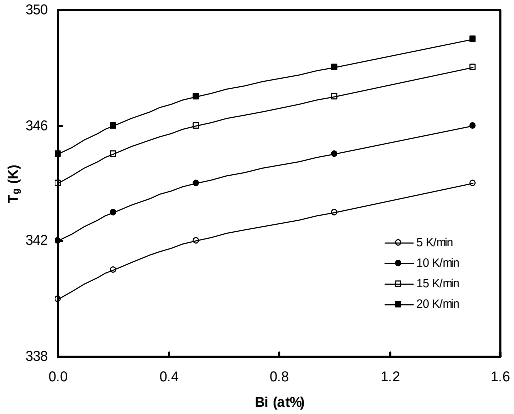

Fig. 2. Variation of T_g with composition of Se_{80-x} $Te_{20}Bi_x$ at different heating rates

The change in B with Bi concentration indicates that the Se-Te-Bi alloy undergoes structural changes with Bi addition [11]. The apparent activation energy for glass transition E_t is calculated using the Kissinger formula [12]

$$\ln\left(\frac{T_g^2}{\alpha}\right) + \text{const.} = \frac{E_t}{\mathrm{R}T_g} \tag{2}$$

where R is the gas constant. The $\ln\left(\frac{T_g^2}{\alpha}\right)$ versus $1000/T_g$ (Fig.4) is found to be linear for all the samples and the values of apparent activation energy E_t for glass transition, obtained from their slopes, are listed in Table 1. The glass transition activation energy is the amount of energy that is absorbed by a group of atoms in the glassy region so a jump from one metastable state to another [13]. In other words, the activation energy is involved in the molecular motions and rearrangements of the atoms around the glass transition temperature [14]. When the sample is reheated in the DSC furnace, the atoms undergo infrequent transitions between the local potential minima separated by different energy barriers in the configuration space where each local minimum represents a different structure. The most stable local minimum in the glassy region has lower internal energy. Accordingly, the atoms in a glass having minimum activation energy have a higher probability to jump to the metastable state (or local) of lower internal energy and hence is the most stable [13]. Therefore, one can argue that the addition of Bi reduces the stability of the glasses under investigation.

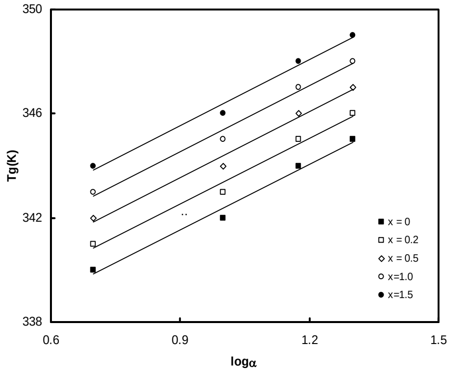

Fig. 3. Variation of T_g with heating rates (α) for Se_{80-x} $Te_{20}Bi_x$ system

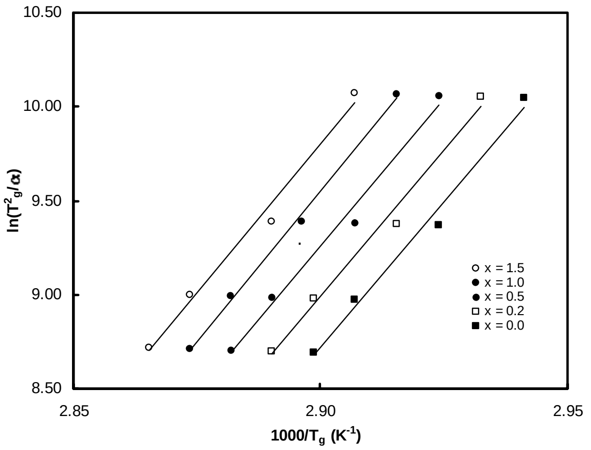

Fig. 4. ln $\left(\frac{T_g^2}{\alpha}\right)$ vs $1000/T_g$ for $Se_{80-x}Te_{20}Bi_x$

Activation energy for crystallization is calculated from the modified Kissinger equation [15,16]

$$\ln\left(\frac{\alpha^n}{T_p^2}\right) = -\frac{mE_c}{\mathrm{R}T_p} + \ln K \tag{3}$$

where K is a constant, containing the factors depending on the thermal history of samples, n and m are constants depending upon the morphology of the growth. The value of $\frac{mE_c}{n}$ calculated from the slope of logα versus $1000/T_p$ (fig.5). According to Matusita relation [17]

$$\ln[-\ln(1-X)] = -n\ln(\alpha) - 1.052\frac{mE_c}{\mathrm{R}T} + \text{const.} \tag{4}$$

where X is the volume fraction of crystals precipitated in the glass heated at a uniform rate, E_c is the activation energy for crystallization and R is the gas constant. The slope of ln [-ln (1-X)] versus ln (α) (Fig. 6) gives the value of n. The value of m is taken as m=n-1 if there is no previous heat treatment and m=n if the sample undergone a heat treatment [23]. In the present case no heat treatment was given, however, the presence of an endothermic peak indicates that a thermal relaxation has taken place. Also, due to the lower value of the T_g, it can be reasonably assumed that the sample might have undergone a heat treatment at room temperature. Hence, the value of m is taken as equal to n in the present case for further analysis. The values of both m and n are reported in Table1. The slope of ln [-ln (1-X)] versus 1000/T gives the value of mE_c shown in Fig.7. The calculated values of E_c shown in columns 7 and 9 of Table 1 show similar behavior but a discrepancy in the values of E_c evaluated may be attributed to the different approximations that have been adopted while arriving at the final equation. In addition, the temperature and pressure gradients in the sample (resulting from heat effect e.g. heating rate) vary randomly and such random variations have predominant effects on kinetic parameters. Hence, the variation in the value of E_c is expected to occur in the light of the reasons mentioned above. Similar variations in the activation energy have also been observed in various other chalcogenide glasses [7,18,19].

Table 1. Parameters determined from heating rate dependence of $Se_{80-x}Te_{20}Bi_x$ glassy System.

X	B	E_t (KJ/mol)	mE_c/n (KJ/mol)	n	m	E_c (KJ/mol)	mE_c (KJ/mol)	E_c (KJ/mol)
0.0	16.61	125.16	97.35	4.05	4	97.35	380.18	95.04
0.2	12.21	185.70	86.06	2.45	2	86.06	267.00	133.50
0.5	11.47	197.00	69.20	2.01	2	69.20	237.00	118.50
1.0	9.74	236.00	63.30	2.30	2	63.30	299.00	149.50
1.5	8.43	272.62	72.14	1.96	1	72.14	247.57	247.57

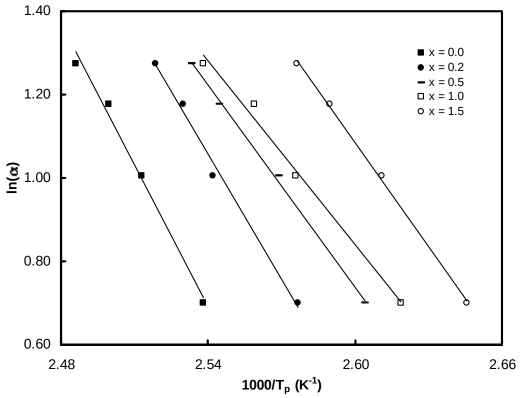

Fig. 5. log (α) vs $1000/T_p$ for $Se_{80-x}Te_{20}Bi_x$

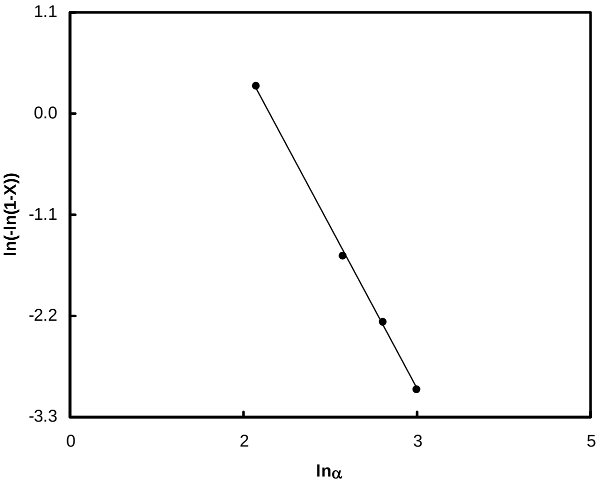

Fig. 6. ln (-ln (1-X)) vs ln(α) for $Se_{80-x}Te_{20}Bi_x$ (x=1.0)

The ease in glass formation is determined by calculating the reduced glass transition temperature $T_{rg} = \frac{T_g}{T_m}$ [20]. The value obtained obey the two-thirds rule which states

$$\frac{T_g}{T_m} = \frac{2}{3} \tag{5}$$

Two-third rule holds well for this composition. The difference between T_c and T_g, which is an indication of the thermal stability of glasses against crystallization decreases with increase in bismuth content. This indicates a decrease in the thermal stability of glass with increase in bismuth concentration in Se-Te-Bi glass system. The glass forming parameter is calculated using Hruby's parameter [21]

$$K_{gl} = \frac{T_c - T_g}{T_m - T_c} \tag{6}$$

The values of K_{gl} are found to decrease with increasing Bi content. The values of T_c-T_g, K_{gl} and T_{rg} are listed in Table2. The theoretical calculations of the viscosity have been done using data of heating rate (α) dependence of T_g and T_p. The theoretical curves for temperature dependence of viscosity (η) have been generated with the help of Vogel-Tamman-Fulcher equation [22]

$$\eta \approx \eta_0 \exp\left(\frac{B'}{\mathrm{R}(T - T_0)}\right) \tag{7}$$

The activation energies for glass transition E_t and for crystallization E_c, which has been evaluated using Kissinger equation, have been used for evaluation of the viscosity using [23]

$$T_o = \frac{\left(\sqrt{A}T_{g-}T_p\right)}{\left(\sqrt{A} - 1\right)} \tag{8}$$

$$B' = \frac{E_t}{A}\left(\frac{T_g - T_o}{T_g}\right)^2 \tag{9}$$

$$\text{where } A = \frac{E_t}{E_c}\left(\frac{T_p}{T_g}\right)^2 \tag{10}$$

substituting the values of B' and T_o and assuming the viscosity at T_g to be 10^{12} poise, the theoretical curves of viscosity as a function of temperature have been generated and are shown in the Fig.8

Table 2. Values of (T_c - T_g), K_{gl} and T_{rg} calculated from DSC thermograms taken at 10K/min heating rate for $Se_{80-x}Te_{20}Bi_x$ glassy system

x	**T_g (k)**	**T_c (k)**	**T_m (k)**	**(T_c - T_g)**	**(T_m- T_c)**	**K_{gl}**	**T_{rg}**
0.0	337	402	521	65	119	0.54	0.64
0.2	343	389	529	46	140	0.32	0.64
0.5	344	384	530	40	146	0.27	0.64
1.0	345	380	534	35	154	0.22	0.64
1.5	346	375	536	29	161	0.18	0.64

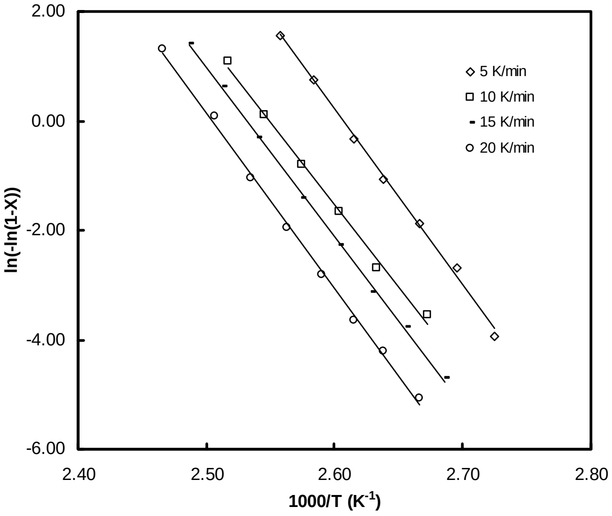

Fig. 7. ln (-ln (1-X)) vs 1000/T for $Se_{80-x}Te_{20}Bi_x$ (x=1.0).

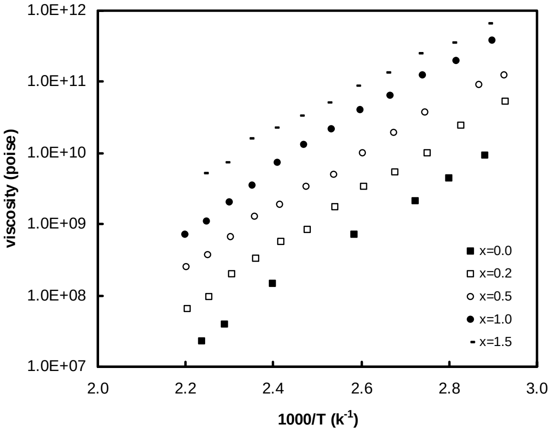

Fig. 8. Variation of viscosity as a function of temperature at α = 10 K/min for $Se_{80-x}Te_{20}Bi_x$ (x = 0, 0.2, 0.5, 1.0, 1.5).

4. Conclusion

The high value of the crystallization temperature well above the room temperature in these materials can prevent self-transition between the two phases making them attractive for recording applications. The decrease of T_c-T_g at higher bismuth concentration leads to the conclusion that stable glasses can be obtained only with low bismuth concentration. Viscosity calculations indicate that addition of bismuth increases the viscosity.

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