

EFFECT OF Bi INCORPORATION ON THE GLASS TRANSITION KINETICS OF $\text{Se}_{85}\text{Te}_{15}$ GLASSY ALLOY

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Bulk samples of $\text{Se}_{85-x}\text{Te}_{15}\text{Bi}_x$ glassy alloys are obtained by melt quenching technique. Differential scanning calorimetry has been applied to determine the thermal properties of Se-rich $\text{Se}_{85-x}\text{Te}_{15}\text{Bi}_x$ glassy alloys at different heating rates. The glass transition temperature (T_g) is found to shift to a higher temperature with increasing heating rate and with Bi addition. Activation energy and fragility of the system is also calculated. Specific heat is evaluated and a jump in heat capacity is observed at T_g . Theoretical parameters viz; density, molar volume, number of atoms per unit volume, lone pair electrons and cohesive energy of the system are also reported.

Keywords: cohesive energy, glass transition, molar volume, specific heat capacity

Introduction

In contrast to amorphous silicon and other group IV tetrahedrally bonded semiconductors, the chalcogenide glasses have attracted much attention due to their interesting optical, electrical and physical properties which can be controlled by changing their chemical composition. Chalcogenides with their twofold coordination and lone pair orbital offers dual channels of structural and electronic flexibility for removal of dangling bonds in the network. As a consequence a typical chalcogenide has a relatively sharp optical absorption edge, a single electrical activation energy and efficient photoexcited conductivity and luminescence. All these properties are characteristics of a well defined, clean forbidden gap. Nevertheless, field effect and doping experiments indicate that Fermi level of these chalcogenide glasses is nearly pinned. These glasses are used for fabricating active devices such as infrared transmitting optical fiber, infrared lasers, optical amplifiers and blue laser diodes [1–3].

Amorphous Se rich semiconducting alloys are of particular interest due to their current uses as photoconductors in high definition TV pick up tubes and particularly in digital X-ray imaging. Recent studies indicate that structure of a-Se having two-fold coordination consists of randomly mixed long polymeric Se_n chains in which various portions of a chain have ring fragments [4–6]. Te enters the structure by an isoelectronic substitution so that its coordination remains two. Addition of Te brings about changes in van der Waals bonds, or interchain secondary bonds because the Te atom is larger than the Se atom and has

more electrons in its orbital. One can therefore argue an increase in secondary bonding between chains due to Te addition. Te addition will also increase the valence alteration pair (VAP) type defects, connecting neighboring chains and limiting molecular mobility. The addition of third element expands the glass forming area and also creates compositional and configurational disorder in the system. The addition of impurities like Bi is particularly of much interest as it has produced a remarkable change in the optical, electrical and thermal properties of chalcogenide glasses. The conductivity of chalcogenide glasses changes from p to n type due to Bi addition [7–10]. An increasing concentration of Bi in Se–Te glassy alloy is responsible for the band tailing and broadening of valence band which is further known to reduce the width of optical band gap [11]. As Bi is introduced to host Se–Te alloy the coordination number of the system increases resulting in cross-linking of chains. This leads to increase in glass transition temperature (T_g) with Bi content [12–14]. The present work reports the effect of Bi incorporation on thermal and physical properties of $\text{Se}_{85}\text{Te}_{15}$ glassy alloy.

Experimental

Glasses of $\text{Se}_{85-x}\text{Te}_{15}\text{Bi}_x$, where $x=0, 1, 2, 3, 4, 5$ were prepared by the melt quenching technique. The materials (5N pure) were weighed according to their atomic percentages and sealed in evacuated (at $\sim 10^{-4}$ Pa) quartz ampoules. The sealed ampoules were kept inside a furnace where the temperature was

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increased up to 1000°C at a heating rate of 3–4°C min⁻¹. The ampoules were frequently rocked for 15 h at highest temperature to make the melt homogeneous. The quenching was done in ice-cold water. Glasses were obtained by breaking the ampoules. The bulk samples are characterized by the X-ray diffraction technique (Rigaku Geiger Flex 3KW Diffractometer) using CuK_α source and are found to be amorphous in nature as no prominent peak was observed in their spectra. Thermal behavior of the sample is recorded using Mettler Toledo Star^c DSC system. In each study approximately 10 mg bulk material is used. DSC runs are taken at four heating rates (5, 10, 15, 20 K min⁻¹) for each of the composition.

Results and discussion

Glass transition temperature and activation energy

Differential scanning calorimetric (DSC) curves are recorded for Se_{85-x}Te₁₅Bi_x glassy alloys at different heating rates. Well defined endothermic peaks are observed at glass transition temperature as shown in Fig. 1 (typically at 10 K min⁻¹ heating rate). It has been observed that glass transition temperature increase with heating rate as well as with Bi concentration (Table 1). The rate dependence of glass transition temperature has been studied using the empirical relation of the form [15]

$$T_g = A + B \ln \beta \quad (1)$$

where A and B are constants and β is heating rate. While the value of B is calculated from the slope of T_g vs. $\ln \beta$ plots (Fig. 2), the intercept on y axis provides the value of A (Table 1). The change in the value of B with increasing Bi concentration indicates that the system undergoes structural changes with Bi addition. The activation energy for glass transition is the amount of energy absorbed by a group of atoms in the glassy region so that a jump from one metastable state to another metastable state is possible. In the present system under study, the activation energy E_t for glass transition is calculated using modified Kissinger

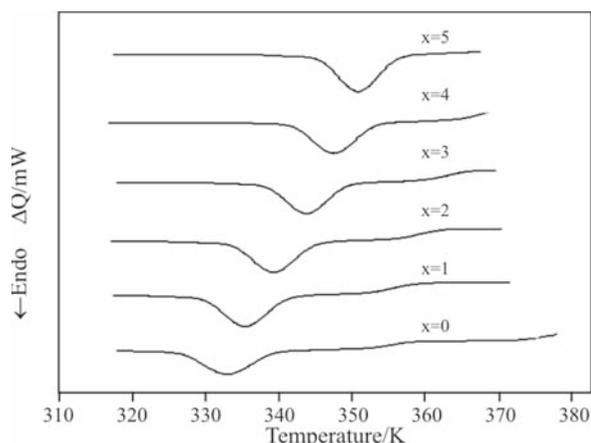


Fig. 1 Plot of DSC curves for Se_{85-x}Te₁₅Bi_x alloy

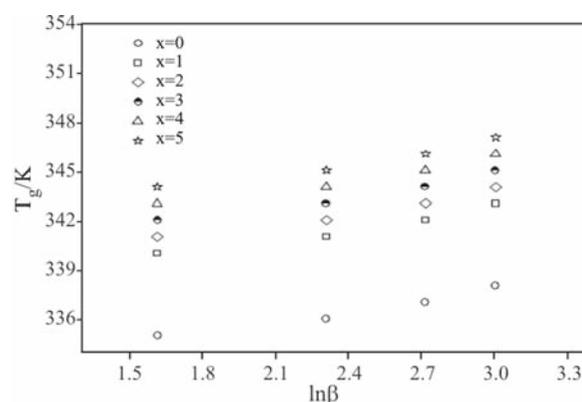


Fig. 2 Plot of T_g vs. for $\ln \beta$ Se_{85-x}Te₁₅Bi_x alloy

formula [16, 17] and it is found to increase with increasing Bi content as shown in Fig. 3 and Table 1. It implies that the probability of atoms to jump to the metastable state of lower internal energy decreases with increasing Bi concentration and hence the stability of system decreases with Bi content. The heating rate dependence of chalcogenide glasses is interpreted in terms of thermal relaxation phenomena. 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 $H_C(T)$ according to formula [18]

Table 1 Value of $\langle r \rangle$, T_g , A , B , E_t , F , C_p and ΔC_p for Se_{85-x}Te₁₅Bi_x glassy system

Bi/at.%	$\langle r \rangle$	T_g/K	B	A	$E_t/kJ mol^{-1}$	F	$C_p/J g atom^{-1} K^{-1}$	$\Delta C_p/J g atom^{-1} K^{-1}$
0	2.00	335	2.10	331	111.00	0.1439	74.60	0.270
1	2.01	339	2.11	338	114.32	0.1464	68.27	0.261
2	2.02	341	2.12	340	115.19	0.1467	62.73	0.248
3	2.03	343	2.13	341	116.36	0.1473	54.93	0.239
4	2.04	344	2.14	342	117.48	0.1483	49.20	0.223
5	2.05	345	2.15	343	118.26	0.1488	42.81	0.131

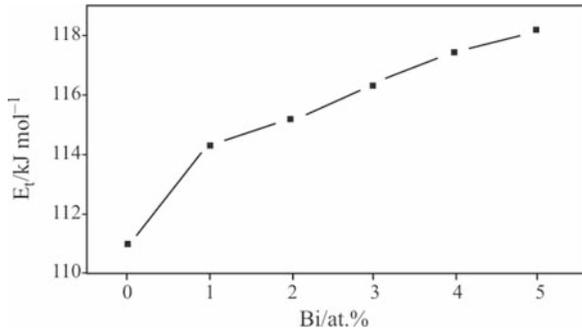


Fig. 3 Plot of E_t vs. Bi (at.%) for $\text{Se}_{85-x}\text{Te}_{15}\text{Bi}_x$ alloy

$$\left(\frac{\delta H}{\delta t}\right)_T = -\frac{(H - H_C)}{\tau} \quad (2)$$

where τ is known as structural relaxation time. The structural changes in the host Se–Te glassy alloy with Bi concentration may be explained on the basis of coordination number of the system. The mean coordination number $\langle r \rangle$ of $\text{Se}_\alpha\text{Te}_\beta\text{Bi}_\gamma$ system is defined by

$$\langle r \rangle = \frac{\alpha N_{\text{Se}} + \beta N_{\text{Te}} + \gamma N_{\text{Bi}}}{\alpha + \beta + \gamma} \quad (3)$$

where N_{Se} , N_{Te} and N_{Bi} are the coordination number of Se, Te, Bi and α , β and γ are their respective atomic ratios. The calculated value of $\langle r \rangle$ for the present system is also listed in Table 1. Bi being an element of group V, can bond with 3 or 5 Se atoms and immediately increases the average coordination number. Three-fold coordination will result in less structural strain than five-fold coordination and would be more favorable. Bi atom in the structure can crosslink chains and thus enables a better covalent network structure to be developed. This leads to observed rise in T_g with Bi addition. The glass transition temperature T_g of chalcogenide glasses shows coordination number dependence. It increases linearly with increase in coordination number and follows the relation [19]

$$\ln T_g = 1.6\langle r \rangle + C \quad (4)$$

where $C=2.3$. Eq. (4) follows the same trend as that of the experimental values obtained for T_g . The above results can also be discussed on the basis of a parameter called fragility (F), which characterizes and quantifies the anomalous non-Arrhenius transport behavior of glassy materials near the ergodicity breaking glass transition region [20–22]. Fragile glasses are substances with non-directional interatomic/intermolecular bonds. Strong glasses are those which show resistance to structural degradation and usually associated with a small ΔC_p . Fragility (F) is calculated by using the following relation [23]

$$F = \frac{E_t}{T_g \ln 10} \quad (5)$$

where all the symbols have their usual meaning. The value of (F) is found to increase with $\langle r \rangle$ as stated in Table 1. This behavior indicates that the glasses become more fragile and their tendency to structural rearrangement increases with increasing non-directional interatomic bonds.

Evaluation of specific heat

Specific heat is very sensitive to the way in which atoms or molecules are dynamically bound in a solid [24]. An abrupt change in specific heat at glass transition temperature is the characteristic of all chalcogenide glasses. The parameter detects sensitively the change in microstructure of glass which can be seen by the jump of specific heat close to Dulong and Petit value of $C_p=3R$.

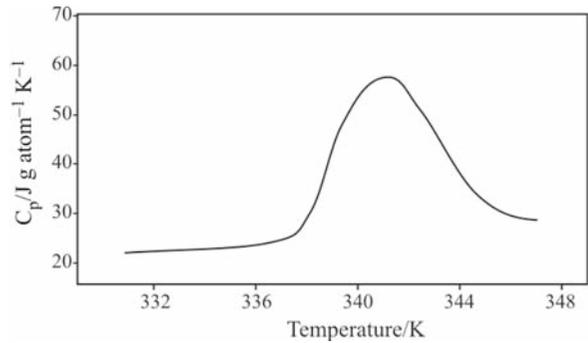


Fig. 4 Plot of C_p vs. temperature (T) for $\text{Se}_{85-x}\text{Te}_{15}\text{Bi}_x$ ($x=2$) alloy

Figure 4 shows typical C_p vs. T plot obtained for $\text{Se}_{83}\text{Te}_{15}\text{Bi}_{2.0}$ glass at 10 K min^{-1} heating rate. It has been observed that below T_g , the C_p values agrees with the classical limit of Dulong and Petit for the vibrational heat capacity of solids. The observed increase in C_p at glass transition temperature is due to the addition of translational and/or rotational modes made available by the breakage of bonds forming the glass network [25, 26]. The value of C_p is found to decrease with increasing Bi content (Table 1). This behavior is may be due to the non-availability of the larger number of degrees of freedom in the alloy which could absorb heat energy. The heat capacity jump (excess heat capacity at T_g) is expressed as

$$\Delta C_p = (C_{p1} - C_{pg})_{T=T_g} \quad (6)$$

where C_{p1} and C_{pg} are the heat capacity of liquid and glassy states across the glass transition. ΔC_p reflects the amount of configurational change occurring in the network during glass to liquid transition. The excess

heat capacity ΔC_p , during glass transition is evaluated using the relation [27]

$$\Delta C_p = \frac{\Delta H}{Qm} \quad (7)$$

where ΔH the change of heat flow through the investigated sample with mass m at glass transition and Q is the heating rate. It has been observed that ΔC_p decrease with increasing Bi content as shown in Fig. 5 and Table 1. The observed decrease in ΔC_p may be due to the fact that with increasing Bi content the concentration of defect states increases. It leads to a decrease in structural relaxation time and hence further responsible for the fall in ΔC_p .

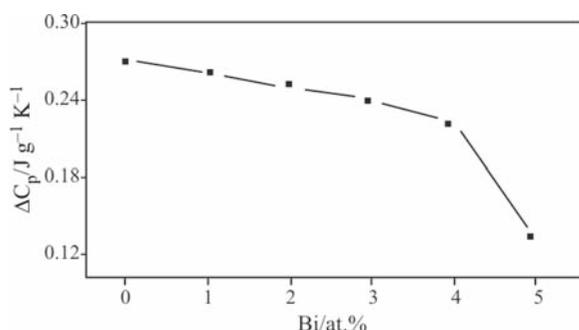


Fig. 5 Plot of ΔC_p vs. Bi (at.%) for $\text{Se}_{85-x}\text{Te}_{15}\text{Bi}_x$ alloy

Theoretical parameters

The rise in T_g with Bi and microscopic changes taking place in the system can be understood in the light of various physical parameters of the system. T_g can be related to

- i) Density of the system which increases monotonically with Bi.
- ii) Average number of bonds per unit volume and number of lone pair electrons.
- iii) Average bond strength of the system.

Density is an important physical parameter and is a measure of rigidity of the system. It can be deduced by using formula [28]

$$\rho = \left(\sum m_i / d_i \right)^{-1} \quad (8)$$

where m_i is the fraction of mass and d_i is the density of i^{th} structural unit density. The density of above glassy system is also determined experimentally by Archimedes method and is tabulated in Table 2. Using the value of density obtained from Eq. (8), the molar volume of the system is calculated by using the formula

$$V_m = \frac{1}{\rho} \left(\sum x_i M_i \right) \quad (9)$$

where x_i represents the atomic fraction of component i and M_i is its atomic mass. The molar volume is also found to increase with Bi content, which is a result of substituting Se atoms with the heavier and larger Bi atoms in the glass network. The theoretical density and molar volume calculated using above two relations is presented in Table 2 for the mentioned glassy system.

In chalcogenide glasses the valence band originates from lone pair electron states whereas the conduction band arises from antibonding states. The energy of the conduction band edge is decided by the number of atoms per unit volume and is determined by using the formula [28]

$$n_b = \langle r \rangle \left(\frac{N_A}{V_m} \right) \quad (10)$$

where N_A is the Avogadro number. n_b is found to increase with Bi content (Table 2). In terms of Pauling viewpoint [29], the chemical bonds with lone pair electrons decreases the strain energy in the system and structures with large number of lone pair electrons favor glass formation. The number of lone pair electrons is calculated by using following relation

$$L = V - \langle r \rangle \quad (11)$$

where L is the number of lone pair electrons and V is the number of valence electrons. The results are listed in Table 2. It has been found that the number of lone pair electrons decrease with increasing Bi content. This behavior is caused by the interaction between the Bi ion and lone pair electrons of bridging Se atom. The interaction decreases the role of lone pair electrons in the glass

Table 2 Value of ρ , ρ_{exp} , V_m , n_b , L , excess Se–Se bonds and CE for the system

Bi/at.%	$\rho / \text{g cm}^{-3}$	$\rho_{\text{exp}} / \text{g cm}^{-3}$	V_m / cm^3	n_b	L	Excess Se–Se bonds	CE/eV
0	5.07	5.57	17.01	$0.7790 \cdot 10^{23}$	4.00	140	2.76
1	5.13	5.68	17.06	$0.7803 \cdot 10^{23}$	3.99	135	2.70
2	5.20	5.70	17.09	$0.7828 \cdot 10^{23}$	3.98	130	2.63
3	5.25	5.81	17.17	$0.7830 \cdot 10^{23}$	3.97	125	2.56
4	5.31	5.96	17.21	$0.7851 \cdot 10^{23}$	3.96	120	2.50
5	5.37	6.04	17.26	$0.7866 \cdot 10^{23}$	3.95	115	2.43

formation. According to a simple criterion proposed by Zhenhua [30] for a binary system the number of lone pair electrons must be larger than 2.6 and for a ternary system it must be larger than 1.

The cohesive energy, defined as stabilization energy of an infinitely large cluster of the material per atom is a measure of average bond strength of the system. It is determined by summing the bond energies of the consequent bonds expected in the material. This behavior is equivalent to assuming a simplified model consisting of non interacting electron pair bonds highly localized between adjacent pair of atoms. The cohesive energy (*CE*) of prepared bulk samples is evaluated using the relation [28]

$$CE = \sum(C_i D_i / 100) \quad (12)$$

where C_i and D_i are the number of expected chemical bonds and energy of each bond respectively. The bond energy of heteropolar bonds is calculated by using Pauling method [31]. According to chemical bond approach (CBA) [32], atoms combine more favorably with atoms of different kind rather than with the same kind and bonds are formed in the sequence of decreasing bond energies until all the available valences are satisfied. Consequently bonds between like atoms will only occur if there is an excess of certain type of atoms. In the above mentioned system Bi is expected to combine preferably with Se because the bond energy of Bi–Se (170.4 kJ mol⁻¹) bond is higher than that of Bi–Te (125.6 kJ mol⁻¹). This results in decrease of Se–Se (190.08 kJ mol⁻¹) bonds and is further responsible for lowering the average bond energy and hence *CE* of the system. The excess Se–Se bonds and *CE* of the system is calculated and tabulated in Table 2.

Conclusions

The glass transition temperature, activation energy, and fragility of the system is calculated and the effect of increasing Bi concentration on these parameters has been studied. It has been observed that Bi atom leads to the cross-linking of chains and increases the coordination number of the system. The specific heat capacity and change in heat capacity at glass transition is also evaluated and has been found that both the parameters decrease with increasing Bi concentration. This decrease is attributed to non availability of the larger number of degrees of freedom in the alloy which could absorb the heat energy. Various physical parameters are also calculated theoretically and were found that density, molar volume and number of atoms per unit volume increases, whereas the lone pair electrons decreases with Bi concentration. Cohesive energy of the system

is also evaluated on the basis of chemical bond approach and also shows the same trend as that of lone pair electrons.

References

- 1 V. Trnovcova, I. Furar and D. Lezal, *J. Non-Cryst. Solids*, 353 (2007) 1311.
- 2 A. Zakery and S. R. Elliott, *J. Non-Cryst. Solids*, 330 (2003) 1.
- 3 N. Goyal, A. Zolanvari and S. K. Tripathi, *J. Mater. Sci.: Mater. Electr.*, 12 (2001) 523.
- 4 S. K. Tripathi, V. Sharma, A. Thakur, J. Sharma, G. S. S. Saini and N. Goyal, *J. Non-Cryst. Solids*, 351 (2005) 2468.
- 5 T. Akiyama, M. Uno, H. Kituara, K. Narumi, K. Nishiuchi and N. Yamada, *Jpn. J. Appl. Phys.*, 40 (2001) 1598.
- 6 T. Ohta, *J. Opto-Electron. Adv. Mater.*, 3 (2001) 609.
- 7 N. Tohge, Y. Yamamoto, T. Minami and M. Tanaka, *J. Appl. Phys. Lett.*, 34 (1979) 640.
- 8 N. Tohge, T. Minami, M. Tanaka, *J. Non-Cryst. Solids*, 59–60 (1983) 1015.
- 9 P. Nagels, M. Rotti and W. Vikhrov, *J. Phys. (Paris)*, 42 (1981) 907.
- 10 P. Nagels, L. Tichey, A. Tiska and H. Ticha, *J. Non-Cryst. Solids*, 59–60 (1983) 999.
- 11 P. Sharma, M. Vashistha and I. P. Jain, *J. Opto-Electron. Adv. Mater.*, 7 (2005) 2647.
- 12 N. Mehta, S. K. Agrahari and A. Kumar, *Phys. Scr.*, 74 (2006) 579.
- 13 M. Saxena and P. K. Bhatnagar, *Bull. Mater. Sci.*, 26 (2003) 547.
- 14 N. Suri, K. S. Bindra, P. Kumar, M. S. Kamboj and R. Thangaraj, *J. Ovonic Res.*, 2 (2006) 111.
- 15 N. Mehta and A. Kumar, *J. Therm. Anal. Cal.*, 7 (2007) 343.
- 16 H. E. Kissinger, *J. Res. Nat. Bur. Stand.*, 57 (1956) 217.
- 17 N. Mehta and A. Kumar, *J. Opto-Electron. Adv. Mater.*, 7 (2005) 1473.
- 18 J. M. Saiter, *J. Opto-Electron. Adv. Mater.*, 3 (2001) 685.
- 19 S. O. Kasap and S. Yannacopoulos, *J. Mater. Res.*, 4 (1989) 893.
- 20 R. Boomer, K. L. Nagi, C. A. Angell and D. J. Plazek, *J. Chem. Phys.*, 99 (1993) 4201.
- 21 P. S. L. Narasimham, A. Giridhar and S. Mahadevan, *J. Non-Cryst. Solids*, 43 (1981) 301.
- 22 S. A. Fayek, M. R. Balboul and K. H. Marzouk, *Thin Solid Films*, 515 (2007) 7281.
- 23 L. Pauling, *The Nature of the Chemical Bond*, 3rd Ed. (Cornell University Press, Ithica NY), 1960.
- 24 L. Zhenhua, *J. Non-Cryst. Solids*, 127 (1981) 298.
- 25 L. Pauling, *Die Nature der Chemischen Bindung*, VCH, Weinheim 1976, pp. 80–89.
- 26 J. Biecerano and S. R. Ovshinesky, *J. Non-Cryst. Solids*, 74 (1985) 75.

Received: May 28, 2008

Accepted: September 18, 2008

Online First: January 12, 2009

DOI: 10.1007/s10973-008-9312-8