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Effect of Bismuth incorporation on some thermo-mechanical properties of glassy $Se_{78}Te_{20}Sn_2$ alloy

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We have synthesized some novel chalcogenide glasses from the Se-Te-Sn-Bi system. The basic thermo-mechanical parameters such as micro-hardness, volume (V_h) and formation energy (E_h) of micro-voids in the glassy network, as well as the modulus of elasticity E have been calculated in present glasses. The composition dependence of micro-hardness is also discussed.

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1. Introduction

In recent years, the physical properties of chalcogenide glasses were intensively investigated because of their wide range of applications in several technological fields [1-6]. Studies on various properties of these materials have revealed many possibilities for their application in different emerging fields like integrated and diffractive optics [1, 2], threshold and memory switching devices [3] and so on. Multi-component systems have recently been used successfully for such applications [4]. These glasses show transmission in the middle-infrared region. Recently, these glasses have been used as bio-sensors in evanescent wave spectroscopy of bio-molecules in human lung cells [5, 6]. The impact of toxic agents on cell health is investigated by recording IR signatures [5, 6]. But an obstacle for such applications is the poor mechanical stability of these glasses. For example, glasses of Se-Ge and Te-As-Se system show poor mechanical properties [7].

From above discussion, it is clear that the mechanical properties of these materials play important role for their practical applications and are intimately connected with their structure and other physical and chemical properties. In particular, the hardness of glass is of direct practical importance since it is apparently related to bonding in these materials. It has often been used as an approximate measure of strength. Although hardness is extensively measured and many techniques are available for its measurement, there is still no satisfactory definition as far as glass is concerned. Among the various experimental techniques, the indentation hardness testing is frequently used for the determination of mechanical properties of these materials in the form of bulk samples and thin films [8, 9].

Recently, we have synthesized some multi-component chalcogenide glasses by incorporating Bi in ternary $Se_{78}Te_{20}Sn_2$ alloy, which a poor glass former and has low thermal stability. We have observed a significant increase in both glass forming ability and thermal stability after the addition of Bi in the parent $Se_{78}Te_{20}Sn_2$ alloy. This motivates us to see the effect of Bi incorporation on thermo-mechanical properties of ternary $Se_{78}Te_{20}Sn_2$ alloy. In the present, an effort has been made to study the variation of micro-hardness and the related thermo-mechanical properties with the Bi content in glassy $Se_{78-x}Te_{20}Sn_2Bi_x$ ($0 \le x \le 6$) alloys. The Vickers hardness test method is used for this purpose. This method is one of the most common and reliable methods for hardness measurements. It provides useful information concerning the mechanical behaviour of brittle solids.

2. Theoretical basis

Hardness of glasses is a function of the strength of individual bonds and the atomic packing density [10]. The Vickers hardness number (VHN) H_V, obtained by measuring the diagonal length of the indentation produced by the penetration of a square-based pyramid indenter is normally taken as a measure of the micro-hardness of the material. VHN is determined using the relation [11]:

$$H_V = \frac{1854.4F}{d^2} \tag{1}$$

Here F is the load applied (in kg) and d is the length (in mm) of the diagonal of the indentation. During indentation, a glass undergoes both compression and shear, resulting in its elastic deformation, flow and densification [12]. The bond strength of a certain compound determines the ratio of recoverable and irreversible deformation. High bond

strength results in high elastic modulus, which in turn prevents bond breakage. On the other hand, low bond strength results in bond breaking concomitant irreversible, plastic flow.

According to the free-volume theory, Sanditov [13] proposed a following equation for micro-hardness of glasses:

$$H_V = \frac{E_h}{V_h} \tag{2}$$

Here E_h is the energy of micro-void creation in a volume V_h. According to Bartenev [14] and Nemilov [15] the micro-hardness is related to the modulus of elasticity (E) and Poisson's coefficient, μ, by the relation:

$$H_V = \frac{(1-2\mu)}{6(1+\mu)}E \tag{3}$$

On the other hand, the variation of the coefficient of thermal expansion at glass transition temperature T_g can be expressed as
[11]:

$$\Delta\alpha = 3(1-2\mu)\frac{H_V}{T_g E} \tag{4}$$

Further, the product of the variation of the coefficient of thermal expansion Δα and the glass transition temperature T_g is:

$$\Delta\alpha T_g \approx 0.1 \tag{5}$$

The equation (5) is valid for the glasses possessing equal values of Poison's coefficients [16]. Combining the equations (3) and (4) we can write the relation:

$$\Delta\alpha T_g = \frac{(1-2\mu)^2}{2(1+\mu)} \tag{6}$$

According to Bartenev and co-authors [17], we have:

$$\Delta\alpha T_g = f_g \ln\left(\frac{1}{f_g}\right) \tag{7}$$

Thus at $T = T_g$ the partition of fluctuational free volume, f_g, depends also on the Poison's coefficient $f_g=f(\mu)$.Then we have:

$$H_V = T_g\left(\frac{gk}{V_h}\right) \tag{8}$$

Here k is the Boltzmann's constant and $g = \ln\left(\frac{1}{f_g}\right)$.

Integration of the equations (1) and (7) gives the relation of T_g, as well as H_V, towards f_g and E_h:

$$T_g = \left(\frac{1}{gk}\right)E_h \tag{9}$$

From the equations' systems (5) and (6), and (5) and (7) we can determine $\mu = 0.25$ and $f_g \cong 0.028$ ($g \cong 3.58$). In order to determine the values of V_h, E_h and E, the relations (8), (9) and (3) we can be written as:

$$V_h = 3.58k\left(\frac{T_g}{H_V}\right); \tag{10}$$

$$E_h = 3.58kT_g \tag{11}$$

and

$$E = 15H_V \tag{12}$$

Thus, knowing the values of T_g, and H_V, one can determine the above thermo-mechanical parameters.

3. Experimental

Bulk $Se_{78-x}Te_{20}Sn_2Bi_x$ ($0 \le x \le 6$) glasses were prepared by the melt quenching technique. Appropriate amounts of high purity elements were taken in quartz ampoules. The ampoules were flame sealed after evacuating the ampoule to 10^{-6} Torr pressure. A high vacuum pumping system (Hindhivac, Model: VS65D) with a liquid nitrogen trap is used for this purpose. The sealed ampoules were heated in a furnace up to 900 °C and then dropped into ice-cooled water rapidly. To check the glassy nature of the samples, XRD technique was used.

The alloys, thus prepared, were ground to make fine powder for DSC studies. 10 to 20 mg of each sample was heated at a constant heating rate of 10 °C-min^{-1} and the changes in heat flow relating to an empty aluminum pan were measured. For the present observations, Auto Q20 Modulated Differential Scanning Calorimetry (T. A. instruments, U.S.A.) was used for obtaining DSC scans at chosen heating rate.

The peak values of glass transition temperature (T_g) determined from Modulated Differential Scanning Calorimeter (T.A. Instruments, Model: Auto Q20) under a constant heating rate of 10 °C-min^{-1} are tabulated in Table 1. Polished samples were indented using an automated digital Vickers micro-hardness tester (Vaiseshika Electron Devices,

Model: DHV-1000). The microscope of micro-hardness tester is calibrated with the screen resolution of computer attached with the tester. For this micrometer disc is placed on the specimen platform of the micro-hardness tester. The image of linear scale on micrometer disc is focused with the help of rack and pinion arrangement. All measurements were made at room temperature.

Table 1 Glass transition temperature and Vickers hardness of glassy $Se_{78-x}Te_{20}Sn_2Bi_x$ $(0 \le \xi \le 6)$ alloys

x	T_g (K)	H_v (kgf / mm^2)
0	340.3	71.1
2	350.3	48.7
4	353.2	41.0
6	352.7	52.6

4. Results and discussion

Fig. 2 shows the typical DSC scans for present glassy alloys at heating rate of 10 K / min. It is clear from Fig. 1 that well defined endothermic and exothermic peaks are observed at glass transition temperature (T_g) and crystallization temperatures (T_c) respectively. The values of ($T_c - T_g$), which is the indicator of thermal stability is found to be increased significantly in quaternary alloys. This is an important advantage of these alloys, which is essential to prevent self-transition between the two phases: amorphous and crystalline. Hence, one can expect each of these alloys to remain stable in its amorphous and crystalline phases at room temperature.

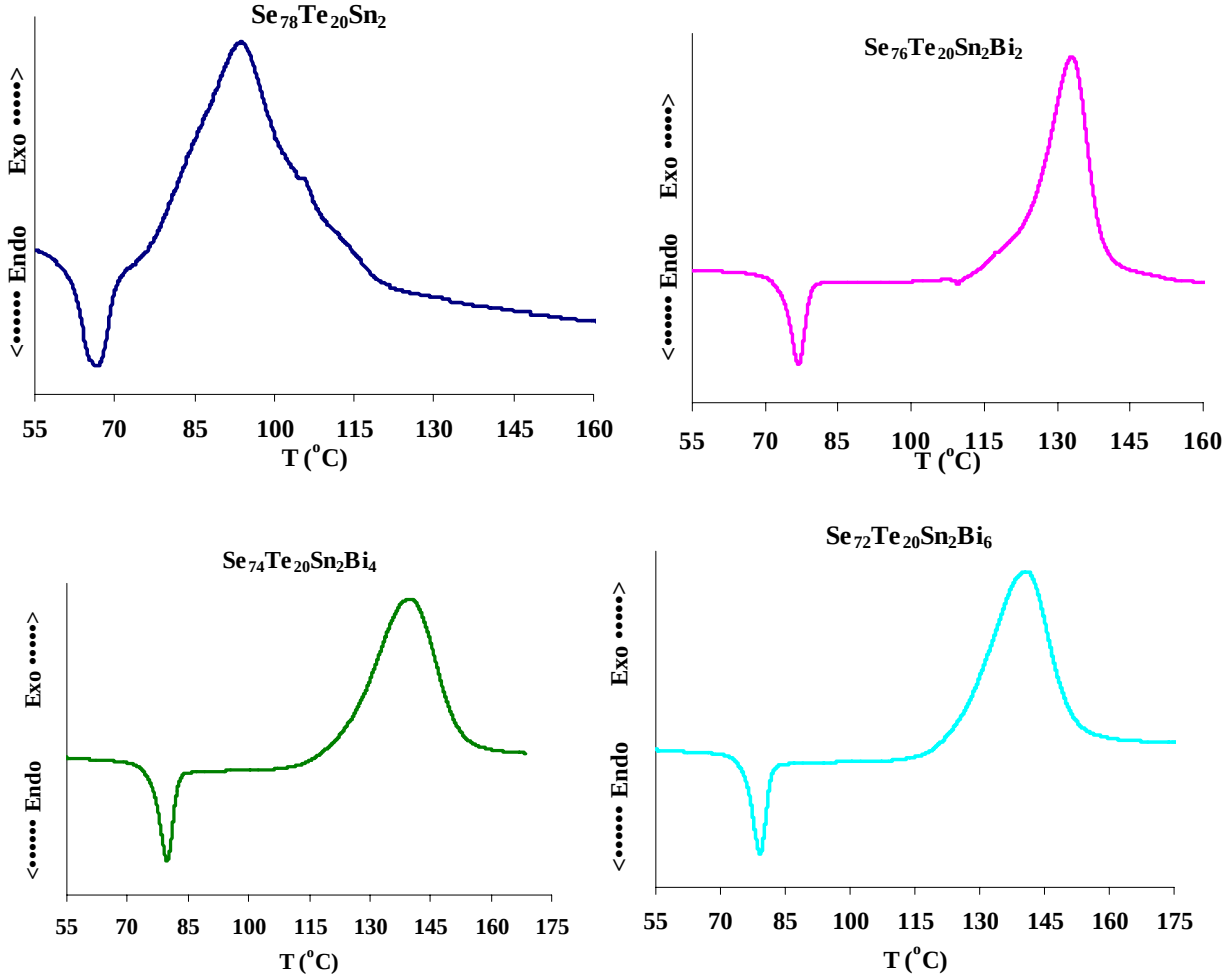

Fig. 1 DSC scans of glassy $Se_{78-x}Te_{20}Sn_2Bi_x$ $(0 \le x \le 6)$ alloys at heating rate of 10 °C-min^{-1}.

Fig. 2 shows typical photographs of Vickers indented marks, for different glassy alloys. The value of H_V is calculated using the average values of indentation diagonals. All glass samples were uniformly subjected to a load of 100 g for 10 seconds duration. The micro-hardness value of each glassy alloy is given in Table 1. The value shown in this table is the average of at least ten indents made on each sample.

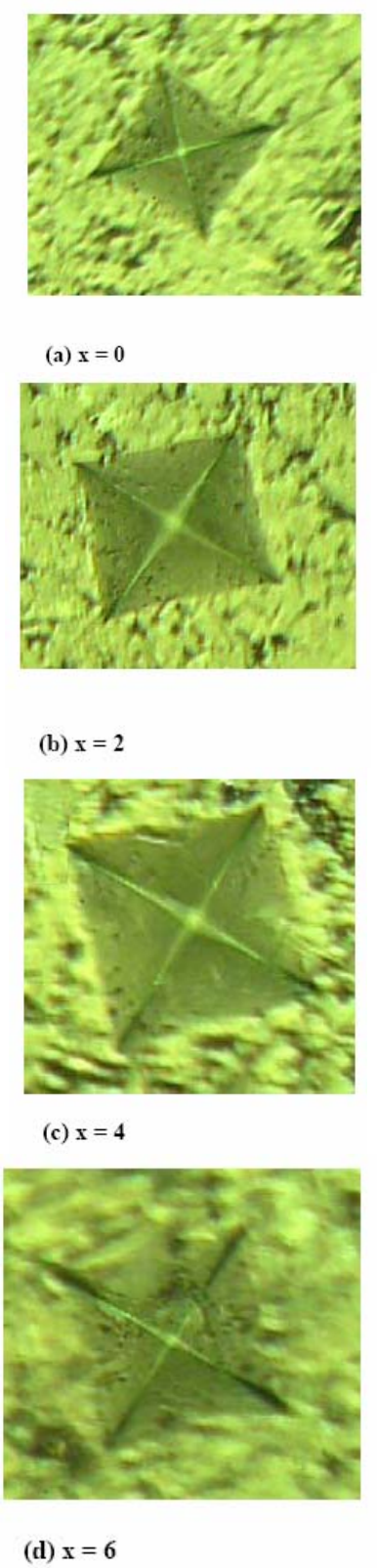

Fig. 2 Micrographs of Vickers indent on surface of bulk samples of glassy $Se_{78-x}Te_{20}Sn_2Bi_x$ ($0 \le x \le 6$) alloys

For the glassy $Se_{78-x}Te_{20}Sn_2Bi_x$ ($0 \le x \le 6$) alloys, the average coordination number <*r*> can be calculated using the formula.

$$< Z >= \frac{\alpha N_{Se} + \beta N_{Te} + \gamma N_{Sn} + \delta N_{Bi}}{100} \qquad (13)$$

Here α, β. γ and δ are the atomic percentages of Se, Te, Sn and Bi and N_{Se}, N_{Te}, N_{Sn} and N_{Bi} are their respective coordination numbers. The values of N_{Se}, N_{Te}, N_{Sn} and N_{Bi} have been taken from literature survey and these values are 2, 2, 4 and 4 respectively.

The composition dependence of both T_g and H_V is shown in Fig. 3 in terms of average coordination number <Z>. From this figure, it is clear that reversal in the respective increasing and decreasing trends of T_g and H_V is obtained at <Z> = 2.12.

From Table 1, one can see that the value of H_V is decreased after the incorporation of Bi in parent glass $Se_{78}Te_{20}Sn_2$. This can be explained in terms of average heat of atomization of the present glassy alloys. In the present glassy system, Bi has been incorporated at the cost of Se. The heat of atomization of Bi (207 kJ / mol) is less than that of Se (227 kJ / mol). Thus, the average heat of atomization of quaternary alloys is less as compared to average heat of atomization of parent ternary alloy. This is probably the reason of decrease in the micro-hardness. Similar correlation between micro-harness and average heat of atomization was reported by Pattanaik et al [18] in past. Thus, our results confirm the possibility of such correlation between these two parameters. After incorporation of Bi, when we increase the concentration of Bi, we see that the variation in H_V for quaternary alloys is not monotonic. Thus, an exact description of the variation of H_V with increase in Pb concentration is difficult due to complexity of disordered structure of present quaternary glasses. Future experiments in this direction could reveal the exact origin.

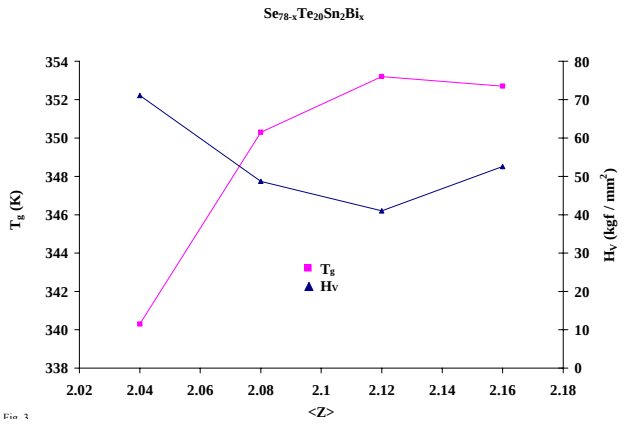

Fig. 3 Plots of glass transition temperature (T_g) and Vickers hardness (H_V) against the average coordination number (<Z>) for glassy $Se_{78-x}Te_{20}Sn_2Bi_x$ ($0 \le x \le 6$) alloys.

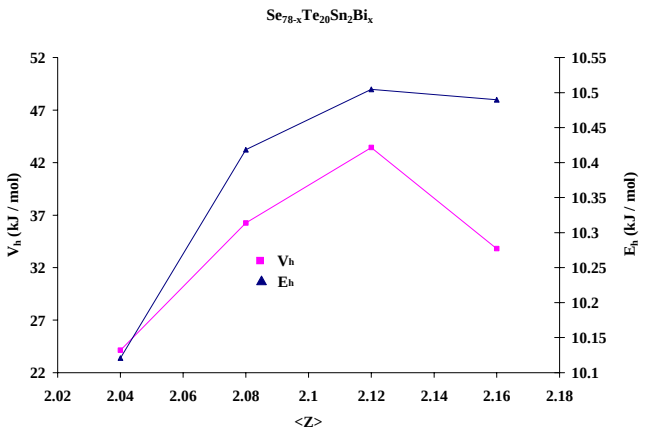

Fig. 4Plots of thermo-mechanical parameters Vh and Eh against the average coordination number (<Z>) for glassy $Se_{78-x}Te_{20}Sn_2Bi_x$ ($0 \le x \le 6$) alloys.

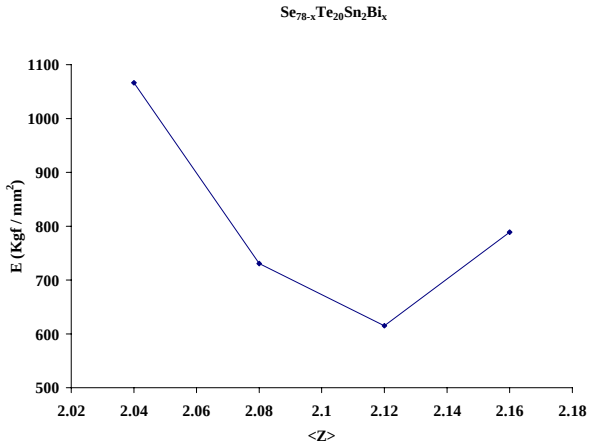

Fig. 5 Plots of modulus of elasticity E against the average coordination number (<Z>) for glassy $Se_{78-x}Te_{20}Sn_2Bi_x$ ($0 \le x \le 6$) alloys.

Knowing the value of T_g and H_V, the values of other thermo-mechanical parameters are calculated using Equation (10), (11) and (12). The values of these parameters are given in Table 2 for various glassy alloys. The composition dependence of volume (V_h) and formation energy (E_h) of micro-voids in the glassy network of present glasses is shown in Fig. 4. This figure shows that both V_h and E_h exhibit similar composition dependence. The reversal in the increasing trends of V_h and E_h is also obtained at <Z> = 2.12. The composition dependence of modulus of elasticity E is shown in Fig. 5. From this figure, we find that the value of E is decreased after incorporation of Bi. The minimum value is obtained at 4 at% of Bi.

Table 2 Thermo-mechanical characteristics of glassy $Se_{78-x}Te_{20}Sn_2Bi_x$ ($0 \le x \le 6$) alloys

x	V_h (Å^3)	E_h (kJ / mol)	E (kgf / mm^2)
0	24.1	10.12	1066.5
2	36.2	10.42	730.5
4	43.4	10.50	615.0
6	33.8	10.48	789.0

5. Conclusion

Some novel glasses of Se-Te-Sn-Bi system have been prepared. The calorimetric and micro-hardness measurements have been performed in glassy $Se_{78-x}Te_{20}Sn_2Bi_x$ alloys. The effect of Bi substitution on the micro-hardness of these glasses has been interpreted in terms of the variation in the average heat of atomization of the glasses with composition. The maximum or minimum values of different thermo-mechanical parameters in quaternary alloys are obtained at 4 at% of Bi.

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