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Study of the physical properties with compositional dependence of bi content in Te-Se-Bi glassy system

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ABSTRACT

The effect on the physical properties with the addition of Bi content, viz glass transition temperature (T_g), mean bond energy <E>, cohesive energy (CE), average heat of atomization (H_S), coordination number (m), constraints (N_{con}) and lone pair electrons (L) of $Te_{18}Se_{82-x}Bi_x$(x= 0,1.5,2.5,3.5,4.5) glassy alloy have been examined theoretically. It has been found that the mean bond energy <E> is proportional to the glass transition temperature (T_g). The glass transition temperature has been estimated by using Tichy – Ticha approach and found to increase with the addition of Bi content. The cohesive energy has been calculated by using chemical bond approach (CBA) method. It has been found that mean bond energy, transition temperature, coordination number and constraints increases whereas all the other parameters decreases with the increasing Bi content in Te- Se-Bi system.

INTRODUCTION

The study of chalcogenide materials is becoming a great field of interest due to their vast application in view of the fabrication of various solid state devices [1]. These materials have their vast electrical, optical and technological applications, such as in memory devices, optical fibers, xerography, photolithography, infrared lenses, optical amplifiers, blue laser diodes and in solar cells [2-7], make them more attractive for their investigation. New applications of amorphous materials such as image sensors, thermoelectric properties and optical recording [8] have become possible due to recent improvements in preparation techniques. The properties of chalcogenide materials like optical, electrical and physical can be controlled by changing their chemical composition [9]. These materials are emerged as multipurpose materials by the

modification in their properties when doped with metal impurities [10]. Among the amorphous chalcogenide alloys, mostly selenium (Se) based materials are preferred due to their commercial uses. Selenium (Se) rich chalcogenide materials are preferred due to their uses as photo conductors in high definition TV pick up tubes and particularly in digital X-ray imaging [11]. The pure Se has short life time and low sensitivity, but it characterized by high viscosity [12]. This problem can be overcome by alloying selenium with some impurities such as Ge, Te, Bi, Sb, As. etc. which in turn gives high sensitivity greater hardness, higher crystallization temperature and smaller aging effects as compared to pure Se glass [12-13]. The addition of tellurium (Te) has a catalytic effect on the crystallization of selenium. The presence of Te in Se chains probably favors their thermal dissociation as the Se-Te bond being weaker than Se-Se bond [14]. The addition of third element in binary chalcogenide glass system is found to be useful in obtaining stable glassy alloys as well as to understand the basic physics of these materials and expands the glass forming area and also creates compositional and configurational disorder in the glassy material. The addition of Bi in Se-Te system affects the electrical and optical properties and leads to cross linking of chains results in the increase of coordination number and also glass transition temperature of the system [15-17]. The series Se-Te has been used as a base material for the incorporation of Bi as reported earlier by several workers [8,13,16-20]. But no work has been reported so far as on the effect of Bi addition in $Te_{18}Se_{82-x}Bi_x$ chalcogenide alloy for the investigation of physical, thermal, electrical and optical properties. In the present work the correlation between mean bond energy and glass transition temperature has been studied theoretically by using the Tichy-Ticha approach [21,22] and a theoretical prediction of various physical parameters namely lone-pair electrons (L), coordination number (m), cohesive energy (CE), electronegativity and heat of atomization has also been investigated. The variation of these various parameters with Bi content has been discussed for $Te_{18}Se_{82-x}Bi_x$ (x=0, 1.5, 2.5, 3.5, 4.5) composition.

RESULTS AND DISCUSSION

2.1 average coordination number and constraints:

In chalcogenide glasses the coordination number of the covalent atoms is given by the 8-N rule [23]. Nearest-neighbor coordination number (m) in a $Te_{18}Se_{82-x}Bi_x$(x = 0, 1.5, 2.5, 3.5, 4.5) ternary system is suitable for testing the validity of topological concept [24] because of its large glass forming region. The average coordination number (m) in $Te_{18}Se_{82-x}Bi_x$ system is calculating by using the relation

$$m = \frac{(X)N_{Te} + (Y)N_{Se} + (Z)N_{Bi}}{X + Y + Z} \qquad (1)$$

Where X, Y and Z are the at % of Te, Se and Bi respectively and N_{Te}, N_{Se} and N_{Bi} are their respective coordination numbers. The calculated values of average coordination number (m) for $Te_{18}Se_{82-x}$ Bi_x (x=0, 1.5, 2.5, 3.5,and 4.5) system are listed in table 1. Covalent networks in a glassy system constrained mechanically by interatomic valence forces such as bond stretching and bond bending. In optimal glass formation the enumeration of mechanical constraints gives m/2, bond stretching constraints (N^{α}) and 2(m)-3, bond bending constraints (N^{β})[25]. The calculated values of average coordination number (m) and average number of constraints (N_{con}= N^{α}+ N^{β}) from table1, indicated that m increases with increase of Bi content concludes that Bi

atom leads to the cross linking of chains and hence increases the coordination number of the system.

2.2 Lone pair electrons and glass forming ability

The view point proposed by Pauling [26], increasing in the number of lone-pair electrons decreases the strain energy in a system and structures with large numbers of lone–pair electrons favors glass formation. The number of lone–pair of electrons is calculated using the relation [27].

$$L = V - m \tag{2}$$

Where L is the number of lone pair electrons, V is the valance electron and m is the average coordination number. The results of Lone-pair electron for $Te_{18}Se_{82-x}$ Bi_x system are tabulated in table 2.Variation of lone-pair electrons with Bi content is shown in fig.1. It is clear from the variation of lone-pair electrons that with the increase of Bi content, the number of lone–pair electrons decreases continuously in $Te_{18}Se_{82-x}Bi_x$ system. This behavior is caused by the interaction between the Bi ion and lone-pair electrons of bridging Se atom [11]. The role of lone-pair electrons in the glass formation decreases by this interaction. Zhenhua [27] proposed a simple criterion for a binary system and ternary system i.e. for a binary system the number of lone-pair electrons must be larger than 2.6 and for ternary system it must be larger than 1. This is clear from the table 2, that the minimum value of lone-pair electrons for $Te_{18}Se_{82-x}$ Bi_x system is 3.73, concludes that the present system under study is good glass former.

2.3 Deviation of stoichiometry, mean bond energy and glass transition temperature:

2.3.1 Determination of R:

The parameter R which determines the deviation of stoichiometry is defined as the ratio of covalent bonding possibilities of chalcogen atom to that of non-chalcogen atom. The quantity R is given by [21,22]

$$R = \frac{YN_{Se} + XN_{Te}}{ZN_{Bi}} \tag{3}$$

Where X, Y and Z are the atomic fractions of Te, Se and Bi respectively.

For R>1, the system is chalcogen rich and for R<1, the system is chalcogen poor. The threshold at R=1 (the point of existence of only hetropolar bonds) is evident. For the $Te_{18}Se_{82-x}$ Bi_x system the calculated value of R>1 is listed in table 3 .For the present investigating system $Te_{18}Se_{82-x}$ Bi_x system the value of R are greater than 1, leading the system to chalcogen-rich region.

2.3.2 Correlation between mean bond energy <E> and transition temperature (T_g)

Glass transition temperature (T_g) represents the temperature above which an amorphous matrix can attain various structural configurations and below which matrix is frozen into structure which cannot easily change to another structure [28]. The value of glass transition temperature (T_g) should not be only related to connectedness of the network (which is related to the average coordination number m), but should also be related to the quality of connections, i.e. mean bond energy between the atoms of the network firstly pointed out by Tichy ad Ticha [22]. Since the difference in the bond energies of hetropolar and homopolar bonds is substatinal [24] ;

chemically ordered networks are expected where the number of hetropolar bonds is maximized . Since bulk glasses are considered a chemical bond ordering model is assumed. So for the chalcogenide rich system we can determine the mean bond energy by using the correlation proposed by Tichy [22].

The mean bond energy $\langle E \rangle$ for the $Te_XSe_YBi_Z$ system is given by the relation:

$$\langle E \rangle = E_C + E_{rm} \tag{4}$$

Where E_c is the overall contribution towards bond energy arising from strong hetropolar bonds and is given by

$$\langle E \rangle = P_r D_{hb} \tag{5}$$

Here P_r is the degree of cross linking and is given by

$$P_r = \frac{XN_{Te} + ZN_{Bi}}{X + Y + Z} \tag{6}$$

D_{hb} is the average hetropolar energy and is suggested to be

$$D_{hb} = \frac{YN_{Te}E_{Se-Te} + ZN_{Bi}E_{Se-Bi}}{YN_{Te} + ZN_{Bi}} \tag{7}$$

E_{rm} is the average bond energy per atom of the "remaining matrix" and is given by

$$E_{rm} = \frac{2[0.5(m) - P_r]E_{Se-Se}}{m} \tag{8}$$

Where $E_{Se\text{-}Se}$ is the homopolar bond energy of Se-Se bonds. The values of the overall mean bond energy <E> for the glass alloy $Te_{18}Se_{82\text{-}x}Bi_x$ are listed in table 3, and are found to increase with increasing Bi content. A graphical variation of <E> with increasing Bi content and R are given in fig. 2.and fig. 3. respectively.

The glass transition temperature (T_g) for Te-Se-Bi glassy alloy is predicted theoretically by using the relation given by Tichy and Ticha [21,22], illustrated an impressive correlation of T_g for a set of 186 glasses, ranging from (320-760 K), with <E> in the form of given relation:

$$T_g = 311[\langle E \rangle - 0.9] \tag{9}$$

Where <E> is the mean bond energy of the system. The calculated values of T_g for $Te_{18}Se_{82\text{-}x}Bi_x$ system are listed in table 3. and it evident from the table that T_g is proportional to <E> with increase of Bi content in Te-Se glassy alloy, <E> along with glass transition temperature (T_g)

increases. The variation of T_g with Bi (at %) is shown in fig.4.Similar trend in the increase in T_g with the addition of Bi content has been experimently reported earlier[11,17-18,20] .

2.4. Calculation of Bond energy, Cohesive energy (CE) and electronegativity

The bond energies for hetronuclear bonds have been calculated by Pauling [26], using the relation:

$$D(A-B) = \left[D(A-A)D(B-B)\right]^{\frac{1}{2}} + 30(\chi_A - \chi_B)^2 \quad (10)$$

Where D(A-B) is the bond energy of hetronuclear bond, D(A-A) and D(B-B) are the bond energies of the homonuclear bonds. The D(A-A) values for Bi, Se and Te are 47.9, 44.0 and 33.0 (kcal/mol) [29]. χ_A and χ_B are the values of electronegativities of A and B respectively. The electronegativity values of the atoms involved used are 2.55 for Se, 2.0 for Bi and 2.1 for Te respectively. Values of electronegativity for the $Te_{18}Se_{82-x}Bi_x$ system are calculated by using Sanderson's principle [30]. According to this principle electronegativity of the alloy is the geometric mean of electronegativity of its constituent elements.

The cohesive energy (CE) of the system is the measure of the strength of a chemical bond and is defined as the stabilization energy per atom. By using the chemical bond approach (CBA) method [31], the cohesive energy for investigated samples has been calculated. The cohesive energy for the Te-Se-Bi system are calculated by summing the bond energies over all bonds expected in the system by using the relation:

$$CE = \Sigma\left(\frac{C_i D_i}{100}\right) \quad (11)$$

Where C_i and D_i are the number of expected chemical bonds and energy of each bond respectively. The calculated values of cohesive energy along with bond energy, electronegativity and the excess of Se-Se bonds for all the compositions are tabulated in table 4. The results indicate that the cohesive energy of the investigated glassy system decreases with increasing of Bi content.. It is also evident from the table 4 that the value of electronegativity also decreases with increasing Bi content. The same trend has been reported earlier[11-12,18,32]for the similar material and for the addition of Ge to the Se-Te system. The variation of cohesive energy with Bi (at %) content is given in fig.5.

2.5. The average heat of atomization.

The heat of atomization $\overline{H}_S(A-B)$ of a binary semiconductor formed from atoms A and B at standard temperature and pressure, as proposed by Pauling[34], is the sum of the heat of formation ΔH and the average heats of atomization $\overline{H}_S^A$ and $\overline{H}_S^B$, that corresponds to the average non-polar bond energy of the two atoms is given by the relation:

$$\overline{H}_S(A-B) = \Delta H + \frac{1}{2}(\overline{H}_S^A + \overline{H}_S^B) \quad (12)$$

The term ΔH in the above equation (12) is Proportional to the square of the difference between the electronegativities of two atoms involved.
i.e.

$$\Delta H \ \alpha \ (\chi_A - \chi_B)^2 \tag{13}$$

In case of ternary and higher order semiconductor compounds [34], the average heat of atomization proposed for a AxByCz system as a direct measure of the cohesive energy and the average bond strength and is given by the relation:

$$\overline{H}_S = \frac{XH_S^A + YH_S^B + ZH_S^C}{X + Y + Z} \tag{14}$$

Where X, Y and Z are the ratios of A, B and C respectively. The values of average heat of atomization for Te-Se-Bi ternary system is calculated by using relation in equation (14), using the values of heat of atomization in the units of kcal/g atom 49.4, 46.0 and 43.11 for Se, Te and Bi respectively. The average heat of atomization ($\overline{H}_S$) and average single bond energy ($\overline{H}_S$) are given in table 5, where m is the average coordination number. It is clear from the table that the value of average heat of atomization decreases with Bi addition in Te-Se-Bi alloy. A graphical representation of average heat of atomization per single bond as a function of composition parameter x (at %) is given in fig.6.

CONCLUSION

Various physical parameters like, transition temperature, mean bond energy, cohesive energy, lone-pair electrons, coordination number and heat of atomization are calculated theoretically for $Te_{18}Se_{82-x}Bi_x$ (x= 0,1.5,2.5,3.5 and 4.5) glassy alloy. It has been observed that Bi atom leads to the cross linking of chains and increases the coordination number of the system. Transition temperature, mean bond energy and constraints increases with increasing Bi content in Te-Se-Bi glassy alloy. The Cohesive energy of the investigated samples has been calculated by using the chemical bond approach (CBA) and has been found to decrease with increase in Bi content. The number of lone pair electrons found to decrease with the addition of Bi content has a minimum value 3.73, which is much more than 1, indicating that the compositions for present investigation are good glass forming ability and the same behavior is exhibited by the heat of atomization. Thus the addition of Bi content to $Te_{18}Se_{82-x}Bi_x$ glassy alloy leads to change in the physical properties.

Table 1.Values of average coordination number (m) and average number of constraints ($N_{con} = N^{\alpha} + N^{\beta}$) for $Te_{18}Se_{82-x}Bi_x$ composition

Composition	m	N^{α}	N^{β}	$Ncon = N^{\alpha} + N^{\beta}$
$Te_{18}Se_{82}$	2.18	1.090	1.360	2.450
$Te_{18}Se_{80.5}Bi_{1.5}$	2.19	1.095	1.380	2.475
$Te_{18}Se_{79.5}Bi_{2.5}$	2.20	1.100	1.400	2.500
$Te_{18}Se_{78.5}Bi_{3.5}$	2.21	1.105	1.420	2.525
$Te_{18}Se_{77.5}Bi_{4.5}$	2.22	1.110	1.440	2.550

Table 2.Values of the number of lone-pair electrons for $Te_{18}Se_{82-x}Bi_x$ composition.

Composition	M	V	L=V-m
$Te_{18}Se_{82}$	2.18	6.00	3.82
$Te_{18}Se_{80.5}Bi_{1.5}$	2.19	5.98	3.79
$Te_{18}Se_{79.5}Bi_{2.5}$	2.20	5.97	3.77
$Te_{18}Se_{78.5}Bi_{3.5}$	2.21	5.96	3.75
$Te_{18}Se_{77.5}Bi_{4.5}$	2.22	5.95	3.73

Table 3. Deviation of stoichiometry (R), mean bond energy<E> and glass transition temperature (T_g) for $Te_{18}Se_{82-x}Bi_x$ composition.

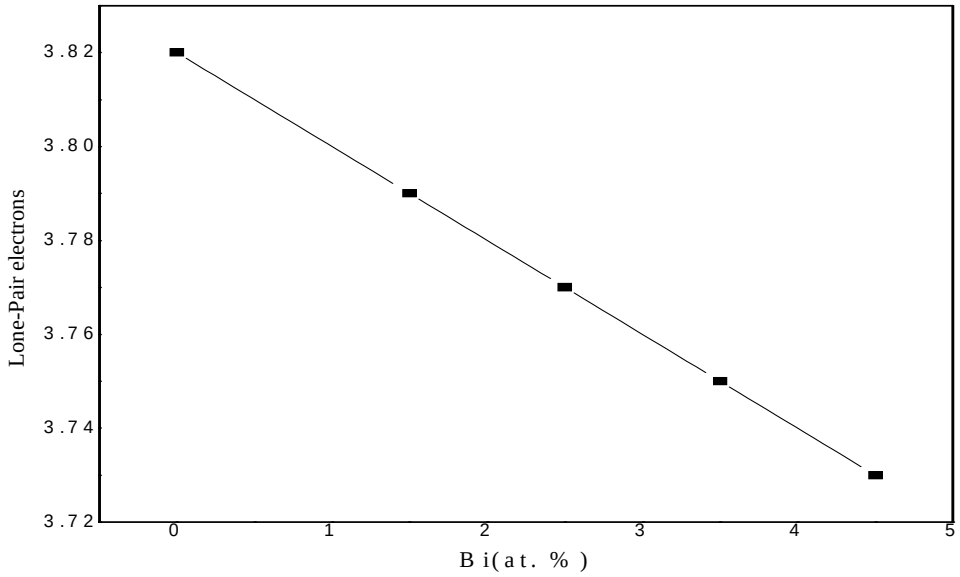
Composition	R	<E> (eV/atom)	Tg (K)	Bonds	Bond Energies (kcal/mol)
$Te_{18}Se_{82}$	∞	1.97	333	Se-Se	44.00
$Te_{18}Se_{80.5}Bi_{1.5}$	47.77	1.98	336	Se-Te	43.15
$Te_{18}Se_{79.5}Bi_{2.5}$	28.40	1.99	339	Se-Bi	40.70
$Te_{18}Se_{78.5}Bi_{3.5}$	20.09	2.00	342	Bi-Te	29.02
$Te_{18}Se_{77.5}Bi_{4.5}$	15.48	2.01	345	Te-Te	33.00

Table 4. Values of electronegativity (χ), excess Se-Se bonds and cohesive energy (CE) for $Te_{18}Se_{82-x}Bi_x$ composition.

Composition	χ	Excess Se-Se bonds	Cohesive energy(CE) (kcal/mol)
$Te_{18}Se_{82}$	2.43	110	43.29
$Te_{18}Se_{80.5}Bi_{1.5}$	2.41	102	43.19
$Te_{18}Se_{79.5}Bi_{2.5}$	2.40	97	43.15
$Te_{18}Se_{78.5}Bi_{3.5}$	2.39	92	43.12
$Te_{18}Se_{77.5}Bi_{4.5}$	2.38	87	42.96

Table 5.Values of average heat of atomization (H_s) and average single bond energy (H_s/m) for $Te_{18}Se_{82-x}Bi_x$ composition.

Composition	m	$\overline{H}_s$ (kcal/g atom)	$(\frac{\overline{H}_s}{m})$ (kcal/g atom)
$Te_{18}Se_{82}$	2.18	48.78	22.38
$Te_{18}Se_{80.5}Bi_{1.5}$	2.19	48.69	22.23
$Te_{18}Se_{79.5}Bi_{2.5}$	2.20	48.63	22.10
$Te_{18}Se_{78.5}Bi_{3.5}$	2.21	48.56	21.97
$Te_{18}Se_{77.5}Bi_{4.5}$	2.22	48.50	21.84



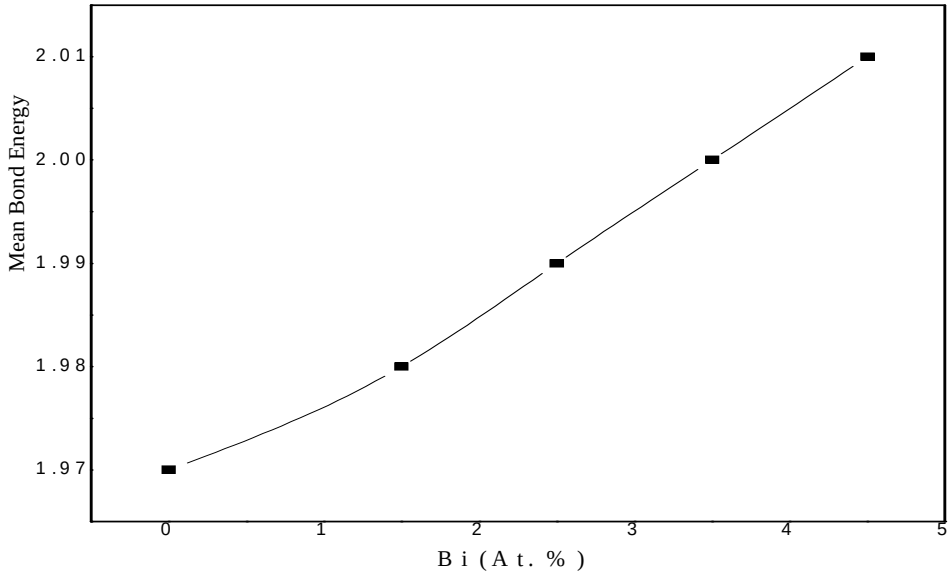
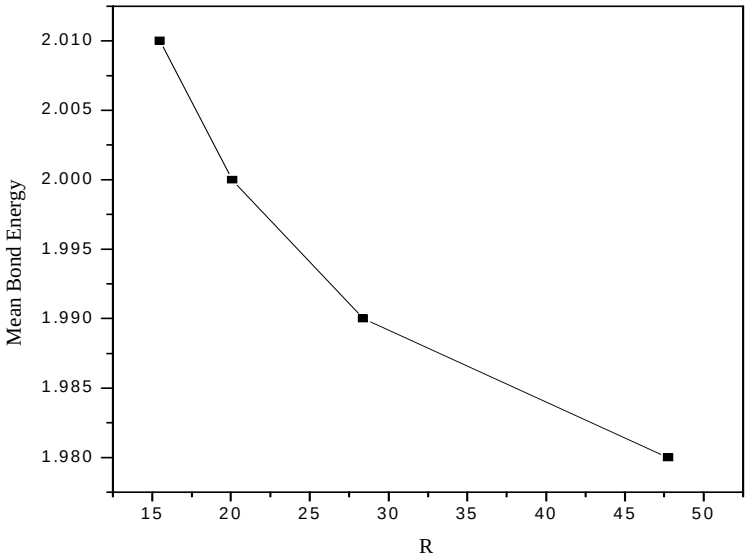


Fig. 1. Lone-pair electrons (L) versus Bi content (at %) for $Te_{18}Se_{82-x}Bi_x$ (x=0,1.5,2.5,3.5,4.5) system.

Fig. 2. Variation of mean bond energy <E> with Bi content (at%) for $Te_{18}Se_{82-x}Bi_x$ (x=0,1.5,2.5,3.5,4.5) system.



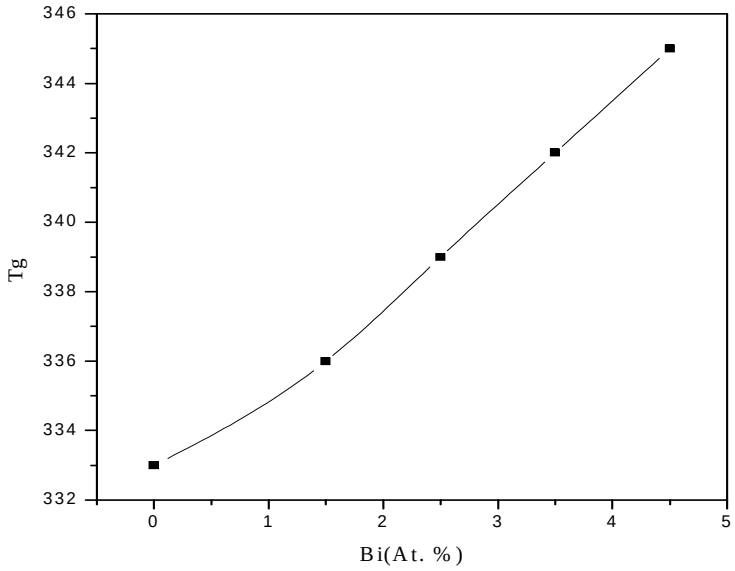
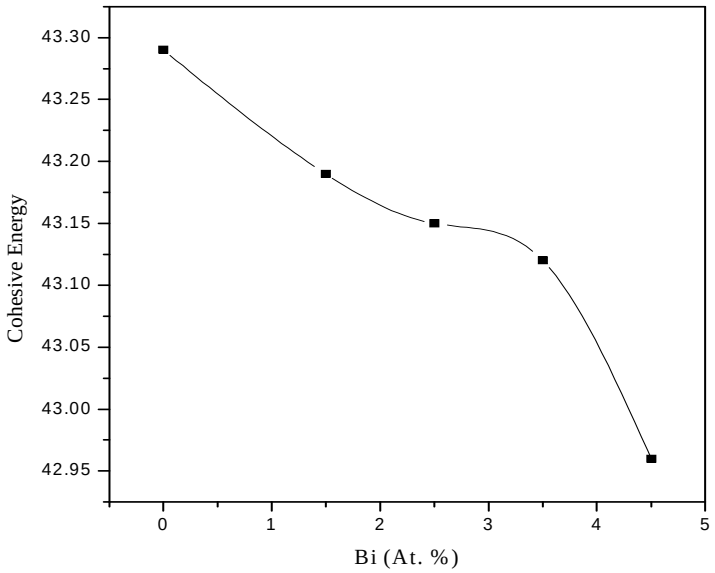


Fig. 3. Variation of mean bond energy <E> with R for $Te_{18}Se_{82-x}Bi_x$ (x=0,1.5,2.5,3.5,4.5) system.

Fig. 4. Variation of T_g with Bi content (at%) for $Te_{18}Se_{82-x}Bi_x$ (x=0,1.5,2.5,3.5,4.5) system.



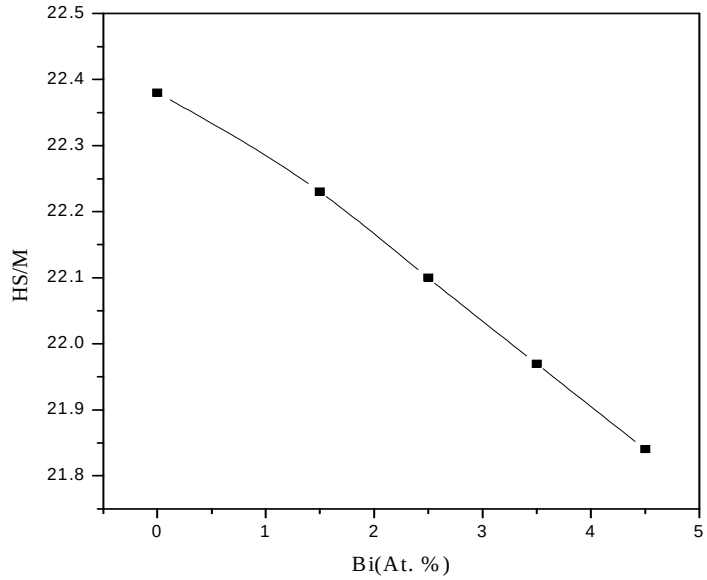


Fig. 5. Variation of cohesive energy (CE) with Bi content (at%) for $Te_{18}Se_{82-x}Bi_x$ (x=0,1.5,2.5,3.5,4.5) system.

Fig. 6. Variation of H_s/m with Bi content (at%) for $Te_{18}Se_{82-x}Bi_x$ (x=0,1.5,2.5,3.5,4.5) system

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