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A Study of the Physical Properties of $Te_{15}(Se_{100-x}Bi_x)_{85}$ Glassy Alloys

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Abstract
In the present communication, a study was made of the compositional variation of physical properties: average coordination number (<*r*>), average number of constraints (N_{con}), number of lone-pair electrons (L), mean bond energy (<*E*>), cohesive energy (CE), average heat of atomization (H_s), glass transition temperature (T_g), density (ρ) and theoretical energy gap (E_g) for $Te_{15}(Se_{100-x}Bi_x)_{85}$ (x = 0, 1, 2, 3, 4, 5at%) glassy alloys. The mean bond energy and the cohesive energy have been calculated using the chemical bond approach (CBA). The glass transition temperature was calculated using the Tichy-Ticha approach, and has been found to increase with Bi content. The mean bond energy is found to be proportional to the glass transition temperature and the average coordination number. It has been found that the average coordination number, average number of constraints, mean bond energy and density increase, whereas the cohesive energy, average heat of atomization and theoretical energy gap decrease with increasing Bi content in Se-Te alloys.

1. Introduction
Chalcogenide glasses are of great scientific interest because of their properties and new application possibilities. These are used in solid state devices, xerography, switching IR lasers and memory devices etc. [1-3]. The properties of Se rich chalcogen glasses are of interest because of their use as photoreceptors in TV vidicon pick up tubes and digital X-ray imaging [4,5]. Pure Se glassy alloys have short life time, low sensitivity and low thermal stability. Recently it has been pointed out that Se-Te alloys have more advantages than a-Se because of their greater hardness, higher crystallization temperature, higher photo sensitivity and smaller aging effects [6-8]. Several workers have reported the impurity effects in various chalcogen glasses [9-14]. The physical properties of the glassy alloys are highly composition dependent. Understanding of physical properties of chalcogenide glasses is important for them to be considered for different practical applications. The addition of third element expands the glass forming region, creates compositional and configurational disorder and produces changes in the physical, electrical and optical properties of the new glassy alloys [13-15]. We have chosen Bi as the third element because it may change the optical, electrical and thermal properties of the chalcogen glasses. Addition of Bi to Se-Te binary is reported to change the conductivity from p to n type [16].
In the present work, the compositional dependence of physical properties such as density (ρ) coordination number <*r*>, number of lone pair electrons (L), number of constraints (N_{con}), mean bond energy <*E*>, glass transition temperature (T_g), cohesive energy (CE) and theoretical energy gap (E_g) of Te-Se-Bi glassy alloys have been investigated. Transition temperature has been correlated with mean bond energy using Tichy-Ticha approach [17,18] and cohesive energy of the

samples has been found using chemical bond approach [19,20]. Variation of these parameters has been discussed in terms of variation of Bi content in Se-Te glassy alloys.

Table 1
Values of average coordination number (<r>), bond stretching constraints (N^{α}), bond bending constraints (N^{β}), average number of constraints (N_{con}) and lone pair electrons for $Te_{15}(Se_{100-x}Bi_x)_{85}$ (x = 0, 1, 2, 3, 4, 5 at.%) glassy alloys

Composition	<r>	N^{α}	N^{β}	N_{con}	V	L
x=0	2.150	1.075	1.300	2.375	6.000	3.850
x=1	2.158	1.079	1.317	2.396	5.991	3.833
x=2	2.167	1.083	1.334	2.417	5.983	3.816
x=3	2.175	1.088	1.351	2.439	5.974	3.799
x=4	2.184	1.092	1.368	2.460	5.966	3.782
x=5	2.192	1.096	1.385	2.481	5.957	3.765

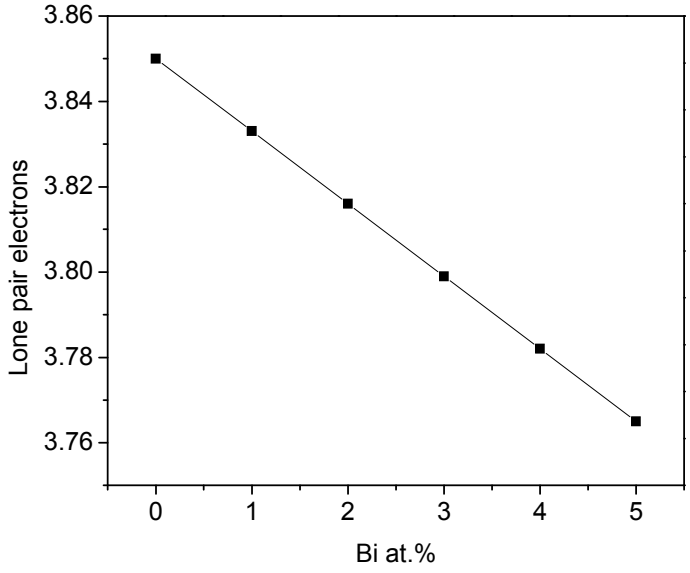

Figure 1
Lone pair of electrons versus Bi content (at%) for $Te_{15}(Se_{100-x}Bi_x)_{85}$ (x = 0, 1, 2, 3, 4, 5at%) glassy alloys

Table 2
Values of density (ρ), molar mass (M_m), molar volume (V_m) and compactness (δ) for $Te_{15}(Se_{100-x}Bi_x)_{85}$ (x = 0, 1, 2, 3, 4, 5at%) glassy alloys

Composition	ρ (g/cm^3)	M_m (g/mol)	V_m(cm^3/mol)	Compactness (δ)
x=0	4.96	86.26	17.391	-0.04042
x=1	5.01	87.36	17.437	-0.05256
x=2	5.04	88.47	17.554	-0.06657
x=3	5.09	89.57	17.597	-0.07616
x=4	5.13	90.67	17.674	-0.08640
x=5	5.19	91.78	17.684	-0.09236

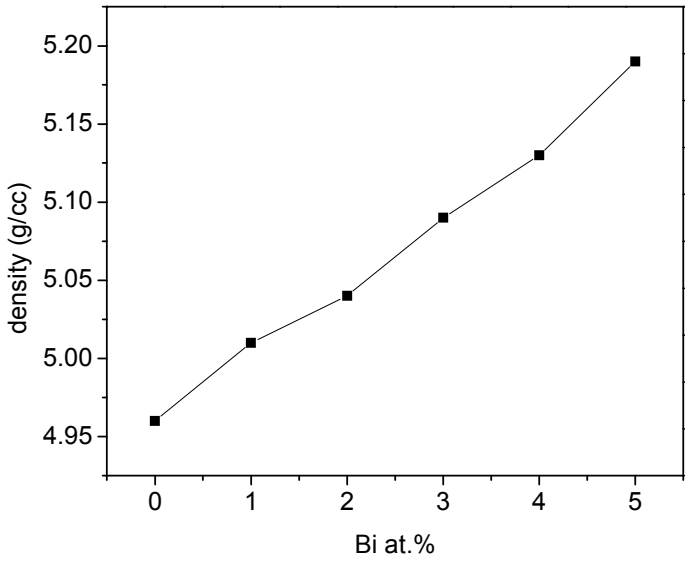

Figure 2
Density versus Bi content (at%) for $Te_{15}(Se_{100-x}Bi_x)_{85}$ (x = 0, 1, 2, 3, 4, 5at%) glassy alloys

2. Experimental Details

$Te_{15}(Se_{100-x}Bi_x)_{85}$ glassy alloys for (x = 0,1, 4, 3, 4, 5 at.%) have been prepared by the melt quenching technique. Se, Te and Bi of high purity (99.999%) were weighed according to their atomic percentages. These materials were sealed in cleaned quartz ampoules of length 10 cm and internal diameter 0.8 cm at a vacuum of 10^{-3} Pa. The ampoules were kept in a vertical furnace and heated to a temperature of 1073 K at a heating rate of 3-4 K/min. The ampoules were heated at this temperature for 12 hours. During heating the ampoules were frequently rocked to make the melt homogenous. The quenching was done in ice cold water. The materials were obtained after breaking the ampoules. The amorphous nature was confirmed as no sharp peak was observed in their x-ray diffraction spectra.

Table 3
Values of electronegativity (χ), cohesive energy (*CE*) and distribution of chemical bonds in $Te_{15}(Se_{100-x}Bi_x)_{85}$ (x = 0, 1, 2, 3, 4, 5at%) glassy alloys

Composition	χ	Distribution of chemical bonds			Cohesive Energy(kcal/mol)
		Se-Te	Se-Se	Se-Bi	
x=0	2.450	0.2647	0.7353	--	43.15
x=1	2.441	0.2674	0.7175	0.0151	43.09
x=2	2.431	0.2701	0.6993	0.0306	43.03
x=3	2.422	0.2729	0.6807	0.0464	42.97
x=4	2.413	0.2757	0.6618	0.0625	42.91
x=5	2.405	0.2786	0.6424	0.0789	42.84

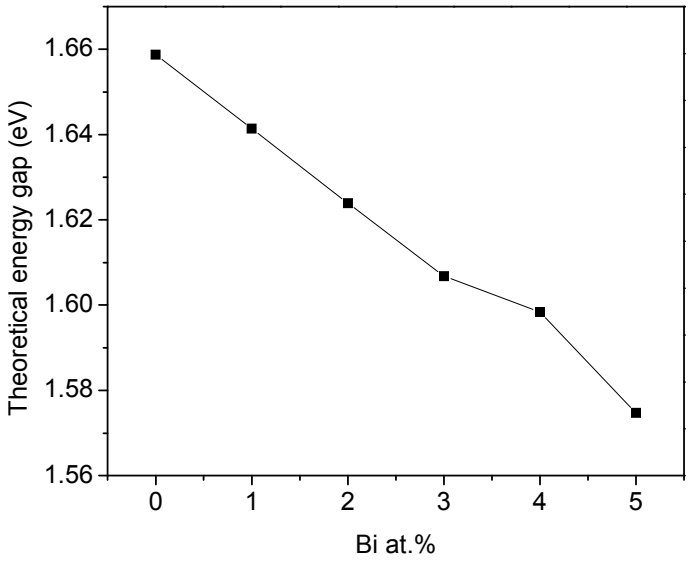

Figure 3
Theoretical energy gap versus Bi content (at%) for $Te_{15}(Se_{100-x}Bi_x)_{85}$ (x = 0, 1, 2, 3, 4, 5at%) glassy alloys

3. Results and Discussion

3.1 Average coordination number and constraints

In chalcogenide glasses the coordination number of covalent atoms is given by the 8-N rule, [21] where N is the number of outer shell electrons in a given atom. Te does not satisfy the 8-N rule in glasses with Te rich environment and shows a coordination number higher than two [22,23]. The coordination number of Te has been taken 3 by various workers [24]. The concept of average coordination number is useful in describing the cross linking in chalcogen glasses. It is defined as the atom-averaged covalent coordination of the constituents. The average coordination number has been calculated using the relationship

$$< r >= \frac{a(CN_{Te}) + b(CN_{se}) + c(CN_{Bi})}{a + b + c} \quad (1)$$

Table 4
Values of *R*, heat of atomization (H_s), mean bond energy <*E*>, transition temperature (T_g) and theoretical energy gap (E_g) for $Te_{15}(Se_{100-x}Bi_x)_{85}$ (x = 0, 1, 2, 3, 4, 5at%) glassy alloys

Composition	R	H_s (kcal/mol)	<E> (eV)	T_g (K)	E_g (eV)
x=0	3.778	48.89	1.9059	312.83	1.6587
x=1	3.539	48.83	1.9090	313.80	1.6414
x=2	3.325	48.78	1.9124	314.86	1.6239
x=3	3.132	48.72	1.9162	316.04	1.6068
x=4	2.956	48.67	1.9202	317.28	1.5984
x=5	2.796	48.62	1.9246	318.65	1.5747

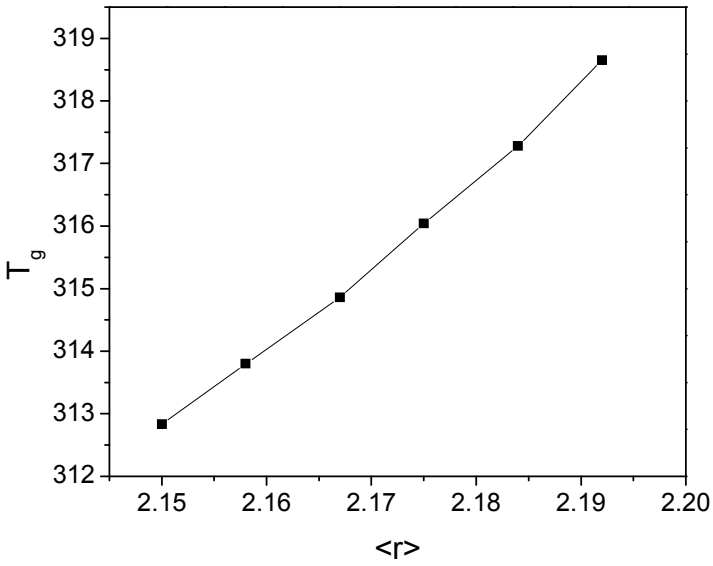

Figure 4
Transition temperature versus average coordination number for $Te_{15}(Se_{100-x}Bi_x)_{85}$ (x = 0, 1, 2, 3, 4, 5at%) glassy alloys

where *a*, b and c are the at.% of Te, Se and Bi respectively and $CN_{Te} = 3$, $CN_{Se} = 2$ and $CN_{Bi} = 3$ are their respective coordination numbers. <r> is found to increase with Bi content and this increase may be correlated with the increase in compactness of the structure of $Te_{15}(Se_{100-x}Bi_x)_{85}$ (x=0, 1,

2, 3, 4, 5 at.%) glassy alloys. Bi atom in the structure can crosslink the chains and thus enables a better covalent network structure to be developed. This leads to increase in T_g with Bi content. In a glassy system, covalent network can be mechanically constrained by inter-atomic valance forces such as bond stretching and bond bending. In the glassy alloys there are $<r>/2$ bond stretching constraints (N^{α}) and $2<r> - 3$ bond bending constraints (N^{β}). The average number of constraints is given by [25]

$$N_{con} = N^{\alpha} + N^{\beta} \tag{2}$$

The average number of constraints increases with an increase in Bi content.

3.2 Lone pair electrons and glass-forming ability

The number of lone pair electrons is equal to all the valance electrons of the system minus the shared electrons. It is reported that increasing the number of lone pair electrons decreases the strain energy in a system and a structure with large number of lone pair of electrons favours glass formation [26]. For a single element system the number of lone pair of electrons must be larger than 4, for a binary system the number of lone pair electrons must be larger than 2.62 and for ternary system the number of lone pair of electrons must be larger than 1.0 [27]. If a system has enough lone pair electrons, a thermally stable state can be obtained. The lone pair electrons are given by [28]

$$L = V - < r > \tag{3}$$

A graphical representation of L and Bi composition is given in Fig. 1. It is seen from the figure that the number of lone pair electrons decreases with increasing Bi content. This is caused by the interaction between Bi ion and lone pair electrons of Se atoms. It can be concluded that some lone pair electrons in the structure of a system is a necessary condition for obtaining the system in glassy state. Values of average coordination number $<r>$, average number of constraints (N^{α}, N^{β} and N_{con}), valance electrons (V) and number of lone pair electrons (L) for Te_{15} $(Se_{100-x}$ $Bi_x)_{85}$ (x=0, 1, 2, 3, 4, 5 at.%)glassy alloys are listed in table 1.

3.3 Density and molar volume

The density of the samples has been calculated using the relation

$$\rho = \left[\frac{w_1}{w_1 - w_2} \right] \rho_{water} \tag{4}$$

where w_1 and w_2 are the weight of the samples in air and water respectively. Each sample was weighed four times and the average density was recorded. The recorded densities are shown in Fig. 2. The density has been found to increase with increase in Bi content. This increase in density is due to replacement of less denser Se (4.79 g/cm^3) by denser Bi (9.78 g/cm^3)

Molar volume (V_m) has been determined using the equation

$$V_m = \frac{1}{\rho} \sum_i x_i M_i \tag{5}$$

where M_i and x_i are the molecular weight and the atomic percentage of the i^{th} element in the sample. The calculated values of the molar volume and density are listed in table 2 and are found to increase with increase in Bi content. This increase may be due to replacing of Se atoms by the heavier and larger Bi atoms in the glassy network. The atomic radius of Se atom is 116 pm whereas the atomic radius of Bi is 160 pm. The compactness (δ) of the samples has been determined using the relationship

$$\delta = \frac{\sum_i c_i A_i / \rho_i - \sum_i c_i A_i / \rho}{\sum_i c_i A_i / \rho} \quad (6)$$

where c_i is the atomic fraction, A_i is the atomic weight, ρ_i is the atomic density of i^{th} element and ρ is the measured density of the samples. The compactness is a measure of change in mean atomic volume due to chemical interaction of the elements forming the sample.

3.4 Cohesive energy and electronegativity

The cohesive energy of a system is defined as the stabilization energy per atom. The cohesive energy has been calculated using the chemical bond approach (CBA) [19,20]. According to CBA the bonds are formed in the sequence of decreasing bond energy until the available valance of atoms is satisfied. The cohesive energy of the prepared samples was calculated by summing the bond energies over all bonds expected in the material by using the equation

$$CE = \frac{\sum C_i D_i}{100} \quad (7)$$

where C_i and D_i are the number of expected chemical bonds and the energy of corresponding bonds. With increase in Bi content, Bi is expected to combine preferably with Se because bond energy of Bi-Se bond (170.4 kJ/mol) is higher than that of Bi-Te bond (125.6 kJ/mol) [29]. This results in a decrease in Se-Se bonds and is further responsible for a decrease in the cohesive energy of the system. The electronegativity has been calculated using Sanderson's principle [30]. According to this principle, the electronegativity of an alloy is the geometric mean of the electronegativities of the constituent elements. Values of electronegativities (χ), distribution of chemical bonds and cohesive energy for $Te_{15}(Se_{100-x}Bi_x)_{85}$ (x 0, 1, 2, 3, 4, 5at%) glassy alloy compositions are listed in table 3.

3.5 Average heat of atomization and deviation of stoichiometry

The average heat of atomization is the quantity of heat required to change one mole of an element in its standard state at 298K to gaseous atoms. For ternary semiconductors, the average heat of atomization H_s has been calculated using the formula [29]

$$H_S = \frac{aH_s^A + bH_s^B + cH_s^C}{a+b+c} \quad (8)$$

The value of H_s was obtained by using the values of heat of atomization 49.4, 46 and 43.11 in kcal/mol for Se, Te and Bi respectively. The ratio (R) of covalent bonding possibilities of the chalcogen atom to that of the non-chalcogen atom is a measure of deviation of stoichiometry. Value of R greater than 1 means the chalcogen rich material and R less than 1 means chalcogen poor material. The quantity R is defined by [17,18]

$$R = \frac{b(CN_{Se})}{a(CN_{Se}) + c(CN_{Bi})} \quad (9)$$

R is found to decrease with Bi addition. The calculated values of R, H_s, $\langle E \rangle$ and T_g are listed in table 4.

3.6 Theoretical energy gap

The theoretical energy gap (E_g) for amorphous glassy alloys described by random bond network is given by the Shimkawa relationship [31]

$$E_g = XE_g(A) + YE_g(B) + ZE_g(C) \quad (10)$$

where X, Y, Z are the volume fraction of element A, B , C and E_g(A), E_g(B) and E_g(C) are the energy-gaps of elements A, B and C respectively. The calculated values of energy band gap are found to decrease with increase in Bi content and are reported in table 4. This decrease in energy gap is explained on the basis of a decrease in cohesive energy. The decrease in cohesive energy decreases the energy of the conduction-band edge, which causes a reduction in the gap between bonding (σ) and anti-bonding (σ*) orbitals; thus resulting in a decrease in the energy gap. The plot of E_g with bismuth content is shown in Fig. 3. Further we can also correlate the decrease in theoretical energy gap with the decrease of heat of atomization.

3.7 Mean bond energy and glass transition temperature

The glass transition temperature (T_g) is that characteristic temperature below which the glassy system frozes into a structure which can not change into another structure and is related to the magnitude of the cohesive forces in the system. Thus T_g is assumed to be proportional to system parameter which strongly depends on cohesive forces in the system. One such parameter is mean bond energy. The bond energies of heteropolar bonds calculated from Pauling relation are quite different from bond energies of weak homopolar bonds so chemically ordered networks are expected. Based on chemical bond ordering model the mean bond energy is given by

$$< E >= E_c + E_{rm} \quad (11)$$

where E_c is the overall contribution towards bond energy due to strong heteropolar bonds and E_{rm} is the contribution due to weak homo-polar bonds. For Se rich glass system, the values of E_c and E_{rm} are given in [32]

$$E_c = 3aE_{Se-Te} + 3cE_{Se-Bi} \quad (12)$$

and

$$E_{rm} = \frac{2b - 3a - 3c}{< r >} E_{Se-Bi} \quad (13)$$

Tichy and Ticha [17,18] illustrated an impressive relation of T_g with <*E*> in the form

$$T_g = 311[< E > -0.9] \quad (14)$$

The glass transition temperature (T_g) is found to increase with average coordination number <*r*>. A graphical representation of T_g with <*r*> is given in Fig.4.

4. Conclusion

The cohesive energy (*CE*), number of lone pair electrons (*L*), average coordination number <r> and glass transition temperature (T_g) are calculated for $Te_{15}(Se_{100-x}Bi_x)_{85}$ (x=0, 1, 2, 3, 4, 5 at.%) glassy alloys. *CE* is found to decrease with increase of Bi content. It is related with decrease of stronger Se-Se bonds. The density increases as lighter Se atoms are replaced by heavier Bi atoms. The number of lone pair of electrons decreases with increase in Bi but still has a minimum value 3.6, which is much more than 1 indicating that the compounds under study are good glass formers. The decrease in theoretical energy gap with increase in Bi content is correlated with decrease in cohesive energy.

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