Experimental and theoretical determination of physical parameters of $(Se_{80}Te_{20})_{100-x}Ag_x$ (0<x< 4) glassy alloys

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In this paper we have theoretically predicted the physical parameters viz. coordination number, constraints, molar volume, fraction of floppy modes, number of lone pair electrons, glass transition temperature, bond energy, cohesive energy, heat of atomization, mean bond energy and viscosity for $(Se_{80}Te_{20})_{100-x}Ag_x$ (0<x< 4) glassy alloys. It has been found that average number of constraints, cohesive energy and mean bond energy increases with the increase in Ag content. The mean bond energy is calculated using the chemical bond approach of Tichy and Ticha and it was found that the mean bond energy and number of lone pair electrons of the system decrease with increase in Ag content.

1. Introduction

The properties of chalcogenide glasses in dependence on chemical composition are of interest, especially in considering the effects of average coordination number, number of covalent bonds per atom [1]. The structure of glasses is an important issue, knowledge of which is necessary for understanding the material's properties and also for the material engineering. Chalcogenide glasses are interesting candidates for reversible phase change optical recording devices [2–4]. There has been an increased interest in the properties of Se-rich chalcogenide glassy alloys due to their current use as photoreceptors in TV vidicon pickup tubes [5] and in digital X-ray imaging [6]. Selenium is considered to be one of the most important semiconductors due to its unusual structure [7] and it exhibits the unique property of reversible phase transformation [8]. It has the wide commercial applications like switching, memory and xerography which make it attractive. But in the pure state it has the disadvantages of short lifetime and low sensitivity and low thermal instability. This problem can be removed by alloying Se with some impurity atoms which gives higher sensitivity, higher crystallization temperature and smaller ageing effects [9-11]. It has been pointed out that addition of Te to Se improves the corrosion resistance [12] and lengthens the crystallization time of amorphous selenium [13]. Glassy alloys of the Se-Te system based on selenium have become materials of considerable commercial importance and are widely used for optical recording media because of their excellent laser writing sensitivity [14] but these advantages depend on material stability [15]. The Se-Te alloys have been found to be useful from the technological point of view due to their greater hardness, higher crystallization temperature T_C, and smaller ageing effects as compared to a-Se [16]. Experimental results indicate that the properties of the Se-Te alloys are highly composition dependent. Addition of Ag will expand the glass forming area and also create compositional and configurational disorder in the system and has large effect on their structural, physical, optical, electronic and thermal properties [17]. The present paper is concerned with the experimental and theoretical prediction of the physical parameters related to composition, *viz*: coordination number, constraints, molar volume, density, compactness, fraction of floppy modes, number of lone pair electrons, bond energy, cohesive energy, heat of atomization, glass transition temperature, mean bond energy, optical band gap, and viscosity for Se-Te-Ag glassy system.

2. Experimental

Bulk samples of $(Se_{80}Te_{20})_{100-x}Ag_x$ (0≤x≤4) were prepared by conventional melt quenching technique. High-purity (99.999%) elements with appropriate atomic percentage were sealed in a quartz ampoule (length ~100mm and internal diameter ~6mm) in a vacuum of 10^{-5} mbar. The ampoules were kept inside a vertical furnace for 72 h. The temperature was raised to 1373K, at a rate of 4-5 K/min. 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 dissolving the ampoule in $HF+H_2O_2$ solution for approximately 48 h. The amorphous nature of the bulk samples was confirmed by the absence of sharp peaks in the X-ray diffractogram. XRD studies were done using Phillips PAN ANALYTICAL machine and X-ray of Cu K_α line to check the amorphous nature of the materials. The thermal behaviour of the samples was investigated using Perkin Elmer (Pyris Diamond) DSC System. In each study approximately 10 mg of the bulk material was used.

3. Results

3.1 Coordination number and constraints

The average coordination number $< r >$ in our system is defined by

$$< r > = \frac{\alpha X + \beta Y}{\alpha + \beta} \qquad (1)$$

Where α and β are the % atomic weights of $(Se_{80}Te_{20})_{100-x}$ and Ag_x respectively, and X=2 and Y=2 are their respective coordination number. The atomic species with coordination number $< r >$ having the number of constraints per atom arising from bond bending $N_\beta = 2< r > - 3$ and from bond stretching $N_\alpha = < r >/2$. Knowing the average number of constraints $N_{con} = N_\alpha + N_\beta$ and the average coordination number $< r >$ for different composition of $(Se_{80}Te_{20})_{100-x}Ag_x$ (0<x< 4) glassy system, the effective average coordination number $< r_{eff} >$ can be calculated [18] using the formula

$$\left\langle r_{eff} \right\rangle = \frac{2}{5}\left(N_{con} + 3\right) \qquad (2)$$

Table 1 shows the values of $< r >$, N_α, N_β, N_{con} along with $< r_{eff} >$ for the $(Se_{80}Te_{20})_{100-x}Ag_x$ (0<x< 4) glassy system.

Table 1 Values of $< r >$, N_α, N_β, N_{con}, and $< r_{eff} >$ for $(Se_{80}Te_{20})_{100-x}Ag_x$ glassy system.

Composition	$< r >$	N_α	N_β	N_{con}	$< r_{eff} >$
a- $(Se_{80}Te_{20})_{100}$	2.00	1.00	1.00	2.00	2.000
$(Se_{80}Te_{20})_{99}Ag_1$	2.02	1.01	1.04	2.05	2.008
$(Se_{80}Te_{20})_{98}Ag_2$	2.04	1.02	1.08	2.10	2.016
$(Se_{80}Te_{20})_{97}Ag_3$	2.06	1.03	1.12	2.15	2.024
$(Se_{80}Te_{20})_{96}Ag_4$	2.08	1.04	1.16	2.20	2.032

3.2 Density, compactness, molar volume and fraction of floppy modes of $(Se_{80}Te_{20})_{100-x}Ag_x$ (0<x< 4) glassy system

The Archimedes method was used for the measurement of the density of as-prepared glasses. The weight of the piece of Se-Te-Ag glassy alloy was measured in air and in dibutyl phthalate using an electrical balance as w_1 and w_2 respectively, w_3 is the weight of the thread used for weighing the sample. The density of dibutyl phthalate (ρ_{Dbp}) is 1.05gcm^{-3} at 20°C. The density of the glassy alloy was calculated from the formula

$$\rho = \left[\frac{w_1}{w_2 - w_3}\right]\rho_{Dbp} \qquad (3)$$

The calculated values of density are reported in Table 2. It is clear from the table that measured density decrease with the addition of Ag content to the $(Se_{80}Te_{20})_{100-x}Ag_x$ (0<x< 4) glassy alloys. The decrease in the density also accounts for the decrease in the refractive index (n) as shown in Table 2. The compactness δ, of the structure of the glass was calculated from the relation [19].

$$\delta = \frac{\Sigma_i(c_i A_i / \rho_i) - \Sigma_i(c_i A_i / \rho)}{\Sigma_i(c_i A_i / \rho)} \qquad (4)$$

where c_i is the atomic fraction, A_i is the atomic weight, ρ_i is the atomic density of the ith element of the glass and ρ is the measured density of the glass. Thus δ is a measure of the normalized change of the mean atomic volume due to chemical interactions of the elements forming the network of a given solid [20], thus it is associated with the flexibility and free volume of the network. From the Table 2, we observed that the compactness having both positive and negative values, which shows that the given Se-Te-Ag system having larger free volume and flexibilities. Consequently, it is more sensitive to changes in the structure of the glass network as compared to mean atomic volume. The molar volume (V_m) was determined from the density data using the following equation

$$V_m = \frac{1}{\rho}\sum_i x_i M_i \qquad (5)$$

where M_i is the molecular weight of the ith component and x_i is the atomic percentage of the same element in the sample. Table 2 summarizes the molecular weight of the investigated compositions and their corresponding

compactness and molar volume. The plot between density (ρ) and molar volume (V_m) with coordination number < r > is shown in Fig. 1. According to M. F. Thorpe [21], the uncoordinated networks having finite fraction of zero frequency normal vibration modes termed as floppy modes in absence of weak long range forces. The fraction f of zero frequency modes is given by

$$f = 2 - \frac{5}{6}\langle r \rangle \qquad (6)$$

f is calculated for varying composition of Ag and is listed in Table 2. It has been observed that with increase in Ag content in the system the value of fraction of floppy modes increased, thus we conclude that with increase in the Ag content the rigidity of the system decreases.

Table 2 Values of n, ρ, M, δ, V_m, f and E^{opt} for $(Se_{80}Te_{20})_{100-x}Ag_x$ glassy system.

Composition	n	ρ (gcm^{-3})	M (g/mol)	V_m (cm^3 mol^{-1})	δ	f	E^{opt} (eV)
a- $(Se_{80}Te_{20})_{100}$	4.29	4.99	92.9561	18.62	0.03638	0.333	0.530
$(Se_{80}Te_{20})_{99}Ag_1$	4.25	4.96	93.1371	18.77	0.02232	1.213	3.76
$(Se_{80}Te_{20})_{98}Ag_2$	4.20	4.92	93.3172	18.96	0.00675	2.422	3.60
$(Se_{80}Te_{20})_{97}Ag_3$	4.15	4.85	93.4968	19.27	-0.01548	3.625	3.44
$(Se_{80}Te_{20})_{96}Ag_4$	4.10	4.73	93.6439	19.79	-0.04713	4.823	3.29

3.3 Theoretical perdition of optical band gap

The calculation of the optical band gap has been carried out by the linear combination of atomic orbitals method [22] by summing over the contributions of different chemical bonds. The optical band gap has been derived from the equations:

$$E^{opt} = 3.6 \quad \{(V_2 + V_3)^{1/2} - 1/2[x_1(V_1^{Se} + V_1^{Te}) + x_2(V_1^{Se} + V_1^{Ag}) + x_3(V_1^{Te} + V_1^{Ag})] + \\ + x_4 V_1^{Se} + x_5 V_1^{Te} + x_6 V_1^{Ag}\}, \qquad (7)$$

$$V_2 = k/(\Sigma x_i d_i)^2, \qquad (8)$$

$$V_3 = x_1 * (\varepsilon_h^{Se} - \varepsilon_h^{Te})/2 + x_2 * (\varepsilon_p^{Se} - \varepsilon_h^{Ag})/2 + x_3 * \\ (\varepsilon_p^{Ag} - \varepsilon_h^{Te})/2, \qquad (9)$$

where x_1 - x_6, x_i* are the molar fractions for the chemical bond, ε_p, ε_h, $V_1^{a,c}$ are atomic terms taken from the generalized periodic table [22], d_i are covalent bond distances, k = 0.16459 eV nm^2. The d_i represents the covalent bond distances that have been used in the calculations [23]. The values of the E^{opt} for all the compositions are tabulated in Table 2.

3.4 Bond energy and cohesive energy

The possible bonds in Se-Te-Ag system are Se-Te, Se-Se and Se-Ag. The CON [24] model suggests that heteropolar bonds are favored over homopolar bonds and they are formed in the sequence of their decreasing bond energy. The bond energy of heteropolar bonds is determined by the method suggested by using the bond energy of homopolar bonds and the electronegativity of the atoms involved [25]. The bond energies D (A-B) for heteronuclear bonds have been calculated by using the following relation

$$D (A-B) = [D(A-A) D(B-B)]^{1/2} + 30 (X_A - X_B)^2 \qquad (10)$$

D (A-A) and D (B-B) are the bond energy of homonuclear bonds. X_A and X_B are the electronegativity values of A and B respectively. Cohesive energy is the stabilization energy of an infinitely large cluster of material per atom and also reflects the average bond strength. Cohesive energy for the investigated samples has been calculated with the help of Chemical bond approach method [26]. According to CBA the bonds are formed in the sequence of decreasing bond energy until the available valence of atoms is satisfied and the bond energies are assumed to be additive. Therefore the cohesive energy was calculated by summing the bond energies over all bonds expected in the material. The values of cohesive energy along with the chemical bond distribution for all the composition are tabulated in Table 3. It has been observed from Table 3 that the C.E increase with increase in Ag content. The electronegativity of the system has been calculated from Sanderson's principle [27]. According to this principle, the electronegativity of an alloy is the geometric mean of electronegativity of its constituent elements. The Se atoms bond strongly to Te and also fill the available valences of the Ag atoms. After all these bonds are formed, there are still unsatisfied Se valences "excess bonds" which must be satisfied by the formation of Se-Se bonds. The numbers of excess bonds of

$(Se_{80}Te_{20})_{100-x}Ag_x$ (0<x< 4) system are listed in Table 3. It has been found that the density of a-$(Se_{80}Te_{20})$ system is higher than that of Se-Te-Ag system which leads to

conclusion that the partial substitution of Ag atoms for Se atoms leads to decrease in "densification" of the structure system as indicated in Table 2.

Table 3. The type of bonds formed with their bond energy and corresponding cohesive energy

Composition	χ	Distribution of chemical bonds			C.E (Kcal mol^{-1})	Excess of Se-Se bonds
		Se-Te	Se-Ag	Se-Se		
a- $(Se_{80}Te_{20})_{100}$	2.4205	0.404002025	-	0.595997974	4262.639307	172.650189
$(Se_{80}Te_{20})_{99}Ag_1$	2.4141	0.404023665	0.034498352	0.561477982	4277.811224	169.341139
$(Se_{80}Te_{20})_{98}Ag_2$	2.4079	0.404001046	0.069700727	0.526298226	4293.307963	166.045906
$(Se_{80}Te_{20})_{97}Ag_3$	2.4016	0.404002026	0.105628975	0.490368997	4309.116054	162.765705
$(Se_{80}Te_{20})_{96}Ag_4$	2.3943	0.404002029	0.142305709	0.453692258	4325.253806	159.49913

3.5 Number of lone pair electrons

Chalcogenide glasses are also called lone pair electron. The criterion which computes the ability of a chalcogenide system to remain in vitreous state is given by L. Zhenhua [28]. According to which the number of lone-pair electrons in the structure of the system are necessary for obtaining the system in its vitreous state. According to Pauling [29] the chemical bonds with lone pair electrons have a character of flexibility. Increasing the number of lone-pair electrons decreases the strain energy in a system and structures with large numbers of lone pair electrons favour glass formation [30]. The number of lone pair

electrons in a chalcogenide glass system can be calculated by using the relation [31]

$$L = V - r \qquad (11)$$

where L and V are the lone pair electrons and valence electrons respectively. The number of lone pair electrons obtained by using equation (11) is listed in Table 4. It has been observed that the lone pair electrons, L, decrease continuously with the increase in Ag content. For a binary system the value of L must be larger than 2.6 and for a ternary system it must be larger than 1 [32].

Table 4 Number of lone pair electrons (L) and valence electrons (V), average heat of atomization H_s, H_s/r and E_{04} for $(Se_{80}Te_{20})_{100-x}Ag_x$ glassy system.

Composition	V	L=V-r	H_s	H_s/r	E_{04}
a- $(Se_{80}Te_{20})_{100}$	5.988	3.988	216.50	108.25	0.73
$(Se_{80}Te_{20})_{99}Ag_1$	5.939	3.919	217.32	107.58	3.96
$(Se_{80}Te_{20})_{98}Ag_2$	5.878	3.838	218.13	106.93	3.80
$(Se_{80}Te_{20})_{97}Ag_3$	5.818	3.758	218.95	106.28	3.64
$(Se_{80}Te_{20})_{96}Ag_4$	5.756	3.676	219.67	105.61	3.49

3.6 Relation between E_{04}, H_s and $< r >$

It is interesting to relate E_{04} with average single bond energy, $(H_s/< r >)$. E_{04} is an arbitrary quantity defined as photon energy, at which optical absorption coefficient has the value of 10^4 cm^{-1}. The photon energy at $\alpha = 10^4$ cm^{-1} is about 0.2 eV larger than the optical band gap (E^{opt}) [33]. The obtained E_{04} values are shown in Table 4. The plot between E_{04} with Ag concentration is shown in Fig. 2. To correlate these values with average single bond energy for the $(Se_{80}Te_{20})_{100-x}Ag_x$ (0<x< 4) system, the average heat of atomization has been calculated. According to Pauling [34] the heat of atomization $H_s(A-B)$ at standard temperature and pressure of a binary semiconductor formed from atoms A and B is the sum of the heat of formation ΔH and the average of the atomization H_s^A and H_s^B that corresponds to the average non-polar bond energy of the two atoms.

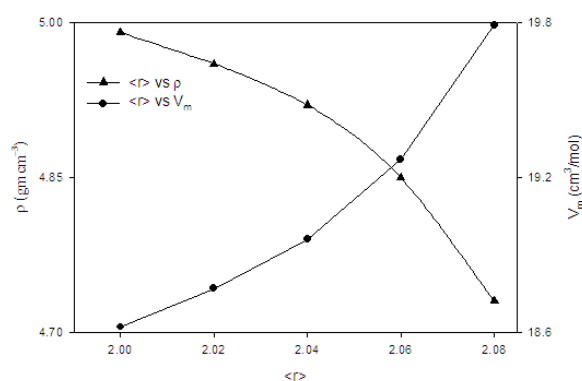$$H_s (A-B) = \Delta H + \tfrac{1}{2} (H_s^A + H_s^B) \qquad (12)$$

Fig. 1. Plot of ρ and V_m with $<r>$ for $(Se_{80}Te_{20})_{100-x}Ag_x$ glassy system.

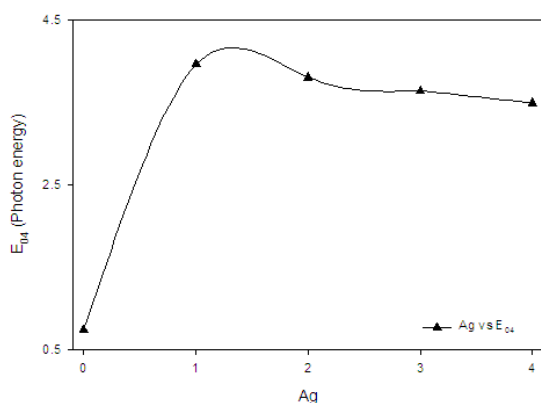*Fig. 2. Plot of E_{o4} with Ag for $(Se_{80}Te_{20})_{100-x}Ag_x$ glassy system.*

The first term in equation (12) is proportional to the square of the difference χ_A and χ_B of the two atoms.

$$\Delta H \quad (\chi_A - \chi_B)^2 \qquad (13)$$

In the few materials for which it is known, the amount of heat of formation ΔH is about 10% of the heat of atomization and is therefore neglected. Hence

$$H_s (A-B) = \tfrac{1}{2} (H_s^A + H_s^B) \qquad (14)$$

The results of H_s for $(Se_{80}Te_{20})_{100-x}Ag_x$ (0<x< 4) using the values of H_s for Se, Te and Ag are 226.4 for Se, 192 for Te and 284.09 KJ/mol for Ag are listed in Table 4, the value of H_s increases with the addition of Ag. The plot between the cohesive energy and $H_s/< r >$ with Ag concentration is shown in Fig. 3. The variation of E_{04} and $H_s/< r >$ with Ag content is given by the Fig. 2 and Fig. 3. From these figures, we observed that there is decrease in E_{04} and $H_s/< r >$ with the Ag addition. It has also been observed that for over-constrained materials with higher connectivity (i.e. $3 \leq r \leq 4$), E_{04} depends more strongly on H_s than for glasses with lower connectivity, $2 \leq r \leq 3$ [35, 36]. In our case, the value of $< r >$ varies from 2.00 to 2.08, which can be correlated with low connectivity glasses. This further suggests that the parameter $H_s/<r>$ is almost constant with composition and has a very negligible effect on E_{04}. Similar results have also been reported for $Te_{46-x}As_{32+x}Ge_{10}Si_{12}$ and $(As_{30}Sb_{15}Se_{55})_{100-x}Te_x$ systems [37, 38].
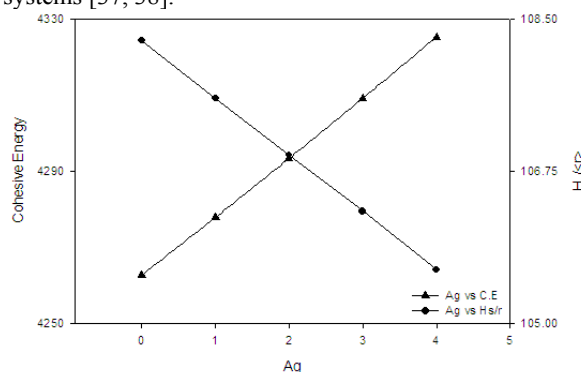
Fig. 3. Plot of cohesive energy and $H_s/<r>$ with Ag of $(Se_{80}Te_{20})_{100-x}Ag_x$ glassy system.

3.7 Mean bond energy $< E >$

We showed that, every $Se_yTe_xAg_z$ system considered the quantity *R*, which determines the deviation of stoichiometry can be expressed by the ratio of the covalent bonding possibilities of chalcogen atoms to that of non-chalcogen atoms. It has been calculated by using the following relation.

$$R = \frac{yCN(Se)}{xCN(Te) + zCN(Ag)} \qquad (15)$$

The value of R has been tabulated in Table 5. The properties of chalcogenide glasses are related to overall mean bond energy $< E >$, which is a function of average coordination number $< r >$, the type of bonds and the bond energy. Using the correlation proposed by Tichy [39, 40].

The overall mean bond energy for the $Se_yTe_xAg_z$ system is given by

$$< E >= E_C + E_{rm} \qquad (16)$$

Table 5 Values of r_{eff}, T_g (experimental and theoretical), $< E >$ and R for $(Se_{80}Te_{20})_{100- x}Ag_x$ glassy system.

Composition	r_{eff}	Glass transition temperature (T_g)			$< E >$ (eV/atom)	R
		Exp.	GDM thr.	T.T thr.		
a- $(Se_{80}Te_{20})_{100}$	2.00	337.14	315.00	286.12	1.82	2.47
$(Se_{80}Te_{20})_{99}Ag_1$	2.05	341.50	328.32	292.32	1.84	2.28
$(Se_{80}Te_{20})_{98}Ag_2$	2.11	340.25	342.28	301.67	1.87	2.11
$(Se_{80}Te_{20})_{97}Ag_3$	2.16	337.13	356.91	311.00	1.90	1.96
$(Se_{80}Te_{20})_{96}Ag_4$	2.21	336.63	372.28	320.33	1.93	1.83

Table 6. Relative probability, ionic character and metallicity of different bonds.

Bond	Bond energy (KJ/mol)	Realtive Probability	R_σ^{AB} (a.u)	R_τ^{AB} (a.u)
Se-Ag	202.45	1	1.38	0.76
Te-Ag	195.76	0.503	-	-
Se-Te	169.82	0.035	0.37	-0.23

Where E_c is the overall contribution towards bond energy arising from strong heteropolar bonds, E_{rm} is the contribution arising from the weaker bonds that remain after the strong bonds have been maximized i.e average bond energy per atom of the 'remaining matrix'. For chalcogen rich systems for $R > 1$ where there are heteropolar bonds and chalcogen–chalcogen bonds.

$$E_c = 2xE_{Se-Te} + 4zE_{Se-Ag} \qquad (17)$$

The mean bond energy (E_c) of the average crosslinking per atom can be given by E_c

$$E_{rm} = \left[\frac{2y - 2x - 4z}{< r >} \right] E_{Se-Se} \qquad (18)$$

For all glasses, we calculated the values of the overall mean bond energy and are tabulated in Table 5. The plot between mean bond energy $< E >$ and compactness (δ) with coordination number $< r >$ is shown in Fig. 4, it has been found that $< E >$ increases continuously with increasing Ag content. However, the overall compositional trend seems to be influenced mainly by the chemical bond arrangement.
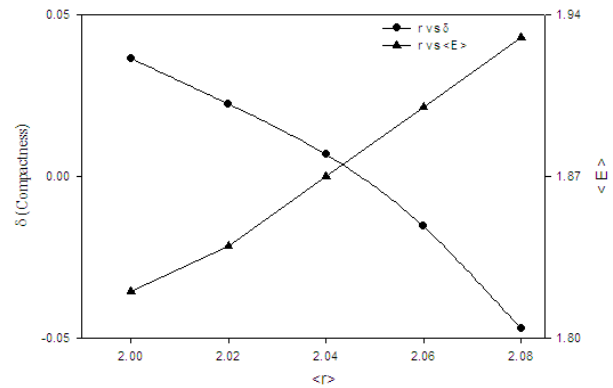

Fig. 4. Plot of δ and $< E >$ with $<r>$ for $(Se_{80}Te_{20})_{100-x}Ag_x$ glassy system.

3.8 Glass transition temperature

Gibbs and Di Marzio have developed a second-order phase transition model and obtained an empirical relationship (GDM equation) between the transition temperature and the density of cross-linking agents inserted inside a system of molecular chains [41, 42]. The glass transition temperature for $(Se_{80}Te_{20})_{100-x}Ag_x$ $(0 < x < 4)$

glassy alloys is predicted theoretically by using modified Gibbs-Di Marzio law in which the effect of chemical ordering is considered [43]. In most of the chalcogenide systems the chemical threshold observed at $r \geq 2.4$ and therefore stochastic description fails, but this description is still useful, if above this coordination number the network can be thought as a set of compound clusters inside a random network. When the effect of chemical ordering is considered the effective coordination number of the system is given by

$$T_g = 311(<E> -0.9) \qquad (19)$$

The value of r_{eff} is tabulated in Table 5. Where r_A, r_B and r_C are the coordination numbers for Se, Te and Ag respectively. The parameter β in this case is given by

$$\beta^{-1} = (r_c - r_A) \ln\left[\frac{r_c}{r_A}\right] \qquad (20)$$

The glass transition temperature T_g is then calculated by using the relation

$$T_g = \frac{T_o}{1 - \beta(r_{eff} - 2)} \qquad (21)$$

Here T_o is the glass transition temperature of chalcogen (here T_o is the glass transition temperature of Se = 316K). Glass transition temperature is also computed by using the relation given by Tichy and Ticha [44, 45].
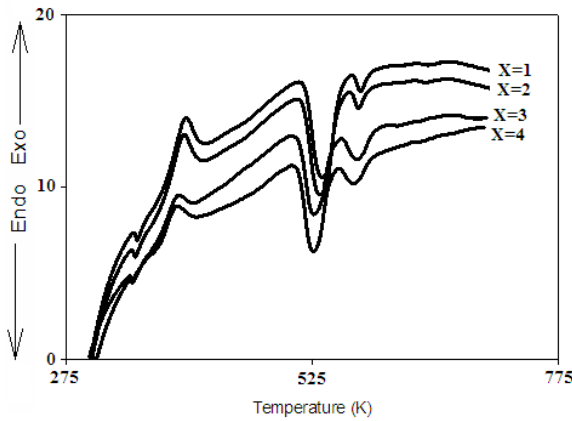
$$T_g = 311(<E> -0.9) \qquad (22)$$

Fig. 5. Typical DSC traces for $(Se_{80}Te_{20})_{100-x}Ag_x$ ($0<x<4$) glass at heating rate of 10K/min.

The value of T_g obtained by above two methods are tabulated in Table 5 along with the experimental value of glass transition temperature obtained by DTA analysis (Fig. 5). The experimental values of T_g has been decreased

with increase in Ag content as given in Table 5. The glass transition temperature represents the strength or the rigidity of the glass network. Larger the value of T_g, larger will be the rigidity of the system [46, 42], which is related to $<r>$ and the quality of connections [47]. The plot between molecular weight (M) and experimental calculated T_g with Ag content is shown in Fig. 6.
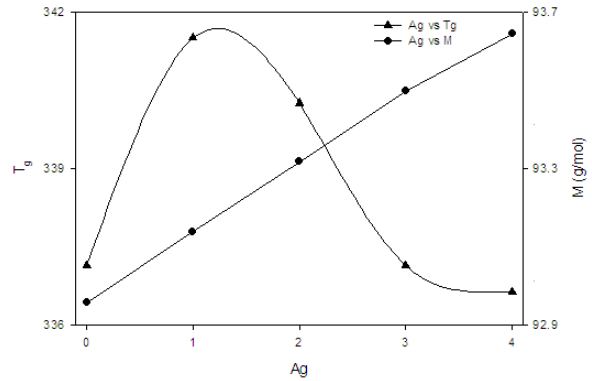

Fig. 6. Plot of T_g (K) and M (g/mol) with Ag for $(Se_{80}Te_{20})_{100-x}Ag_x$ glassy system.

3.9 Ionicity and metallicity

The correlation between the glass forming tendency and the structure of electron shell was given by the A.Winter [48]. According to her P-electrons play a major role in glass formation. Therefore she gave a rule known as the Winter's rule according to which, in order to obtain a compound in the vitreous state, it is necessary that the ratio of number of P-electrons from the component element to the number of atoms in a molecule is higher then 2. But this rule fails to explain the glass forming ability of chalcogenide glasses because the same group of elements have same P-electrons but differ in glass forming ability. This problem has been resolved by the Chlikowsky and Phillips [49] they obtained the orbitally dependent ionic radii from the Pauli force model potential. According to which r_s and r_p corresponds to the orbitally dependent ionic radii of S-orbital and P-orbital respectively. The $R_\sigma{}^{AB}$ and $R_\tau{}^{AB}$ scales correspond to the ionicity and metallicity of an A-B bond respectively, and are defined as [49]

$$R_\sigma{}^{AB} = (r_s{}^A + r_s{}^B) - (r_p{}^A + r_p{}^B) \qquad (23)$$

$$R_\tau{}^{AB} = (r_s{}^A - r_s{}^B) + (r_p{}^A - r_p{}^B) \qquad (24)$$

The relative probability of chemical bonds formation can be calculated by the Boltzmann factors exp (-E/RT) = exp (D/RT), where D is the bond energy, R the gas constant and T the reaction temperature at which the samples were prepared during their synthesis in Kelvins. The orders of bond energies and the relative probabilities listed in Table 6 indicate that the stronger the chemical bond is, the larger is its forming probability. According to

the Ordered Bond Network Model, the chemical bonds in the $(Se_{80}Te_{20})_{100-x}Ag_x$ glasses must be formed in the order of Se-Ag > Te-Ag > Se-Te.

3.10 Structure of Se-Te-Ag

The ternary phase diagram for Se-Te-Ag system is shown in Fig. 7. In the figure, three pseudo binary compositions lines are indicated, the bold line represents the Ag_5Te_3-Ag_2Se composition whereas the dashed line represents the Ag_2Te-Ag_2Se composition.
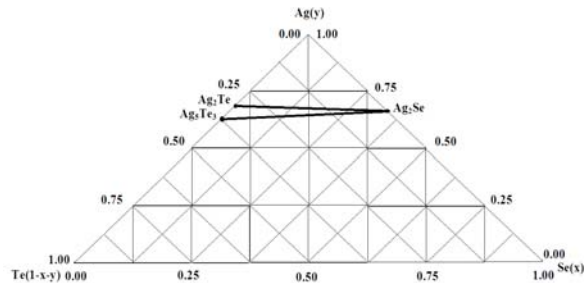

Fig. 7. The ternary phase diagram for Se-Te-Ag system.

3.11 Viscosity

The theoretical calculations of the viscosity have been done using data of heating rate (β) 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 [50]

$$\eta \approx \eta_o \exp\left(\frac{B'}{R(T-T_o)}\right) \quad (25)$$

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 [51].

$$T_o = \left(\frac{\sqrt{A}T_g - T_P}{\sqrt{A}-1}\right) \quad (26)$$

$$B' = \frac{E_t}{A}\left(\frac{T_g - T_o}{T_g}\right)^2 \quad (27)$$

where

$$A = \frac{E_t}{E_c}\left(\frac{T_p}{T_g}\right)^2 \quad (28)$$

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. It has been found that the viscosity decreases with increase in Ag content and in temperature.
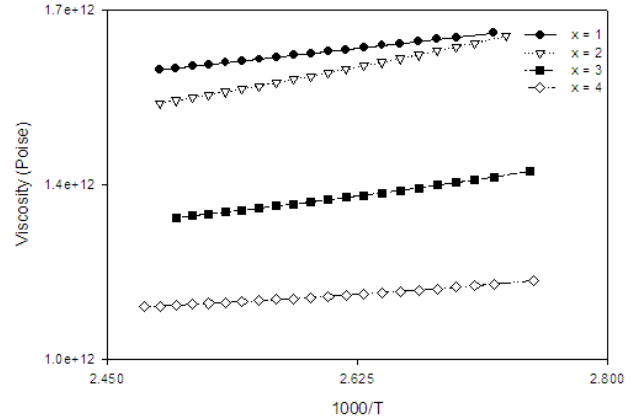

Fig. 8. Plot of viscosity (Poise) with 1000/T for $(Se_{80}Te_{20})_{100-x}Ag_x$ glassy system.

4. Discussion

It is observed that the density of $(Se_{80}Te_{20})_{100-x}Ag_x$ glassy system has been decreased with the increase in Ag content. This shows that the system becomes more and more flexible. This behavior is also supported by the experimental values of T_g. Fig. 5 shows DSC thermograms of samples with various x values at a heating rate of 10K/min. In this system the glass transition temperature is found to decrease with the increase in Ag content. Glassy Se has both chain as well as Se_8 ring structures [52]. Addition of Te leads to increase in the Se-Te mixed rings with simultaneous increase in Se and Te atoms in chain structure but there is decrease in the Se_8 ring concentrations. When Ag is incorporated, it makes bonds with Se and probably is dissolved in the Se chains. Thus there is decrease in the number of long Se-Te polymeric chains and Se-Te mixed rings but there is increase in the Se_8 rings. The decrease in chain length may be causing a decrease in T_g [53]. This reason explains the decrease in T_g with increase in Ag content. It has been observed that the values of glass transition temperature obtained theoretically are different from the experimental approach. This may be due to reason that the Tichy and Ticha method does not account the molecular interactions, which play a vital role in the relaxation process in the glass transition region. It has been found that H_s increase when T_g decrease it means that the heat of atomization or the average bond strength increases when the rigidity of the glass network decrease, so the higher values of H_s corresponds to lower value of T_g. Decreases in value of T_g with Ag content corresponds to decrease in rigidity of the system. It has been observed from Table 3 that the C.E increase with increase in Ag content. The increase of C.E implies higher bonding strength; i.e. lower defect bonds. It can be concluded that decrease of optical band gap with

increasing Ag content is most probably due to a decrease of average stabilization energy and decrease of electronegativity of the system calculated from Sanderson's principle [27]. The lone pair analysis shows that the L decrease with increase in Ag content. The lone pair electrons of $(Se_{80}Te_{20})_{100-x}Ag_x$ $(0<x< 4)$ system is between 3.988 and 3.676 which aggress with the Ref [32], and leads to conclusion that the observed system can form glasses at the ordinary rate. The change in the value of ionicity from Se-Te bond to Se-Ag bond is very important to an understanding of glass-forming ability. As shown in Table 6 the ionicity of Se-Te bond is less than that of Se-Ag bond. As we know that the σ bonds of P-orbitals have a very marked directivity, which leads to well defined structure that are malleable and makes possible, within certain limits, modifications in bond angles and the rotation of the structural elements around bond axes. These properties of σ bonds are in favour of the glass formation. The lower ionicity of Se-Te bond means that the σ bond has preponderance over that of Se-Ag. This means that the small ionicity of Se-Te bonds is the typical of σ bond. A lone-pair electrons and lower ionicity of Se-Te bond are the reasons that Te has better glass forming ability than Ag atom [54]. The decrease in the values of viscosity also favor's the same result given by the density (ρ), compactness (δ), and fraction of floppy modes (f).

5. Conclusion

The physical properties of the $(Se_{80}Te_{20})_{100-x}Ag_x$ $(0<x<4)$ chalcogenide glasses has been changed with the increase in Ag content. Density and the compactness are found to decreases with increase in the Ag content, which shows that the given system having larger free volume and flexibilities. The increase in value of f with Ag content shows that the system becomes more and more flexible. Decrease in value of T_g shows that the rigidity of the system decrease with increase in Ag content. The increases in value of cohesive energy and average heat of atomization implies that bonding strength and average bond strength increase with addition of Ag content. Average single bond energy remains almost constant with composition. No correlation between photon energy and average single bond energy was found for low connectivity glasses. The viscosity of glassy alloys has been decreased with increase in temperature and Ag content.

References

[1] E. Skordeva, D. Arsova, J. Non-Cryst. Sol. **192**, 665 (1995).
[2] Z. L. Mao, H. Chen, Ai-iien jung, J. Appl. Phys. **78**(4), 2338 (1995).
[3] R. Chiba, H. Yamazaki, S. Yagi, S . Fujimori, Jpn. J. Appl. Phys. **32**, 834 (1993).
[4] M. Szukwei, Y. Hanmei, Z. Xiaowei, J. Non-Cryst. Sol. **112**, 204 (1989).
[5] E. Maruyama, Jpn. J. Appl. Phys. **21**, 213 (1982).
[6] D. C. Hunt, S. S. Kirby, J. A. Rowlands, Med. Phys. **29**(11), 2464 (2002).
[7] T. Wagnar, S. O. Kasap, J. Mater. Res. **12**, 1892 (1997)
[8] K. Tanaka, Phys Rev. B 39, 1270 (1989).
[9] K. Shimakawa, J Non- Cryst Sol. **77**, 1253 (1985).
[10] J. Y. Shim, S. W. Park, H. K. Baik, Thin Solid Films **292**, 31 (1997).
[11] J. M. Saitar, J. Ledru, A. Hamou, G. Saffarini, Physica B **245**, 256 (1998)
[12] R. Chiba, N. Funakoshi J Non-cryst Sol. **105**, 149 (1988).
[13] A. Bhargava, A. Williamson, Y. K.Vijay, I. P. Jain, J Non-Cryst Sol. **192**, 494 (1995).
[14] R. M. Mehra, G. Kaur, A. Pundir, P. C. Mathur, Jpn. J. Appl. Phys. **32**, 128 (1993)
[15] Z. Wang, C. Tu, Y. LI, Q. Chen, J Non-Cryst Sol. **191**, 132 (1995)
[16] S. O. Kasap, T. Wagner, V. Aiyah, O. Krylouk, A. Bekirov, L. Tichy, J. Mat. Sci. **34**, 3779 (1999)
[17] M. S. Kamboj, R. Thangaraj, Eur. Phys. J. Appl. Phys. **24**, 33 (2003).
[18] M. Fadel, Vacuum **48**(1), 73 (1997).
[19] M. Vlcek, M. Frumar, J. Non-Cryst. Sol. **97**, 1223 (1987).
[20] L. Tichy, H. Ticha, J. Non-Cryst. Sol. **189**, 141, (1995).
[21] M. F. Thorpe, J. Non Cryst. Sol. **57**, 355 (1983)
[22] W. A. Harrison, Electronic Structure and the Properties of Solids. The Physics of the Chemical Bond, W. H. Freeman & Company, San Francisco, (1980).
[23] N. D. Savchenko, J. Optoelectron. Adv. Mater**. 4**(1), 41 (2002)
[24] S. R Elliot, Physics of Amorphous Solids, Longman Inc, New York, 134 (1984).
[25] K. Sedeek, M. Fadel, Thin Solid Films **229**, 223 (1993).
[26] J. Bicerano, S. R. Ovshinsky, J. Non-Cryst. Sol. **74**, 75 (1985).
[27] R. T. Sanderson, Inorganic Chemistry, Affiliated East-West Press,New Delhi, (1971).
[28] L. Zhenhua, J. Non-Cryst. Sol. **127**, 298 (1991).
[29] L. Pauling, The Nature of the Chemical Bond, 3rd Edition, Cornell University Press, Ithaca, New York, (1960).
[30] Ambika, P. B. Barman, J. Ovo. Res. **3**(1), 21 (2007).
[31] A. George, D. Sushamma, P. Predeep, Chalcogenide Letters **3**(4), 33 (2006)
[32] L. Zhenhua, J. Non Cryst. Sol. **127**, 298 (1991)
[33] J. P. Deneufville, H. K. Rockstad, J. Stuke et al. (eds.), Amorphous and Liquid Semiconductors, Taylor & Francis, London, (1974).
[34] L. Pauling, The Nature of the Chemical Bond, Cornell University Press, New York, (1960).
[35] M. Kastner, Phys. Rev. Lett. **28**, 355 (1972).
[36] M. Kastner, Phys. Rev. B **7**, 5237 (1973).
[37] S. S. Fouad, Vacuum **52**, 505 (1999).

[38] A. A. Othman, K. A. Aly, A. M. Abousehly, Thin
      Solid Films **515**, 507 (2007).
[39] L. Tichy, H. Ticha J. Non-Cryst. Sol. **189**, 141
      (1995).
[40] L. Tichy, H. Ticha, Mater. Lett. **21**, 313 (1994)
[41] G. Adam, J. H. Gibbs, J. Chem. Phys. **43**, 139 (1965)
[42] J. H. Gibbs, E. A. Di Marzio, J. Chem. Phys. **28**, 373
      (1958).
[43] M. Micoulaut, G. G. Naumis, Europhys. Lett.
      47(5), 568 (1999).
[44] L. Tichy, H. Ticha, J. Non Cryst. Sol. **189**, 141
      (1995).
[45] L. Tichy, H. Ticha, Mater. Lett. **21**, 313 (1994)
[46] E. A. Dimarzio, J. H. Gibbs, J. Polym. Sci. **60**, 121
      (1959).
[47**]** L. Tichy, H. Ticha, M. Munzar, R. Vahalova,
      Properties and Applications of Amorphous
      Materials, in: M.F. Thorpe, L. Tichy (Eds.). Kluwer
      Academic Publishers, London, (2001).

[48] A. Winter, C. Renclus, J. Phys. Chem. Glass
      73, 250 (1978).
[49] J. R. Chelikowsky, J. C. Phillips, J. Phys. Rev.
      B **17**, 2453 (1978).
[50] J. P DeNeufuille, H. K. Rockstadt, Amorphous and
      liquid semiconductors, ed. by J Stuke, W Brenig ,
      Taylor and Francis, London, (1974).
[51] H.S. Chen, J. Non-Cryst. Sol. **27**, 257 (1978).
[52] J. Schottmiller, M. Tabac, G. Lucovsky, A. Ward, J.
      Non-Cryst. Sol. **4**, 80 (1970).
[53] A. Eisenberg, Polym. Lett. **1**(4), 177 (1963).
[54] M. Fadel, S. S Fouad, E. G. El-Metwally,
      Chalcogenide Letters **5**(5), 79 (2008).

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