Physical Topology and Bonds Arrangement of As-Se-Tl Chalcogenide Glasses

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Abstract: Topological consideration of As_{20} $Se_{80-x}Tl_x$ ($5 \leq x \leq 35$ at.%) chalcogenide glasses prepared by melt quenching technique, is reported and discussed in light of the ordered bond network model (ORBNM). The DSC results show that the glass transition temperature, T_g is not lineary decrease with increasing Tl content. The crystallization temperature, the thermal stability of the glass and the glass formation ability increases with increasing Tl content until 20 at.% Tl and then decreases. According to CONM the possibility bond distribution is given. An attempt has been made to correlate the optical energy gap, E_g and estimated bond energy, E_s, through the Manca relationship:

- $E_g = 1.61(E_S - 3.11)$

Key word: Chalcogenide · Glasses · Topological · Floppy · Rigid

INTRODUCTION

The growing interest in the investigation of the properties of chalcogenide glasses stems from the actual and potential technological applications of these materials in solid state devices[1]. The As-Se-Tl chalcogenide glasses are semiconducting and infrared transmitting and have gained much industrial and reasarch interest. A wide compositional range of glass formation of the As-Se-Tl system was observed and reported by many authors [2-5]. The measurements of DC conductivity of glassy As_2Se_3 containing Tl have been peformed by many investigators[6-8]. Also the effect of the addition of Tl to As_2Se_3 on differential thermal analysis [9], the conductivity and absorption coefficient[4] and the structural studies [10] have already been demonstrated. The compostion dependence of physical propertice of thin films As-Se-Tl thin films have already been studied [11-13]. They show a continuous change in the physical properties of these alloys with change in chemical composition.

The ordered bond network model [14,15], also known as the chemically ordered network model, is usually used to explain the peculiarities observed in the compositional dependence of physical properties of chalcogenide glasses[16-18]. According to this model, the structure of the glass is assumed to be composed of three-dimensiional (3-D) cross-linked structural units of the stable chemical compounds of the system with excess, if any, of the elements dispersed among these units[19].

The model of bond arrangement[14,20] and topological models such as the constraints model[21,22] and the structural transition model [23], have been used in the interpretation of the compositional dependence of theses properties.

The composition dependence of the mean atomic volume, V_g, a fundamental physiochemical property, is an important aspect in the investigation of chalcogenide glasses. In this paper the compositional dependence of V_g for glasses belonging to the As-Se-Tl system, is reported and discussed in light of the ordered bond network model (OBNM). The composition dependence of the glass formation ability, K_g and the thermal stability of glass, T_c-T_g, have been studied. An attempt is made to estimate the possible bond arrangement of ternary chalcogenide As_{20} $Se_{80-x}Tl_x$ ($5 \leq x \leq 35$ at.%) glasss is given. Estimated band gap, E_s, has been calculated and compared to the experimental optical band gap, E_g, through the Manca relationship.

Experimental Procedure: Bulk glasses of As_{20} $Se_{80-x}Tl_x$ ($5 \leq x \leq 35$ at.%) system were prepared by a standard melt quenching techniques. The appropriate quantities of pure As, Se and Tl (5N) required to prepared 5 g of each composition were introduced in a dry clean silica tubes, which were sealed under vacuum of 10^{-5} Torr.

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The synthesis was carried out in an oscillatory furnace in the following sequence, the temperature was raised to 350 °C for 4 h and then to 650 °C for a further 2h and, finally, a furnace temperature was gradually raised to 875°C and kept at this temperature for approximately 16 h. The molten materials were then quenched in an ice water mixture to obtain the glasses.

The Archimedean's method was used for the measurement of the, ρ_g, of as-prepared glasses The weight of a piece of the As-Se-Tl alloys was measured in air and in water using electronic balance. The accuracy of the density measurement, is estimated to be better than ±2%.

Thermal studies have been carried out on the bulk glasses using a Shimadzu DSC-50 differential scanning calorimetry (DSC). The DSC thermograms of 15 mg of samples were recorded as the temperature of the sample was increased foom room temperature to about 800 k at a uniform rate (α) 10 k/min. The values of the glass transition temperature, T_g, the crystallization temperature, T_c and the melting point, T_m were determined with accuracy ±0.1 k.

The experimental optical band gap, E_g, has been found using the Tauc Plot $(\alpha h\nu)^{1/2} = f(h\nu)$. The absorption coefficient α has been calculated from the optical transmission spectra of the samples.Technological and experimental details are given in [13,24].

RESULT AND DISCUSSION

Topological Consideration: The densities of the glasses, ρ_g, were calculated using the formula:

$$\rho_g = [w_0/(w_0-w_L)]\,\rho_L \qquad (1)$$

where w_0 and w_L are, respectively, the weight of the sample in air and in liquid (water) and ρ_L is the density of the immersion liquid (water) which is equal to 1g cm^{-3} at room temperature. The values of ρ_g for glasses As$_{20}$ Se$_{80-x}$Tl$_x$ (5≤x≤35 at.%) system, measured by using Archimdean technique and the calculated density by using mixing rule are shown in Fig. 1. The densities of pure As, Se and Tl used in the mixing rule calculation were 5.73 g/cm^3, 4.82 g/cm^3 and 11.89 g/cm^3, respectivity [2]. It can be noticed that the experimental densities are less than that of the calculated ones. Its expected since the densities of the As, Se and Tl crystaline solids at room temperature were used in the mixing rule calculation. In the most cases, amorphous materials have a smaller density than their respective crystalline materials [2]. Such linear variation in Fig. 1, indicates the additive nature of the density as a character of glassy structure [8].

The mean atomic volumes of the glasses,V_g, werecalculated from the formula;

$$V_g = \sum_i (c_i\,A_i)/\rho_g \qquad (2)$$

where c_i and A_i are the atomic concentration and the atomic weight of the i-th component, respectively. The mean atomic volume, V_g, as a function of the amount of Tl at.% in the glass is depicted in Fig. 2. It is worth noting that this figure can be looked at as consists of two regions; the first one extending up to Tl-content <20 at.%, while the second one starts at Tl-content > 20 at.% and it exhibits a clear maximum at Tl-content = 20 at.%. The general formula representing this system can be written as As$_2$Se$_3$+Tl$_2$ Se$_3$ + Δc, where Δc an excess of Se or Tl elements. On the basic of the OBNM, the glass structure

Fig. 1: Shows the variation of ρ_g with Tl content for As$_{20}$ Se$_{80-x}$Tl$_x$ (5≤x≤35 at.%) chalcogenide glasses
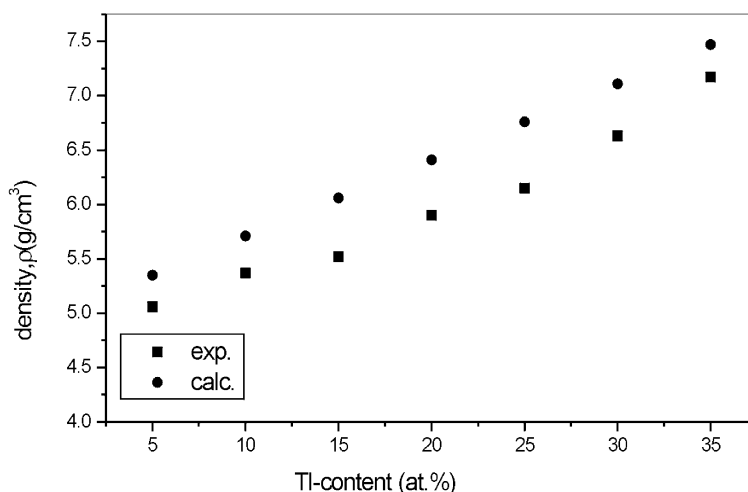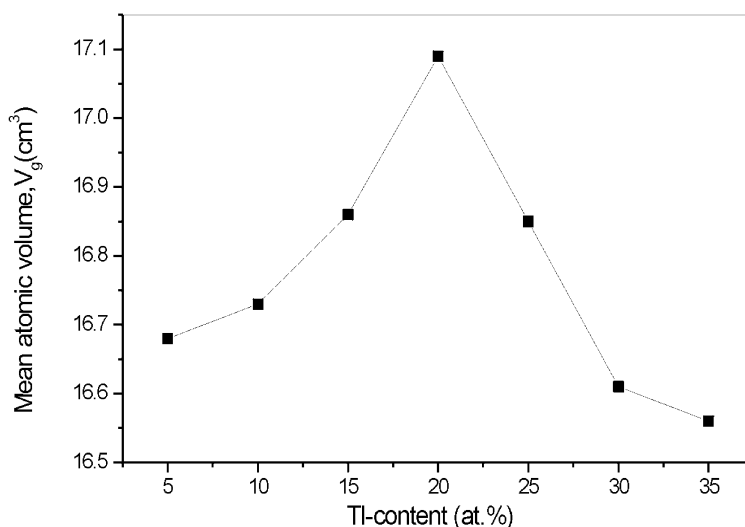
Fig. 2: Shows the variation of V_g with Tl content for $As_{20} Se_{80-x}Tl_x$ ($5 \le x \le 35$ at.%) chalcogenide glasses

of this tie-line composition, defined as the line joining the crystalline compounds As_2Se_3 and Tl_2Se_3, is visualized to be composed of 3-D completely cross-linked As_2Se_3-type and Tl_2Se_3-type structural units consisting of heteropolar bonds only, with no excess of elements for 20 at.%.Tl At Tl content < 20 at.% the glass structure defined as a composed of 3-D completely cross-linked As_2Se_3-type and Tl_2Se_3-type structural units with an excess of Se-element. At Tl content > 20 at.%, it can be defined as a composed of 3-D completely cross-linked of As_2Se_3 and Tl_2Se_3 structural units with an excess of Tl-elements. Therefor, the observed maximum in V_g for the tie-Line composition which contains 20 at.% Tl is ascribed to chemical order effects tacking place at this composition. These chemical ording effects occurring at the tie line composition, were recently reported for Ge-In-Se and Ge-S-Ag glasses[17,19].

Lately, the mean coordination number has been widely used for the description of the structure of network glasses. It is defined as the average number of bonded neighbours per atom in the structure. For $As_x Se_y Tl_z$ system the the mean coordination number <z> is given by;

$$<z> = (xN_{As}+yN_{Se} +yN_{Tl}) \qquad (3)$$

Where x, y and z are the respective atomic concentration of As, Se and Tl and N_{As}, N_{Se} and N_{Tl} are the coordination numbers of As, Se and Tl respectivity. The evaluation of <z>, requires the knowledge of the coordination numbers of the individual atoms in the amorphous alloy. It is well known that the coordination number of Se atoms in Se-containing alloys conform with the Mott (8-N) rule [25] where N is the number of valence electrons. Therefore, coordinations of 3, 2 and 3 for As, Se and Tl atoms, respectively, are used for the evaluation of <z> and Eq. (3) for $As_{20} Se_{80-x}Tl_x$ alloys reduces to the formula

$$<z>=2.2+ 0.01x \qquad (4)$$

The dependence of Tl-content on the mean value of <z> are listed in Table 1.

The variation of V_g with <z> are depicted in Figure 3. It is worth noting that this figure can be looked at as consists of two regions; the first one extending up to <z> < 2.4, while the second one starts at <z> > 2.4 and is characterized by a maxinmum at <z>=2.4. This maximum is

Table 1:   The mean coordination number,<z>, glass transtion temperature, T_g, crystallization temperature, T_c, melting poin, T_m, thermal stability (T_c-T_g), and ability of glass formation, K_g, for $As_{20} Se_{80-x}Tl_x$ ($5 \le x \le 35$ at.%) chalcogenide glasses.

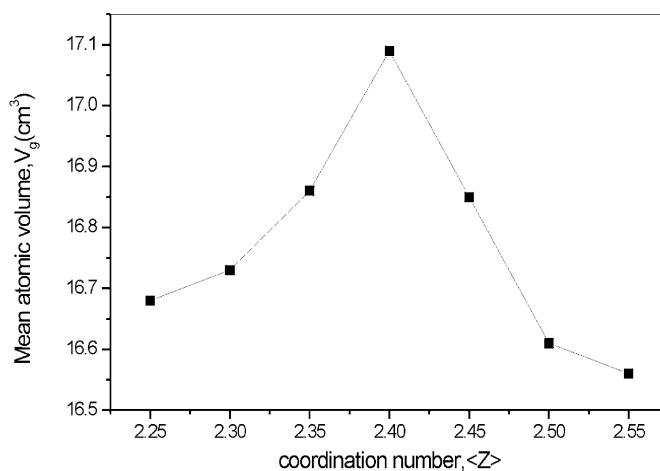| Tl (at.%)	<z>	T_g (K)	T_c (K)	T_m(K)	T_c-T_g(K)	K_g
5	2.25	356	443	713	87	0.322
10	2.30	354	448	708	94	0.362
15	2.35	353.5	583.	701	230.5	2.004
20	2.4	352	593	697	241	2.410
25	2.45	351.5	538	693	186.5	1.218
30	2.5	349	513	687	164	0.943
35	2.55	348	463	683	115	0.523

Fig. 3: Shows the variation of the mean atomic volume, V_g with coordination number $<z>$ for $As_{20} Se_{80-x}Tl_x$ ($5\leq x\leq 35$ at.%) chalcogenide glasses
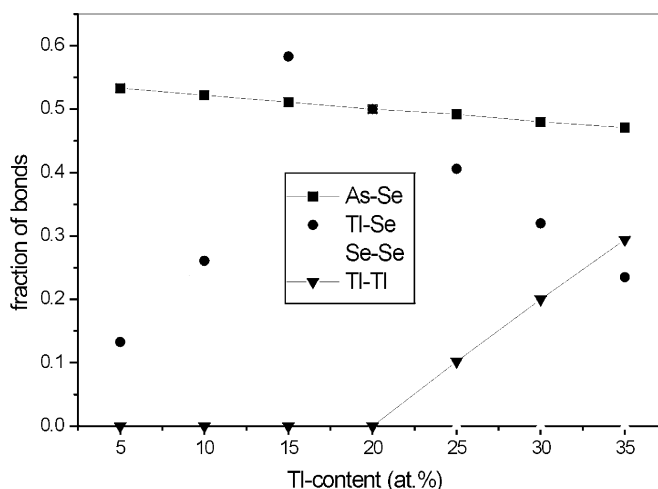

Fig. 4: Shows the variation the number of floppy with Tl content for $As_{20} Se_{80-x}Tl_x$ ($5\leq x\leq 35$ at.%) chalcogenide glasses

understood using the notion of rigidity percolation in covalent glasses which was intitially presented by Phillips and subsequently modified by Thorpe [22,26-28]. They developed a mean field theory for the number of zero-frequency modes in a covalent network glass. Taking into account the constraints by bond-streching and bond-bending force and equating the number of topological constraints per atoms, N_c {N_c= ($<z</2$ +($2<z>$-3) where $<z>/2$ is the constaint on bond length and ($2<z>$-3) is the number of constraints on the bond angle} to the number of degrees of freedom per atom (N_d=3), rigidity percolation exists at $<z>$=2.4. Networks with $N_c< N_d$ are referred to as under-cross-linked and contain large floppy regions with a few rigid inclusions while in those with $N_c>N_d$, referred to as over-cross-linked, the rigid regions have percolated to form a solid with a few floppy inclusions. The network with N_c =N_d for which $<z>$ =2.4, is a percolaction threshold

at which the transition from a floppy to a rigid takes place and at which the mechanical stability of the network is optimized[29]. The stability of the network with $<z>$= 2.4 is associated with atomic arrangements that become more tightly bound and having shorter bond lengths thus resulting in a maximum in V_g as shown in figure 2. The obseved thresholed in the this work at $<z>$ =2.4 making the floppy-to-rigid transition in glasses with 20 at.% Tl.

The fraction,F, of zero-frequenc (floppy) modes F is given by[30];

$$F=2-5/6<z> \qquad (5)$$

Figure 4 shows the fraction of floppy modes, F, against Tl content, we can notice that the values of f decreases with increaing Tl conent reaches to zero at 20 at.% Tl. For tl content $<$ 20 at.%, the number of floppy
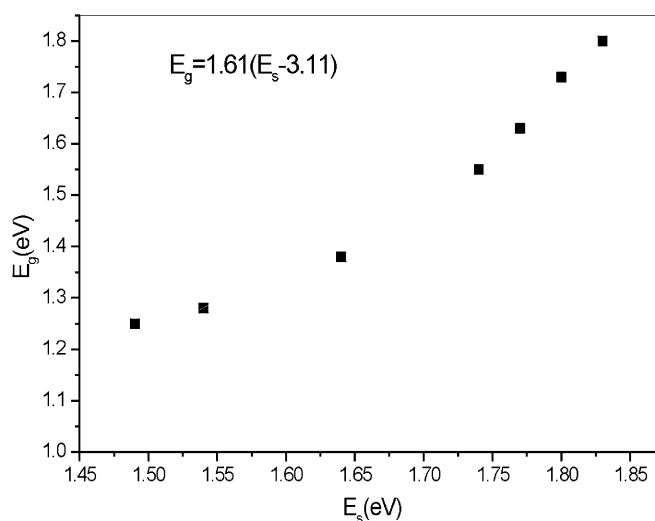
Fig. 5: Shows the variation of glass transition temperature, T_g with Tl content for As_{20} $Se_{80-x}Tl_x$ ($5 \leq x \leq 35$ at.%) chalcogenide glasses

modes, equal to 0.125. Finally, for Tl content > 20 at.%,the number of floppy has a negative values, this meams that, the network becomes rigid as it goses throught a phase transition from floppy to rigid at 20 at.% Tl.

Glass Forming Ability: From the DSC thermogrames obtained at a heating rate of 10 K / min for our system. The values of glass transition temperature,T_g, crystallization temperature, T_c, and melting point, T_m, were measured to an accuracy ±1k. Numerical values of these quantities as well as the values of interval (T_c-T_g) and the ration K_g, =(T_c-T_g)/ (T_m-T_c), are listed in Table 1. It can be seen, that both T_g and T_m decreases with increasing Tl content, while the values of T_c increases with increasing Tl content until 20 at.% Tl. For greater amount of Tl content >20 at.%Tl, the values of T_c is decreases.

Figure 5 shows the variations of T_g wih the amount of Tl present in the glass. It is worth noting that this figure can be looked at as consisting of two regions; the first one extending up to the glassy composition with 15 at.% Tl, while the second one starts at the composition with 20 at.% Tl where a sudden drop in T_g is observed. This is taken as an indication that the underlying glass structure for composition with =20 at.%Tl is different from that corresponding to the compositions with less than 20 at.%.Tl and suggesting that a phase change might be taking place at composition of 20 at.% Tl. In general, the decreases of T_g for a glassy alloy, observed in this work, leads to an inceases in its configurational entropy and thus to a decreases in its stability. A slight contribution to the decreases of the T_g with increasing Tl content in

the glass is attributed to the replacement of the strong As-Se bonds (bond energy = 41.68 kcal/mol) by the weak Tl-Se bonds (bond energy = 38.71 kcal/mol).

The values (T_c-T_g) may be used to assess the thermal stability of the glasses or equivalently the relative ease with which a glass can be formed, where a short interval signifies that the glass contains structural units with a hight crystallization tendency [31]. As seen from Table 1, the values of (T_c-T_g) increases with increasing Tl content in the glass reaches to a maximum values at 20 at.%Tl. For greater amount of Tl content > 20 at.%Tl, the thermal stability of the glasses is increases. The thermal stability for As-Se-Tl, glasses has a maximum for $As_{20}Se_{60}Tl_{20}$ composition, (correspoding to $As_2Se_3+Tl_3Se_3$ structural units).

It has been suggested by Hruby [32] that an appropriate measure for the glass forming ability is given by the ratio:

$$K_g = (T_c-T_g)/ (T_m-T_c) \qquad (6)$$

Figure 6 shows the variation of K_g with Tl content for for As_{20} $Se_{80-x}Tl_x$ ($5 \leq x \leq 35$ at.%) glasses. It could be noticed that the glass formation ability of this glasses increases with increasing Tl content reaches to a maximium values at 20 at.% Tl corresponding to $As_{20}Se_{60}Tl_{20}$ composition.

Bonds Arrangement: In order to estimate the possible bond arrangement in chalcogenide glass systems two models have often been applied: (1) The random bond
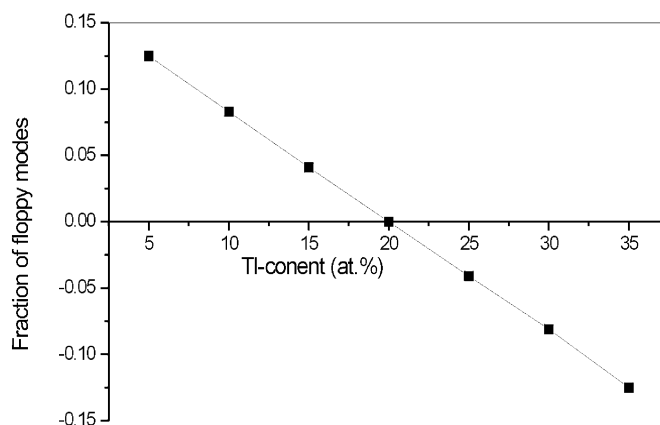
Fig. 6: Shows the variation of glass formation ability, K_g with coordination number for As_{20} $Se_{80-x}Tl_x$ ($5 \leq x \leq 35$ at.%) chalcogenide glasses
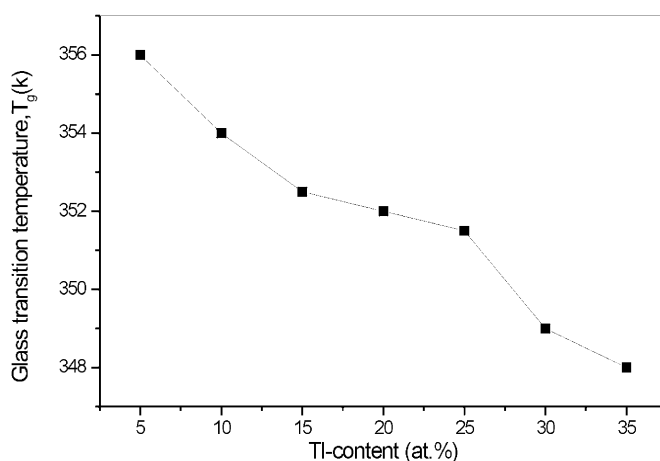

Fig. 7: Shows the variation of the fraction of bonds with Tl-content for As_{20} $Se_{80-x}Tl_x$ ($5 \leq x \leq 35$ at.%) chalcogenide glasses

network model (RBNM). In this model the distribution of the various kinds of bonds is statistical and is determined by the fractional concentration c_i of an atom I and the number of bonds of the same atom. (2) The ordered bond network model (OBNM) suggests the prevalence of heteropolar bonds and minimum number of weak homopolar bonds. In this work we applied the second model, because the first model is suitable only for the characterization of freshly evaporated films where the chemical ordering is very small [33].

According to ordered bond network model (OBNM) in chalcogen rich alloys as in our case, the relative fraction of As-Se, Tl-Se and Se-Se, expected to exist in the As_{20} $Se_{80-x}Tl_x$ alloys at x <20 at.% Tl, while the relative fraction As-Se,Tl-Se and Tl-Tl at Tl content >20 at. % where the Se-Se bond replaced by Tl-Tl bonds. The relative fraction of the bonds is summarized in Table 1 and Figure 7. It is seen from this table that the fraction of As-

Se and Se-Se bonds decreases with increasing Tl content, while the fraction of of Tl-Se bonds increases with incresing Tl content until 20 at.% Tl and then decreses with incresing Tl content.

The heteropolar bond energy E_{A-B} for a covalent bond between atoms A and B is estimated from the Pauling formula [34-36].

$$E_{A-B} = [E_{A-A} E_{B-B}]^{1/2} + 30 (\phi_A - \phi_B)^2 \qquad (7)$$

where E_{A-A} and E_{B-B} are the single bond energies for atoms A and B in kcal/mol, respectively, and ϕ_A and ϕ_B are their corresponding electronegativities. The single bond energies in kcal/mol, are 32.1 for As, 44 for Se and 15.4 for Tl. Using electronegativity values of 2.18, 2.55 and 1.9 for As, Se and Tl, respectivity[37]. The bond energie E_{As-Se} and E_{Tl-Se} are calculated. The types of bond expected to occur in As_{20} $Se_{80-x}Tl_x$ system are As-Se (E_{as-Se} =41.68 kcal/mol), Tl-Se (E_{tl-Se} =38.71 kcal/mol).
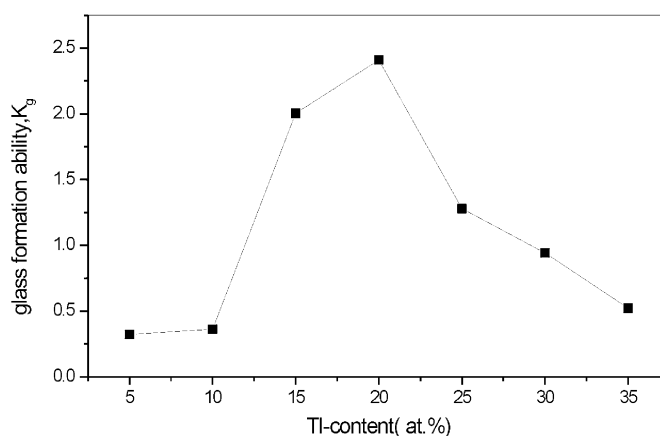
Fig. 8: Shown the dependence of estimated banding engery,E_s, on the opticl energy gap E_g for As_{20} $Se_{80-x}Tl$ ($5 \leq x \leq 35$ at.%) chalcogenide glasses

Table 2: Relative fraction of the bonds (As-Se, Tl-Se, Se-Se and Tl-Tl), the estimated binding energy, E_s and optical energy gap, E $_g$of As $_2$Se $_{80}$Tl $_x$ ($5 \leq x \leq 35$ at.%) chalcogenide glasses

Tl (at.%)	As-Se	Tl-Se	Se-Se	Tl-Tl	E_s (eV)	E_g(eV)[12]
5	0.533	0.133	0.334	--------	1.83	1.80
10	0.521	0.261	0.217	--------	1.80	1.73
15	0.511	0.383	0.106	-------	1.77	1.63
20	0.500	0.500	-------	--------	1.74	1.55
25	0.492	0.406	-------	0.102	1.64	1.38
30	0.480	0.320	-----	0.200	1.54	1.28
35	0.471	0.235	------	0.294	1.49	1.23

For Tl content = 5,10,15 at.%, the excess of bonds are Se-Se (E_{se-Se} =44 kcal/mol) but for Tl content= 25,30 and 35 at.% the number of excess bonds are Tl-Tl bond with (E_{Tl-Tl} =15.4 kcal/mol). This results in a good agreement with the results obtained from $(As_2Se_3)_{1-x}Tl_x$ system [35].

If we now further assume that the bond energies are additive, we can estimate the bond energy (the cohesive energy), E_s i.e the stablization energy of an infinitely large cluster of the material per atom, by summing the bond energies expected in the materials. This is equivalent to assuming a simplified model consisting of non-interacting electron pair bonds highly localized between adjacent pairs of atoms. The average bond energies of the different compositions,E_s, are listed in Table 2, where the E_s of the prepared bulk samples is evaluated from the following equation:

$$E_s = \sum f_i \, E_i / 100 \qquad (8)$$

where f_i and E_i are the number of the expected chemical bonds and the energy of each corresponding bond, respectively. It can be seen from table 2 that the average

bond energy decreaes with increasing Tl content. This decrease of the average bond energy of the system tends to decrease the energy of the conduction band edge, causing a narrow splitting between bonding, σ and antibonding band, σ^*, and thus resulting in the observed decreases in the band gap.

The experimental optical energy gap, E_g, of As_{20} $Se_{80-x}Tl_x$ ($5 \leq x \leq 35$ at.%) thin film are determined by El.Nahass *et al*. [13]. They shows that the values of E_g decreases lineary with increasing Tl content as shown in Table 2. The difference between E_s and E_g of our system deviate by 1.64-17.45%. This difference increases with increasing Tl content until 20.% Tl and then it has a constant value. As is well know, the bond energy, E_s, is clossely connected to the oprical energy gap E_g of the chalcogenide semicondutors and usually $E_s > E_g$[38]. Fig.7 shows the relation beween E_g and E_s for our system. The linear relation has a slope(=1.61) and intercept(=-1.93). An attempt has been made to correlate the optical energy gap, E_g and estimated bond energy,E_s, through the Manca relationship[39]:

$$E_g = 1.61(E_s - 3.11) \qquad (9)$$

CONCLUSION

The variation of mean atomic volune (V_g), with Tl content for chalcogenide As_{20} $Se_{80-x}Tl_x$ ($5 \leq x \leq 35$ at.%) glasses were investigated. The V_g-$<z>$ dependence were discussed in the light of the ordered bond network model (ORBNM). The thermal stability of the glass as well as the glass forming ability has non linear decreases with Tl content. According to CONM the possible bond distribution as well as the binding energy in ternary As_{20} $Se_{80-x}Tl_x$ ($5 \leq x \leq 35$ at.%) glasses are s given.. An attempt has been made to correlate the optical energy gap,E_g and estimated bond energy,E_s, through the Manca relationship

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