

EFFECT OF INDIUM CONTENT ON THE OPTICAL AND OTHER PHYSICAL CHARACTERISTICS OF As – Te GLASS SYSTEM

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The influence of indium (In) on the optical and other physical properties of $As_{40}Te_{60-x}In_x$ ($7.5 \leq x \leq 16.5$) was investigated. The relationship between the optical gap (ΔE_g) and chemical composition has been discussed in terms of the average heat of atomization (H_s) and average coordination number Z . It was found that the magnitude of ΔE_g and H_s increases with increasing indium content. Using the chemical bond approach of Tichy and Ticha the mean bond energy $\langle E \rangle$ has been calculated and it was found to be proportional to the glass transition temperature (T_g), the average coordination number (Z) and the number of lone pair electrons (L) of the system.

Keywords: Chalcogenide glasses, Glass transition temperature, Optical gap, Heat of atomization.

1. Introduction

Chalcogenide glasses are interesting materials because of their technological applications [1] and commercial importance [2]. High attention has been paid to the influence of impurities on the electrical and optical properties of chalcogenide glasses. Many approaches have been proposed to explain the compositional dependence of various physical properties of chalcogenide networks [1,3-6] The relation ship between chemical bonding and the glass transition temperature (T_g) of amorphous semiconducting alloys is an essential feature for any comprehensive theory relating their structural properties [7,8]. Chalcogenide glasses are often called lone-pair semiconductors. The chemical bonds with lone pair electrons have electron flexibility [9]. The lone pair electrons have an important role in chalcogenide glass formation [10]. Because of the electrostatic repulsion and the repulsion caused by the Pauli's exclusion principle, the valence electrons tend to avoid one another. If all the valence electrons of a central atom are used to form bonds, the coordination polyhedra have a strictly symmetrical structure. The configuration of polyhedra with unshared electron pairs is similar to those of polyhedra with shared pairs.

The chemical bonds with lone pair electrons are characterized by flexibility. It is easier to distort a bond with lone pair electrons than a bond with no unshared electrons. Increasing the number of lone pair electrons decreases the strain energy in a system, and structures with large number of lone pair electrons favor glass formation. In this study the influence of indium (In) on the optical and physical properties of As-Te-In glass system is investigated. Also, the variations of the optical gap with composition and average heat of atomization is discussed on the basis of the overall mean bond energy using the available data [11] for the composition $As_{40}Te_{60-x}In_x$ ($x=7.5,10,12.5,13.5,14,15\&16.5$).

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2. Discussions

For the given glass system As-Te-In the average coordination number is calculated by using the formula

$$Z = [3(40) + 2(60-x) + 4(x)]/100 \quad (1)$$

Here the coordination number of As, Te and In is taken to be 3, 2 & 4 respectively [11,12]. Fig. 1 shows the variation of glass transition temperature (T_g) with average coordination number (Z) for various compositions. It is seen from the figure that T_g increases with increasing Z and reaches a maximum value corresponding to Chemical Threshold (CT) where $Z = 2.7$ [12,13]. The rigidity percolation deals with the dimensionality and rigidity of a glass network whereas the chemical ordering deals with the arrangement of molecular species in a chalcogenide glass. The composition/average coordination numbers at which these two topological effects occur are known as rigidity percolation threshold (RPT) and CT respectively.

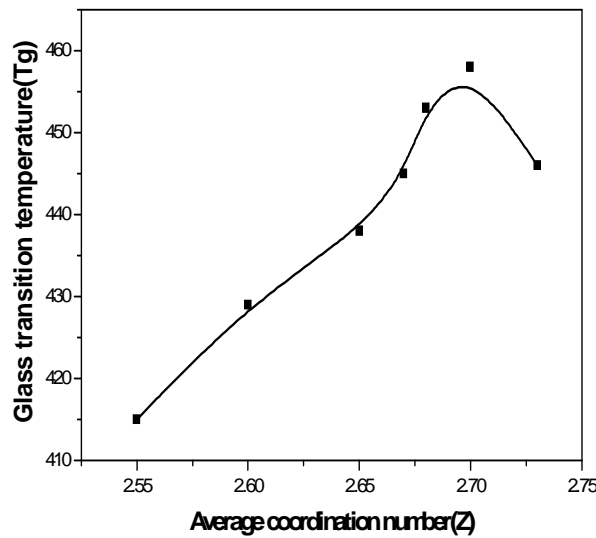


Fig. 1. Variation of glass transition temperature (T_g) average coordination number ' Z '.

3. Role of lone-pair electrons

In order to calculate the number of lone-pair electrons of a chalcogenide glass system, the average coordination number proposed by Phillips [4] was introduced. The number of lone-pair electrons is equal to all the valence electrons of the system minus the shared electrons. i.e.:

$$L = V - Z \quad (2)$$

where L and V are lone-pair electrons and valence electrons, respectively. The number of lone-pair electrons of the given glassy system $As_{40}Te_{60-x}In_x$ was obtained according to equation 2 and is listed in Table 1. It is seen from the above table and from the Fig. 2 that the number of lone-pair electrons decreases continuously with the increase in the content of In (with decrease in the content, Te) in the given glass system. We can conclude from the results given above, that some lone-pair electrons in the structure of a system are a necessary condition for obtaining the system in vitreous state. 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[14].

Table 1. Values of Z, valence electron(V) and lone-pair electrons for the system $As_{40}Te_{60-x}In_x$.

Composition $As_{40}Te_{60-x}In_x$	Z	V	L=V-Z
x=7.5	2.55	5.375	2.825
x=10	2.6	5.3	2.7
x=12.5	2.65	5.255	2.605
x=13.5	2.67	5.195	2.525
x=14	2.68	5.180	2.50
x=15	2.70	5.15	2.45
x=16.5	2.73	5.105	2.375

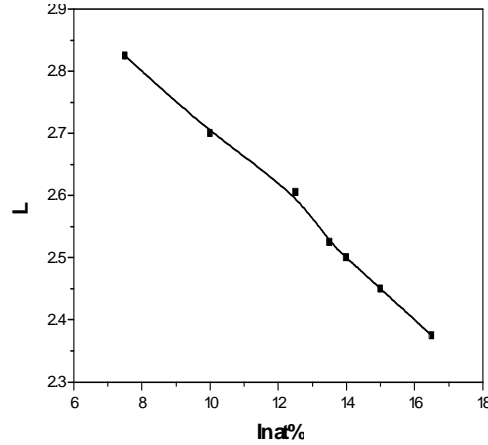


Fig. 2. Variation of In concentration with lone-pair electrons(L).

4. The relationship between the average heat of atomization, the optical gap and the coordination number.

According to Pauling [15] 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 heats of formation ΔH and the average of the heats of atomization H_s^A and H_s^B that correspond to the average non-polar bond energies of the two atoms [16,17].

$$H_s (A-B) = \Delta H + 1/2 (H_s^A + H_s^B) \quad (3)$$

The first term in equation 3 is proportional to the square of the difference between the electro negativity X_A and X_B of the two atoms:

$$\Delta H \propto (X_A - X_B)^2 \quad (4)$$

In order to extend this idea to ternary and higher order semiconductor compounds, the average heat of atomization H_s is defined for the compounds $A_\alpha B_\beta C_\gamma$ as a direct measure of the cohesive energy and that of average bond strength, given by [18,19].

$$H_s = (\alpha H_s^A + \beta H_s^B + \gamma H_s^C) / (\alpha + \beta + \gamma) \quad (5)$$

In this ternary glass system H_s is given by equation 5 is applicable. The values of H_s obtained by using the values of H_s for As, Te and In (the H_s values in units of K cal/gm.atom are 69 for As, 46 for Te and 58 for In) are listed in Table 2. As seen from Table 2, the value of H_s increases with the addition of In. In a given chalcogenide system, decreasing the relative atomic mass of chalcogen (Te) or its proportion in the glass increases the average bond strength and hence the T_g also increases [20]. It is therefore interesting to relate the optical gap ΔE_g with the chemical bond energy, and the parameters we use to specify the bonding are H_s and Z . The relation between the energy gap and average heat of atomization was discussed by Aigrain and Balkanski [21]. According to their study a linear correlation exists for semiconductors of the diamond and zinc blende structure.

$$\Delta E_g = a(H_s - b) \quad (6)$$

where **a** and **b** are characteristic constants. The values of ΔE_g for $As_{40}Te_{60-x}In_x$ with $x=7.5, 10, 12.5, 13.5, 14, 15$ & 16.5 are listed in Table 2. It can be seen that the addition of In (substitution of Te) leads to the increasing H_s as well as ΔE_g . It is suggested by the above equation that the average heats of atomization are a measure of the cohesive energy and represent the relative bond strength, that in turn are correlated with properties like energy gap [22]. If there is a linear relationship between the bond strength and average band gaps to describe the compounds, then the addition of In (substitution of Te) to $As_{40}Te_{60-x}In_x$ will affect the average band gap. By adding In to this glassy system, the average bond strength of the compound increases, and hence ΔE_g will increase. When the bond energies in the alloy are not very different, the increase in the disorder associated with deviation from stoichiometry will tend to push the mobility edges further into the bands (Anderson transition) thereby increasing ΔE_g [23]. Figs. 3 and 4 represents the dependence of H_s and ΔE_g on the composition. All these parameters are gradually increasing with x .

Table 2. Variation of the parameters Z , H_s , ΔE_g , T_g and $\langle E \rangle$ for $As_{40}Te_{60-x}In_x$ composition with x .

Z	H_s [Kcal/g-atom]	ΔE_g [eV]	T_g [°K]	$\langle E \rangle$ [eV]
2.55	56.10	2.366	415	2.23
2.6	56.40	2.373	429	2.279
2.65	56.70	2.379	438	2.308
2.67	56.82	2.382	445	2.330
2.68	56.88	2.383	453	2.365
2.70	57.00	2.386	458	2.372
2.73	57.18	2.390	446	2.334

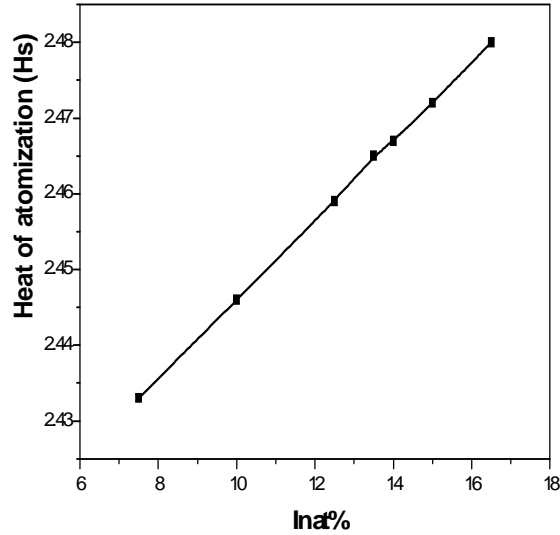


Fig. 3: Variation of indium concentration with average heat of atomization (Hs).

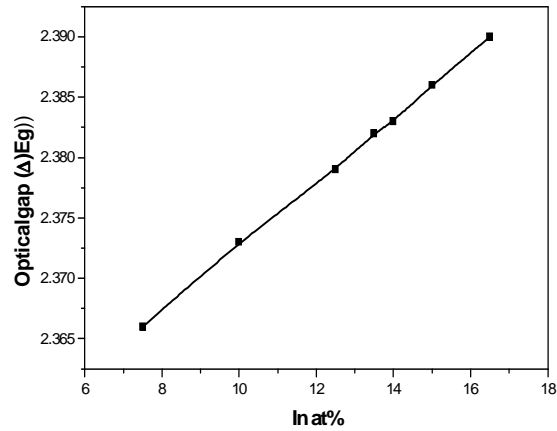


Fig. 4. Dependence of In at% on optical gap width.

The covalent bond approach of Tichy and Ticha [24,25] may be considered as a first approximation in the case of chalcogenide glasses. The glass transition temperature is considered to be proportional to the mean bond energy $\langle E \rangle$, which depends on factors like mean coordination number, degree of cross linking, bond energy and the nature of bonds. Taking account of all these factors, they have examined 186 chalcogenide glasses with T_g ranging from ~ 320 to 760 K, and obtained a good correlation between T_g and $\langle E \rangle$ in the form,

$$T_g = 311[\langle E \rangle - 0.9] \quad (7)$$

which satisfies the Arrhenius relation for viscosity [25]. Applying this model in our problem, we have evaluated mean bond energies for various compositions of As-Te-In system, and it can be seen that T_g is proportional to mean bond energy, $\langle E \rangle$. This shows that when indium content increases,

the mean bond energy of the system increases, reaches a maximum corresponding to the composition $As_{40}Te_{45}In_{15}$, and then decreases as shown in Fig. 5. The major limitation of the model is that, it does not account for the molecular interactions, which plays a vital role in relaxation process in the glass transition region.

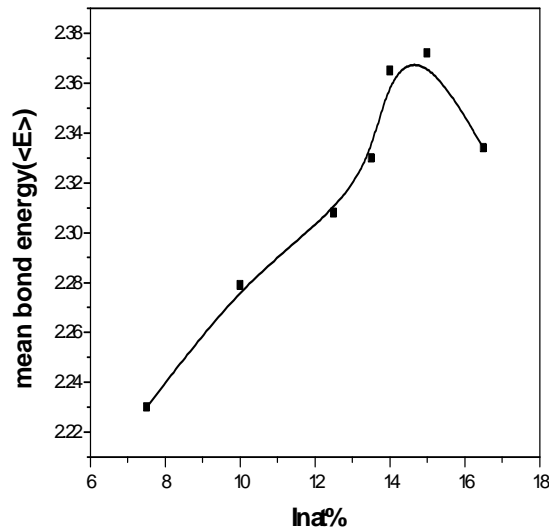


Fig. 5. Variation of indium concentration with mean bond energy $\langle E \rangle$.

The calculated values listed in Table 1 and 2 for all different compositions of $As_{40}Te_{60-x}In_x$ glassy system reveal that the addition of indium leads to a decrease in the number of lone-pair electrons and an increase in the parameters like, average heat of atomization, the mean bond energy and the optical gap.

5. Conclusion

It is seen that the average coordination number, optical gap, average heat of atomization and mean bond energy increase with increasing the In content or decreasing the Te content. This behavior is most likely due to reduction of defected bonds Te-Te and to the increase of the average binding strength. According to the covalent bond approach of Tichy and Ticha the mean bond energy is proportional to the glass transition temperature and it reaches a maximum value corresponding to chemical threshold ($Z=2.7$).

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