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COMPOSITIONAL DEPENDENCE OF PHYSICAL PARAMETERS IN Sn-Se-In CHALCOGENIDE GLASSES

A. KUMAR DIXIT[a*], P. SHARMA[b], A. THAKUR[b], V. MISHRA[c], P. SHARMA[d], V. S. RANGRA[a]
[a]*Department of Physics, H. P. University, Summer Hill Shimla (171005) India.*
[b]*Department of Physics, Abhilashi P.G. Institute of Life Sciences (175008) India.*
[c]*Department of Physics, Sri Sai University, Palampur (176061) India.*
[d]*Department of Physics, Jaypee University of Information Technology, Waknaghat, Solan, H.P. (173215) India.*

The effect of the variation of the composition of the Chalcogenide glasses of $Sn_7Se_{93-x}In_x$ (x = 0, 2, 4, 6, 8, 10) system has been studied on various physical parameters viz. coordination number, lone pair of electrons, number of constraints, bond energy, heat of atomization, glass transition temperature, cohesive energy and mean bond energy by using melt quenching technique. The average number of constraints, average heat of atomization, mean bond energy, glass transition temperature and cohesive energy are found to increase whereas number of lone pair of electrons calculated here decreases with the increase in the Indium content in the composition of the alloy.

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1. Introduction

Recent years have witnessed a growing interest in the field of study of the properties of chalcogenide glasses. Chalcogenide glasses find numerous potential applications owing to their typical electrical and optical properties. So these glassy alloys have been investigated for the modification of their properties. These glasses possess phase reversal property between crystalline and amorphous states [1-4]. This phase reversal property makes them useful in rewritable optical recording [5, 6]. These chalcogenide glasses are semiconductors in nature and have low transmission losses in the infrared region, so these can be used in producing glass sensors, in infrared optical fibers, information transfer xerography, switching and memory devices, photolithography and fabrication of inexpensive solar cells [7-12]. The combination $Sn_7Se_{93-x}In_x$ has the glass forming ability over a wide range of compositional variation [13, 14]. The addition of impurity metal Indium to Se increases its glass forming ability which may also enhance the optical and electrical properties of the system. The addition of metallic impurity also increases the glass forming region as well as it creates disorder in the composition and configuration of the glassy system. The addition of metallic impurity Indium along with the replacement of Se increases the glass transition temperature of the system. Every impurity atom of Indium tries to adjust itself according to the nearest neighbor's environment in Se, so it looks like causing little effect on the glassy system [15]. However recent study indicates that the addition of metallic impurities causes significant effect on the properties of chalcogenide glasses [16]. A continuous change in the physical properties has been observed with the variation in the chemical composition. The effect of compositional variation on the physical properties of the chalcogenide glasses is generally explained by using ordered bond network model also known as chemically ordered network model.

*Corresponding author: arundixit16@gmail.com

The present work is devoted to examine the glassy system $Sn_7Se_{93-x}In_x$ (x = 0, 2, 4, 6, 8, 10) theoretically for various physical parameters like the coordination number, number of constraints, number of lone pair electrons, bond energies of the different bonds formed in the system, heat of atomization, average single bond energy (which is a measure of cohesive energy [17], mean bond energy, glass transition temperature and cohesive energy. Theoretical calculation of glass transition temperature has been done using the model proposed by Tichy and Ticha [18,19].

2. Experimental details

Conventional melt quenching technique was used to prepare the bulk samples of glassy $Sn_7Se_{93-x}In_x$ (x = 0, 2, 4, 6, 8, 10) alloy. High purity (99.999%) elements Sn, Se and In in the appropriate weight proportion, were vacuum sealed (10^{-4} Pa) in quartz ampoules and heated up to 800ºC in a rocking furnace at a heating rate of 3-4ºC/min, the ampoules were frequently rocked at the highest temperature for 8 hrs. The quenching was done in ice-cold water immediately after taking out the ampoules from the furnace. The experimental technique has been given in detail by P. Sharma et. al [20]. The amorphous nature of the bulk samples was confirmed by the X-ray diffraction technique as no sharp peak was observed in spectra.

3. Results and discussion

3.1 Calculation of coordination number (m) and number of constraints in glassy network

Nearest neighbor coordination number (m) is an important tool to test the validity of topological concepts in ternary system because of its large glass forming domain. The average coordination number in the system under investigation has been calculated by using the relation

$$m = \frac{\alpha N_{Se} + \beta NSn + \gamma N_{In}}{100} \tag{1}$$

where α, β and γ are the atomic % of Se, Sn and In respectively and N_{Se}, N_{Sn} and N_{In} are their respective coordination numbers. Nearest neighbor coordination number (m) in the ternary system $Sn_7Se_{93-x}In_x$ (x = 0, 2, 4, 6, 8, 10) is suitable for testing the validity of topological concepts [21,22] because of its large glass forming domain The calculated coordination numbers (m) lie in the range $2.14 \leq m \leq 2.24$ and are given in Table 1.

Table 1 describes the values of the average coordination number < m > , number of constraints arising from bond stretching (N_a), number of constraints arising from bond bending (N_b), average number of constraints (N_c) and effective coordination number <m_{eff}> for $Sn_7Se_{93-x}In_x$ (x = 0, 2, 4, 6, 8, 10).

Composition	m	N_a	N_b	N_c	<m_{eff}>
Sn_7Se_{93}	2.14	1.07	1.28	2.35	2.14
$Sn_7Se_{91}In_2$	2.16	1.08	1.32	2.40	2.16
$Sn_7Se_{89}In_4$	2.18	1.09	1.36	2.45	2.18
$Sn_7Se_{87}In_6$	2.20	1.10	1.40	2.50	2.20
$Sn_7Se_{85}In_8$	2.22	1.11	1.44	2.55	2.22
$Sn_7Se_{83}In_{10}$	2.24	1.12	1.48	2.60	2.24

Bond stretching (N_a) and bond bending (N_b) interatomic valence forces constrain mechanically the covalent bonded glassy network and these mechanical constraints (N_c) are

associated with atomic bonding and effective coordination number < m_{eff} >. $N_b = 2m - 3$ gives the number of constraints per atom arising from bond bending and $N_a = m/2$ gives the bond stretching for the atomic species having coordination number (m). The effective coordination number < m_{eff} > for different compositions of the glassy system $Sn_7Se_{93-x}In_x$ (x = 0, 2, 4, 6, 8, 10) can be calculated by knowing the average number of constraints i.e. $N_c = N_a + N_b$ and the average coordination number (m), as:

$$< m_{eff} >= \frac{2}{5}\left(N_c + 3\right) \tag{2}$$

The calculated values of N_a, N_b, N_c and < m_{eff} > for the glassy system $Sn_7Se_{93-x}In_x$ (x = 0, 2, 4, 6, 8, 10) are listed in Table 1. The system should contain floppy and rigid regions in the range of the glass forming compositions according to Thorpe [22]. In $Sn_7Se_{93-x}In_x$ (x = 0, 2, 4, 6, 8, 10) compositions the average coordination number varies from 2.14 to 2.24.

3.2 Bond Energies of Homo and Heteronuclear Bonds

Heteronuclear bond formation is preferred over homonuclear bond formation according to Zachariasen [23]. The possibility of different types of bond formation in the present system is Sn-Sn, Se-Se, In-In, Se-In, Se-Sn and Sn-In. These bonds are formed in the sequence of their decreasing bond energy. This is equivalent to assume the maximum possible amount of chemical ordering. This means that bonds between like atoms will only occur if there is an excess of a certain type of atom, so that it is not possible to satisfy its valence requirements by bonding it to atoms of different kinds alone. Thus the bonds are formed in the sequence of decreasing bond energy until all available valences of the atoms are saturated. The possible bond distribution at various compositions is expressed using chemically ordered network (CONM) model by Ovshinsky et al [24].

Chemically ordered network model (CONM) leads to conclusion that atoms combine more favorably with atoms of different kinds than with those of same kind. Moreover bonds are formed in the sequence of decreasing bond energy until all available valences of the atoms are saturated. The bond energies E_{A-B} for heteronuclear bonds have been calculated by using the relation [25]

$$E_{A-B} = (E_{A-A} \times E_{B-B})^{0.5} + 30\left(\chi_A - \chi_B\right)^2 \tag{3}$$

where E_{A-A} and E_{B-B} are the bond energies of the homonuclear bonds and χ_A and χ_B are the electro negativities of the atoms involved. The values of the electro negativities of Se, Sn and In are 2.55 and 1.96 and 1.78 respectively. The calculated values for different bonds are given in Table 2.

Table 2 describes the number of lone pair electrons, bond energies of different bonds possible in $Sn_7Se_{93-x}In_x$ (x = 0, 2, 4, 6, 8, 10) glassy alloys and their cohesive energies.

Composition	**m**	**V**	**L = V-m**	**Bonds**	**Bond energy (kCal/mol)**	**Cohesive Energy (kCal/mol)**
Sn_7Se_{93}	2.14	5.86	3.72	Se-In	54.03	44.82
$Sn_7Se_{91}In_2$	2.16	5.80	3.64	Se-Sn	49.25	45.17
$Sn_7Se_{89}In_4$	2.18	5.74	3.56	Se-Se	44.04	45.53
$Sn_7Se_{987}In_6$	2.20	5.68	3.48	Sn-Sn	34.20	45.91
$Sn_7Se_{85}In_8$	2.22	5.62	3.40	Sn-In	32.91	46.30
Sn_7Se_{83In10}	2.24	5.56	3.32	In-In	29.83	46.72

Cohesive energy is the stabilization energy of an infinitely large cluster of material per atom. It gives a measure of the average bond strength. Chemical Bond Approach method [24] has been used to find the cohesive energy of the system under study. According to this method, bonds are formed in the order of their decreasing bond energies. So the cohesive energy is calculated by summing the bond energies over all bonds expected in the present system. The values of the bond energy for the different compositions of the $Sn_7Se_{93-x}In_x$ system are shown in Table 2. The values of cohesive energy show an increasing trend with the increase of In content. This increasing trend of cohesive energy can be attributed to the formation of more and more heteronuclear bonds of Se with In on increasing the In content. These Se-In bonds have the highest value of bond energy for the present glassy alloy.

3.3 Role of lone pair electrons in the glass forming ability

Phillips [21] gives the introduction of average coordination number which leads to the calculation of the number of lone pairs of a chalcogenide glass system. The number of lone pair electrons is given by the difference of all the valence electrons of the system and the shared electrons as

$$L = V - m \tag{4}$$

where L and V are lone pair electrons and valence electrons respectively. For the glassy system $Sn_7Se_{93-x}In_x$ (x = 0, 2, 4, 6, 8, 10) the number of lone pair electrons is obtained by using equation (4) and which are listed in Table 2. For $Sn_7Se_{93-x}In_x$ (x = 0, 2, 4, 6, 8, 10) glassy system, it is clear from Table 2 and Fig. 1 that with the increase in content of In, the number of lone pair of electrons decreases continuously. It shows that bond deformation decreases with increase in In content thereby decreasing the flexibility of the system which is caused by the interaction between the In ion and the lone pair electrons of a bridging Se atom. The interaction decreases the role played by the lone-pair electrons in the glass formation. A simple criterion for computing the ability of a chalcogenide system to retain its vitreous state was introduced by Zhenhua [26]. This criterion contains the number of lone pair electrons which is necessary for obtaining the system in its vitreous state. 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. In our case the values of lone pair electrons lie in the range from 3.72 to 3.32. This explains the fact that the system can be obtained in glassy state.

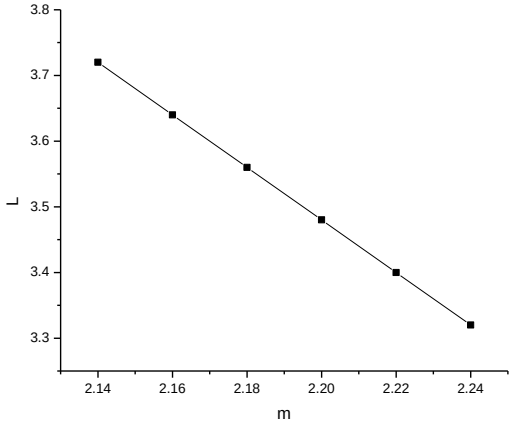

Fig. 1 shows the variation of lone pair of electrons (L) with average coordination number < m > for the glassy system $Sn_7Se_{93-x}In_x$ (x = 0, 2, 4, 6, 8, 10).

3.4 Average heat of atomization

Chalcogenide glasses showing the semiconducting properties containing a high concentration of group VI element, the lone-pair forms the top of the valence band and the antibonding band forms the bottom of the conduction band [27]. The energy difference between

the top of the valence band and the bottom of the conduction band gives the optical gap. Due to the presence of high-energy lone pair group VI atoms form a dative bond with metal atoms without any cost of energy. Dative bonds correspond to empty bonding levels which give localized acceptors states in the gap [28].

Pauling [29] proposed that 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 heat of atomization H_S^A and H_S^B that corresponds to the average non polar bond energy of the two atoms

$$H_S(A-B) = \Delta H + \frac{1}{2}\left(H_S^A + H_S^B\right) \tag{5}$$

The first term in the equation (5) is proportional to the square of the difference between the electronegativities χ_A and χ_B of the two atoms

$$\Delta H \propto (\chi_A - \chi_B)^2 \tag{6}$$

This idea can be extended furthur to ternary and higher order semiconducting compounds and the average heat of atomization $\overline{H}_S$ is defined for that compound. Heat of atomization for the compound $A_\alpha B_\beta C_\gamma$ is considered a direct measure of the cohesive energy and thus of average bond strength and is given as

$$\overline{H}_S = \frac{\alpha H_S^A + \beta H_S^B + \gamma H_S^C}{\alpha + \beta + \gamma} \tag{7}$$

Clearly the $\overline{H}_S$ values do not contain the heat of formation (ΔH) as part of cohesive energy; however $\overline{H}_S$ is a useful parameter for correlating the physical properties of semiconducting compounds. In chalcogenide glasses the heat of formation contributes very little towards the average heat of atomization because the electronegativities of the constituent elements are very similar and in most of the cases of chalcogenide glasses the heat of formation is unknown. Therefore for binary chalcogenide glasses H_S (A − B) is given by

$$H_S(A-B) = \frac{1}{2}\left(H_S^A + H_S^B\right) \tag{8}$$

$\overline{H}_S$ is given by equation (7) for ternary and higher order compounds. The values of heat of atomization for Se, Sn and In elements are 226.0 kJ/mol, 302.0 kJ/mol and 243.0 kJ/mol, respectively. The calculated average heat of atomization and average single bond energy are given in Table 3. It is clear from the Table 3 that the heat of atomization increases with the increase of In content while the average single bond energy ($\overline{H}_S$/m) which is a measure of cohesive energy decreases with the increase of In content. This decrease in the average single bond energy with the increase of In content may cause the decrease of optical band gap [17].

Table 3 describes the values of average heat of atomization ($\overline{H}_S$), average single bond energy ($\overline{H}_S$ /m), mean bond energy < E > and glass transition temperature T_g (K) for $Sn_7Se_{93-x}In_x$ (x = 0, 2, 4, 6, 8, 10) glassy alloys.

Composition	$\overline{H}_S$ **(eV/bond)**	$\overline{H}_S$ **/m (eV/bond)**	**<E> (eV/bond)**	**T_g (K)**
Sn_7Se_{93}	2.400	1.121	2.008	344.59
$Sn_7Se_{91}In_2$	2.404	1.113	2.048	357.03
$Sn_7Se_{89}In_4$	2.407	1.104	2.089	369.78
$Sn_7Se_{87}In_6$	2.411	1.096	2.131	382.84
$Sn_7Se_{85}In_8$	2.415	1.088	2.176	396.84
$Sn_7Se_{83}In_{10}$	2.418	1.079	2.222	411.14

3.5 Mean bond energy and glass transition temperature

Properties of chalcogenide glasses are dependent on their overall mean bond energy <E>. Mean bond energy <E> is a function of average coordination number (m), the type of bonds and the bond energy. The mean bond energy of the system may be calculated using the relation

$$< \mathrm{E} >= \mathrm{E_C} + \mathrm{E_{rm}} \tag{9}$$

where E_c is the overall contribution towards bond energy from strong heteronuclear bonds and E_{rm} is that arising from weaker bonds, i.e. average bond energy per atom of the 'remaining matrix'. For $Sn_xSe_yIn_z$ system (where x+y+z = 1), and in the selenium rich region,

$$E_c = 4xE_{Sn-Se} + 3zE_{Se-In} \tag{10}$$

And

$$E_{rm} = \frac{[2y - 4x - 3z]}{< m >} E_{Se-Se} \tag{11}$$

Table 1 shows the calculated values of the mean bond energy for the system. As is evident from mean bond energy data that when In content increases, the mean bond energy of the system increases.

The glass transition temperature T_g for the chalcogenide glasses is theoretically predicted as a first approximation by covalent bond approach of Tichy and Ticha [18, 19]. According to this approximation, the glass transition temperature T_g is found to be proportional to the mean bond energy <E> which depends on factors like average coordination number, degree of cross linking, bond energy and the nature of the bonds. Tichy and Ticha examined 186 chalcogenide glasses by taking into consideration all the above mentioned factors with T_g ranging from 320K to 760 K, and obtained a good correlation between T_g and <E> in the form

$$\mathrm{T_g} = 311[\langle \mathrm{E} \rangle - 0.9] \tag{12}$$

This equation also satisfies the Arrhenius relation for viscosity.

The variation of glass transition temperature with mean bond energy is shown in Fig. 2. There is a direct proportionality between the glass transition temperature and the mean

bond energy. The glass transition temperature for the different compositions of the chalcogenide system $Sn_7Se_{93-x}In_x$ (x = 0, 2, 4, 6, 8, 10) has been calculated using equation (12) and is given in Table 3. The glass transition temperature of the system under consideration is found to increase with the increase of the In content. This increase in the value of the glass transition temperature with increasing In content in glass forming alloys may be due to the accumulation of three dimensional structural units Sn-Se, In-Se and due to the decrease in the content of chain like formation of excess Se.

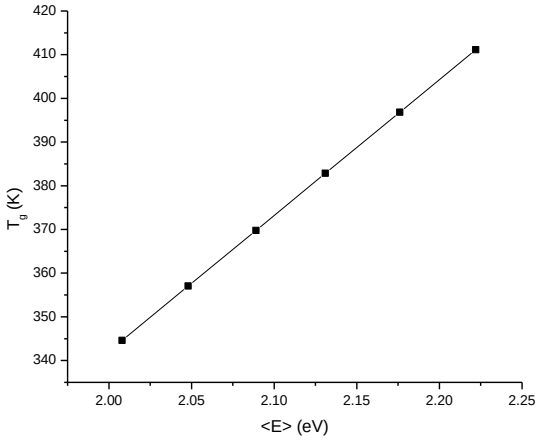

Fig. 2 shows the variation of glass transition temperature (T_g) with mean bond energy < E >in the glassy system $Sn_7Se_{93-x}In_x$ (x = 0, 2, 4, 6, 8, 10).

4. Conclusions

It is evident from the theoretical investigation that the variation in composition of Sn-Se-In system changes almost all the physical parameters. The present work on $Sn_7Se_{93-x}In_x$ (x = 0, 2, 4, 6, 8, 10) glassy system shows that the average coordination number, number of constraints, average heat of atomization, mean bond energy, cohesive energy and glass transition temperature increase with the increase of In content while the number of lone pair of electrons and average single bond energy ($\overline{H}_S$/m) decrease. The increase in glass transition temperature (T_g) and cohesive energy with increasing In content is explained on the basis of chemically ordered network model by which heteronuclear bonds are preferred to homonuclear ones.

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