



Theoretical study of Sb-doped $\text{Se}_{90}\text{In}_{10}$ glassy system

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ABSTRACT

The effect of antimony (Sb) addition in SeIn glassy system is theoretically studied, and important physical properties, such as average coordination number, lone pair electrons, fragility parameter, heat of atomization, mean bond energy and optical band gap are evaluated in addition to thermal stability. The values of average coordination number and heat of atomization were found to increase with increasing Sb content, while the other properties were in decrease. By adding more Sb atoms, the glassy system becomes less stable thermally. According to the number of zero-frequency mode per atom, which was in decrease, the Phillips'-Thorpe threshold cannot be realized for the considered glassy system.

Keywords: Chalcogenide glasses; DSC; SeInSb; coordination number; heat of atomization; bond energy.

INTRODUCTION

Chalcogenide glasses are interesting candidates for reversible phase change recording devices [1-3]. They have been used in infrared optical fibres [4] and in fabrication of inexpensive solar cells [5]. In addition, they found applications in xerography [6] and photolithography [7]. Amorphous selenium holds an important role and is widely used as amorphous semiconductor, but presents various disadvantages such short life time and poor sensitivity [8] which can be improved by alloying it with other materials like Te, Ge, Sb, Bi, etc. Selenium based binary chalcogenide glasses are found to be more useful in practical applications and got several advantages over pure and amorphous selenium [9]. They should be thermally stable with time and temperature during use. Among them, we can cite the *Se-Te* and *Se-In* alloys which have higher photosensitivity, higher crystallization temperature and greater hardness [10,11], in addition to their small ageing effects [12] and present band energy of about 1.3 eV at 300 ° K [13]. The properties of both systems can be varied by adding a third element from Group IV or V of the periodic table for required purpose. The latter binary system *Se-In* doped with antimony has been experimentally studied by our team [14] and we obtained important parameters and results based on several methods using Differential Scanning Calorimetry (DSC) thermograms.

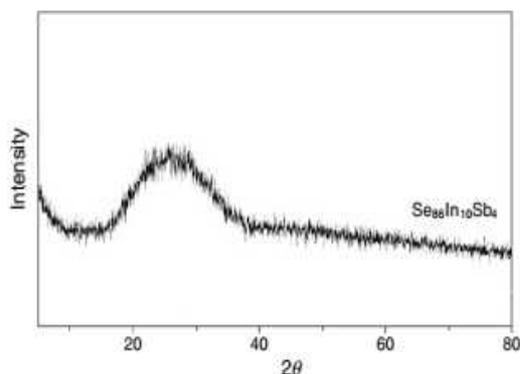
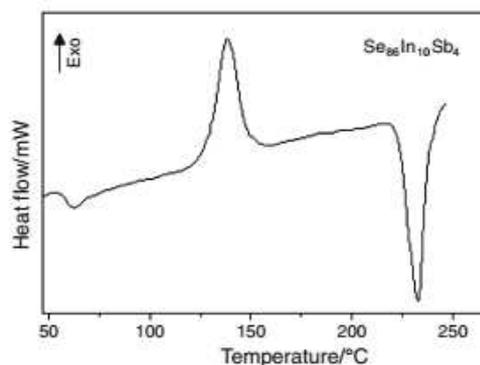
The aim of this paper is to complete the system study by investigating the effect of antimony (Sb) addition on many physical properties such as coordination number, mean bond energy and thermal stability for *SeInSb* system alloys with different Sb contents.

EXPERIMENTAL SECTION

The glassy samples were prepared by melt quenching. The three elements (99.999 % purity) were weighted and introduced in quartz ampoules and sealed in vacuum of 10^{-5} Pa. The ampoules were placed in a horizontally rotating oven and annealed at 1000 °C for 3 h. Then, each ampoule was quenched into ice-cold water to avoid crystallization. The amorphous nature of these alloys was verified by X-Ray diffraction (XRD) technique. As shown in Fig. 1 (XRD pattern of $Se_{86}In_{10}Sb_4$ as an example), the XRD spectra do not contain any prominent peak, which confirms the amorphous nature of the samples.

RESULTS AND DISCUSSION

DSC thermogram for $Se_{86}In_{10}Sb_4$ glassy alloy under non-isothermal condition at a particular heating rate of 10 °C/min is shown in Fig. 1. Well-defined endothermic peaks are observed at glass transition temperature (T_g), crystallization temperature (T_c) and melting temperature (T_m). Very similar DSC thermograms were observed at other heating rates and for different compositions (not shown). The characteristic temperatures are listed in Table 1. The experimental results are fully details in our previous paper [14].

Fig. 1. XRD pattern of $Se_{86}In_{10}Sb_4$ glassy alloy [14]Fig. 2. DSC thermogram of $Se_{86}In_{10}Sb_4$ glassy alloy at 10 °C/min [14]

Knowing the coordinations of the three elements, the average coordination number of the $Se_xIn_ySb_z$ glassy system has been evaluated [15,16]:

$$n = \frac{xN_{Se} + yN_{In} + zN_{Sb}}{x + y + z} \quad (1)$$

where x , y and z are atomic fractions of Se , In and Sb respectively and N_{Se} , N_{In} and N_{Sb} are their respective coordination numbers. The calculated values of the average coordination number are given in Table 1. The average coordination number values increase with increasing Sb content. Sb atoms being from group V can bound with 3 or 5 Se atoms (from group IV), and immediately increase the average coordination number. Three-fold coordination results in less structural strain than five-fold and would be more favourable.

TABLE 1: Average coordination number, measured glass transition and crystallization temperatures (at 10 °C/min) [14] and Dietzel temperature interval of $Se_{90-x}In_{10}Sb_x$ glassy system

Composition	n	T_g (K)	T_c (K)	ΔT (K)
$Se_{90}In_{10}$	2.10	326	405	79
$Se_{89}In_{10}Sb_1$	2.11	329	402	73
$Se_{88}In_{10}Sb_2$	2.12	330	401	71
$Se_{87}In_{10}Sb_3$	2.13	-	-	-
$Se_{86}In_{10}Sb_4$	2.14	330	400	70
$Se_{85}In_{10}Sb_5$	2.15	334	399	65

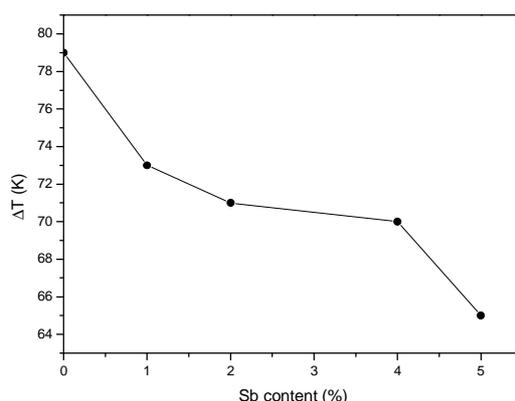


Fig. 3. Dietzel temperature interval versus Sb content in $Se_{90-x}In_{10}Sb_x$ glassy system

In order to evaluate the thermal stability of the system, we used Dietzel criterion by calculating temperature interval; $\Delta T = T_c - T_g$ [17]. According to this criterion, the kinetic resistance to crystallization increases with increasing ΔT . This value gives an indication of the thermal stability of the glassy system, a high value of ΔT means that the glass contains structural units with small crystallization tendency and vice versa.

From Table 1 and Fig. 3, we can see that glass alloy compositions $Se_{89}In_{10}Sb_1$ gives the most stable glass with the maximum value of ΔT .

The presence of maximum in ΔT values can be understood on the basis of Phillips'-Thorpe [15,18-21] constraint theory for glasses with covalent bonds. According to this theory, for alloy compositions having high glass forming ability and where only short range order structures are considered, the number of degrees of freedom, N_d in a covalently bonded glass exhausts the number of constraints, $N_{c\alpha}$ due to bond stretching, and bond bending $N_{c\beta}$, with $N_c = N_{c\alpha} + N_{c\beta}$. The condition $N_c = N_d$, led Philips to conclude that the stability of the network having the critical coordination number $n = 2.4$ is optimized. Thorpe [19] found the same result by counting the number of zero-frequency modes. He showed that under coordinated networks would possess a finite fraction of zero-frequency modes in the absence of the weaker longer range forces. The number of zero-frequency mode per atom is given by:

$$f = 2 - \frac{5}{6}n \quad (2)$$

This number approaches zero as n approaches the critical value of 2.4, where there is a phase transition from under-constrained floppy network to overconstrained rigid network having maximum stability. We consider then that the Phillips'-Thorpe threshold is not realized for the investigated system.

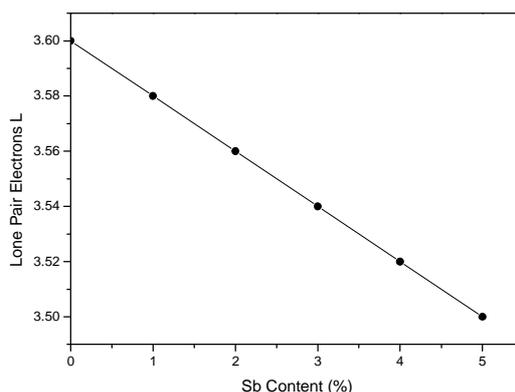
Lone pair electrons of $SeInSb$ glassy system has been evaluated using the following relation:

$$L = V - n \quad (3)$$

where V denotes the valence electrons number of the investigated system.

TABLE 2: Number of constraints, number of zero-frequency mode, valence and lone pair electrons values of $\text{Se}_{90-x}\text{In}_{10}\text{Sb}_x$ glassy system

Composition	N_c	f	V	L
$\text{Se}_{90}\text{In}_{10}$	2.45	0.250	5.70	3.60
$\text{Se}_{89}\text{In}_{10}\text{Sb}_1$	2.46	0.242	5.69	3.58
$\text{Se}_{88}\text{In}_{10}\text{Sb}_2$	2.47	0.233	5.68	3.56
$\text{Se}_{87}\text{In}_{10}\text{Sb}_3$	2.49	0.225	5.67	3.54
$\text{Se}_{86}\text{In}_{10}\text{Sb}_4$	2.50	0.217	5.66	3.52
$\text{Se}_{85}\text{In}_{10}\text{Sb}_5$	2.51	0.208	5.65	3.50

Fig. 4. Lone pair electrons versus Sb content in $\text{Se}_{90-x}\text{In}_{10}\text{Sb}_x$ glassy system

As seen in Table 2, L decreases with increase Sb content, this is caused by interaction between Sb atoms and lone pair atoms of bridging sections and this interaction decreases the role of lone pair electrons in the glass formation. The values of L are always larger than 1 as proposed by Liang for all ternary systems [22]. Fig. 4 shows also that L is linearly dependent with the average coordination number n .

The results can be discussed on the basis of the fragility parameter F , which characterizes and quantifies the anomalous non-Arrhenius transport behaviour of glassy materials near the ergodicity breaking glass transition region [23-25]. Fragile glasses are materials with non-directional interatomic/intermolecular bonds. Strong glasses are those which show resistance to structural degradation and usually associated with a small ΔC_p . Fragility is calculated using the relation [26]:

$$F = \frac{E_g}{T_g \ln 10} \quad (4)$$

Both T_g and E_g (activation energy of glass transition) are taken from our previous paper [14]. The values of F are found to decrease with increasing average coordination number n as seen in Table 3. This indicates that the studied glassy system becomes less fragile when adding more Sb atoms and its tendency to structural rearrangement decreases with increasing non-directional interatomic bonds.

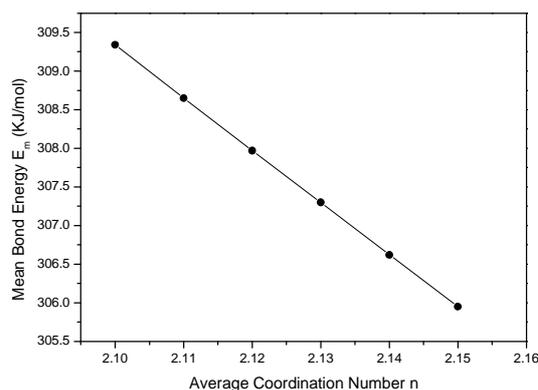
The heat of atomization has also been calculated for the glassy system using the relation:

$$H_s = \frac{xH_s^{Se} + yH_s^{In} + zH_s^{Sb}}{x + y + z} \quad (5)$$

and the calculated values are listed in Table 3, and found to be increasing with increase Sb contents.

TABLE 3: Glass compositions, average coordination number, fragility, heat of atomization, mean bond energy and estimated optical band gap values of $Se_{90-x}In_{10}Sb_x$ glassy system

Composition	n	F	H_s (KJ/mol)	E_m (KJ/mol)	E_g (eV)
$Se_{90}In_{10}$	2.10	0.174	216.95	309.34	1.755
$Se_{89}In_{10}Sb_1$	2.11	0.157	217.31	308.65	1.737
$Se_{88}In_{10}Sb_2$	2.12	0.135	217.66	307.97	1.718
$Se_{87}In_{10}Sb_3$	2.13	-	218.02	307.30	1.700
$Se_{86}In_{10}Sb_4$	2.14	0.123	218.37	306.62	1.681
$Se_{85}In_{10}Sb_5$	2.15	0.114	218.73	305.95	1.663

Fig. 5. Mean bond energy versus average coordination number for $Se_{90-x}In_{10}Sb_x$ glassy system

The covalent bond approach (CBA) [27, 28], given by:

$$E_m = E_{cl} + E_{rm} \quad (6)$$

was used to calculate the mean bond energy E_m of the glassy network; where E_{cl} is the overall contribution towards bond energy arising from strong bonds, and E_{rm} is the contribution arising from weaker bonds that remain after the number of strong bonds becomes maximum. For the system under investigation $Se_xIn_ySb_z$:

$$E_{cl} = 2xD_{Se-In} + 3zD_{Sb-In} \quad (7)$$

where 2, x , 3 and z correspond to the atomic concentration and coordination number of Se and Sb atoms respectively. The heteropolar bond energy is calculated using the relation given by Pauling [26]:

$$D_{A-B} = (D_{A-A} \times D_{B-B})^{0.5} + 30(\chi_A - \chi_B)^2 \quad (8)$$

where, χ_A , χ_B , D_{A-A} and D_{B-B} are respectively the electronegativity and the homopolar bond energies of A and B atoms.

The average bond energy per atom of the remaining matrix is given by:

$$E_{rm} = \left(1 - \frac{2x-3z}{2}n\right) D_{In-In} \quad (9)$$

The calculated values of the mean bond energy E_m are listed in Table 2. It is found to be in decrease with increasing Sb content and thus with increasing average coordination number.

Fig. 5 shows the linear dependency of mean bond energy E_m of the system with the average coordination number. This energy E_m is influenced by the degree of cross-linking, the bond energy, the average coordination number and the bond type, and all these factors influence the glass transition temperature of the glassy system.

The later, is considered as one of the most important parameters used for characterizing a glassy state and can be theoretically predicted using different methods [25, 27-29]. For many chalcogenide systems, this glass transition temperature T_g is found to be proportional to the mean bond energy value of the covalent glassy network [30-32].

In the other hand, the variation of the theoretical band gap E_g values of the system under investigation $Se_xIn_ySb_z$ with composition (as for all alloys) can be described by the following relation [33]:

$$E_g = xE_g(Se) + yE_g(In) + zE_g(Sb) \quad (12)$$

The calculated values of band gap are listed in Table 3, and found to decrease with increase Sb content. As optical absorption depends on short range order in the amorphous state and defects associated with it, the decrease in optical band gap may be explained on the basis of the density of states model in amorphous solids proposed by Davis and Mott. According to this model, the width of the localized states near the mobility edges depends on the disorder and defects present in the amorphous state [34].

CONCLUSION

Using the characteristic temperatures, thermal stability of the glassy system $Se_{90-x}In_{10}Sb_x$ has been studied, and the results showed a low stability according to Dietzel criterion when adding more Sb atoms, and thus the Phillips'-Thorpe threshold is not realized for this system. With addition of Sb atoms, the system becomes less fragile and its tendency to structural rearrangement decreases with increasing non-directional interatomic bonds. The mean bond energy is calculated using the covalent bond approach and is found to be, as the predicted optical band gap, in decrease with increasing Sb contents and thus with increasing average coordination number, while the heat of atomization of the system exhibits the opposite behaviour.

REFERENCES

- [1] Z. L. Mao; H. Chen; Ai-lien Jung, *J. Appl. Phys.*, **1995**, 78(4), 2338-2342
- [2] R. Chiba; H. Yamazaki; S. Yagi; S. Fujimori, *Jpn. J. Appl. Phys.*, **1993**, 32 (2), 834-841
- [3] M. Szukwei ; Yang Hanmei; Zhang Xiaowei, *J. Non-Cryst. Solids*, **1989**,112 (1-3), 204-206
- [4] J. R. Gannon , *Proc. SPIE* , **1981** , 266, 62-68
- [5] J. Fusong; M. Okuda, *Jpn. J. Appl. Phys.*, **1991** ,30 (1), 97-101
- [6] J. H. Dessaur; H. E. Clarke, *Xerography and Related Processes*. Local, London, **1965**, 202-216.
- [7] D.E. Carlson; C. R. Wronski, *Appl. Phys.*, **1976** ,28 (11), 671-672
- [8] S. A. Khan; M. Zulfequar; M. Hussain, *Solid State Commun.*, **2002**,123 (10), 463-458
- [9] S. O. Kasap; T. Wagner; V. Aiyah; O. Krylouk; A. Bekirov; L. Tichy, *J. Mater. Sci.*, **1999** ,34 (15), 3779-3787
- [10] Majeed Khan M.A.; Zulfequar M.; Husain M., *J. Opt. Mater.*, **2003**, 22 (1), 21-29
- [11] Sharma P.; Katyal S.C., *Phys. B*, **2008**, 403 (19-20), 3667-3671
- [12] Mehta N.; Singh K.; Saxena N.S., *Solid State Sci.*, **2010**, 12 (10), 963-965
- [13] Segura A.; Guesdon J.P.; Besson J.M.; Suzuki A., *J Appl Phys.*, **1983**, 54 (2), 876-888
- [14] M. M. Heireche; M. Belhadji; N. E. Hakiki, *J. Therm. Analys. Calorim.*, **2013**, 114 (1), 195-203
- [15] J. C. Phillips, *J. Non-Cryst. Solids*, **1979**, 34 (2), 153-181
- [16] R. Ganesan; A. Srinivasan; K.N. Madhusoodanan; K.S. Sungunni; E.S.R. Gopa, *Phys. Status (b)*, **1999**, 212 (2), 223-228
- [17] A. Dietzel, *Glasstech. Ber*, **1968**, 22 (1), 41-50
- [18] J.C. Phillips; M.F. Thorpe, *Solid State Commun.*, **1985**, 53 (8), 699-702
- [19] M. F. Thorpe, *J. Non-Cryst. Solids*, **1983**, 57 (3), 355-370
- [20] H. He; M. F. Thorpe, *Phys. Rev. Lett.*, **1985**, 54 (19), 2107-2110
- [21] M. F. Thorpe, *J. Non-Cryst. Solids*, **1995**, 182 (2-3), 135-142
- [22] Z. H. Liang, *J. Non-Cryst. Solids*, **1991**, 127 (3), 298-305
- [23] R. Bohmer; K. L. Nagi; C. A. Angell; D. J. Plazek, *J. Chem. Phys.*, **1993**, 99 (5), 4201-4209

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- [24] P. S. L. Narasimham; A. Giridhar; S. Mahadevan, *J. Non-Cryst. Solids*, **1981**, 43 (2), 301-305
[25] S.A. Fayek; M.R. Balboul; K.H. Marzouk, *Thin Solid Films*, **2007**, 515 (18), 7281-7285
[26] L. Pauling: *The Nature of the Chemical Bond*, 3rd Ed. (Cornell University Press, Ithica NY), **1960**, 64-107
[27] L. Tichy; H. Ticha, *Material Letters*, **1994**, 21 (3-4), 313-319
[28] L. Tichy; H. Ticha, *J. Non-Cryst. Solids*, **1995**, 189 (1-2), 141-146
[29] M. H. R. Lankhorst, *J. Non-Cryst Solids*, **2002**, 297 (2-3), 210-219
[30] L. Pauling: *The Nature of the Chemical bond* VCH, Weinheim, **1976**, 80
[31] M. Micoulaut, *C.R. Chimie*, **2002**, 5 (12), 825-830
[32] G. Safarini; J.M. Saiter; J. Matthiesen, *Materials Letters*, **2007**, 61 (2), 432-436
[33] A. Dahshan; K. A. Aly, *Phil. Mag.*, **2008**, 88 (3), 361-372
[34] A. M. Farid, *Egypt. J. Sol.*, **2002**, 25 (1), 23-32