International Journal of Advanced Research in Physical Science (IJARPS)
Volume 1, Issue 7, November 2014, PP 9-16
ISSN 2349-7874 (Print) & ISSN 2349-7882 (Online)
www.arcjournals.org

Study of the Physical Properties with Compositional Dependence of Sb Content in Se-Te-Sb Glassy System

Balbir Singh Patial

Department of Physics
Govt. College Sunni
Shimla, H.P. India
bspatial@gmail.com

Neha, Nagesh Thakur

Department of Physics
H.P. University Summerhill Shimla
H.P, India

S. K. Tripathi

Centre of Advanced Study in Physics
Punjab University Chandigarh,
India

Abstract: *The effect on the physical properties with the addition of Sb content, viz glass transition temperature (T_g), mean bond energy <E>, cohesive energy (CE), average heat of atomization (H_S), coordination number (<r>), constraints (N_c) and lone pair electrons (L) of $Se_{80-x}Te_{20}Sb_x$ (x = 1, 2, 4, 6 and 10) glassy alloys have been examined theoretically. The glass transition temperature has been predicted using Tichy–Ticha approach and found to increase with the addition of Sb content. The cohesive energy has been calculated using chemical bond approach (CBA) method. It has been found that mean bond energy, glass transition temperature, coordination number, heat of atomization and number of constraints increases whereas all the other investigated parameters decreases with increasing Sb content in Se- Te -Sb system.*

Keywords: *Chalcogenide glasses, Physical parameters, XRD, Mean Bond Energy, Glass Transition Temperature.*

1. INTRODUCTION

The study of chalcogenide materials is becoming a great field of interest due to their vast applications in the fabrication of various solid state devices [1]. Chalcogenide glasses containing S, Se and Te are a recognized group of inorganic glassy materials which constitute a rich family of vitreous semiconductors. Now days, in the field of chalcogenide glasses a lot of attention have been devoted to the characterization of chalcogenide glasses, especially for those materials which are used in the switching memories. These materials can be reversibly switched between amorphous and crystalline state and hence have applications in electrically programmable non-volatile memories and in rewri Table optical recording [2-4].

Chalcogenide glasses possess properties intermediate between organic polymers and oxide glasses. These glasses are weakly bonded materials than oxides [5]. Glasses and their properties can be improved according to the requirements of applications by improving their chemical compositions. Glassy alloys of chalcogen elements are more recent improvement in optical recording [6]. The alloy of Se-Te improves the corrosion resistance and optical sensitivity of the alloy [7-8]. The presence of Te in Se chains probably favours their thermal dissociation as the Se-Te bond being weaker than Se-Se bond [9]. The addition of third element in binary chalcogenide system is found to be useful in obtaining sTable glassy alloys and expands the glass forming area and also creates compositional and configuration disorder in the glassy material. The addition of Sb in Se-Te system affects the electrical properties and leads to cross linking of chains which in turn results in the increase of coordination number and also glass transition temperature of the system [10-12].

2. EXPERIMENTAL DETAILS

Bulk glassy alloys of $Se_{80-x}Te_{20}Sb_x$ (x = 1, 2, 4, 6 and 10) are prepared using melt quenching technique. 5N pure materials are weighted according to their atomic percentages and sealed in the quartz ampoules (length = 5 cm, diameter = 12 mm) under a vacuum of 2×10^{-5} mbar. The ampoules have been kept inside the furnace where the temperature is raised to 1000°C at a rate of 3-4°C/min. During heating, the ampoules are rocked constantly to make the melt homogenous. After rocking for about 12 hours, the obtained melts are cooled rapidly by removing the furnace and dropping into ice-cooled water very rapidly to prevent crystallization. The ingots of the samples are then taken out by breaking the quartz ampoules.

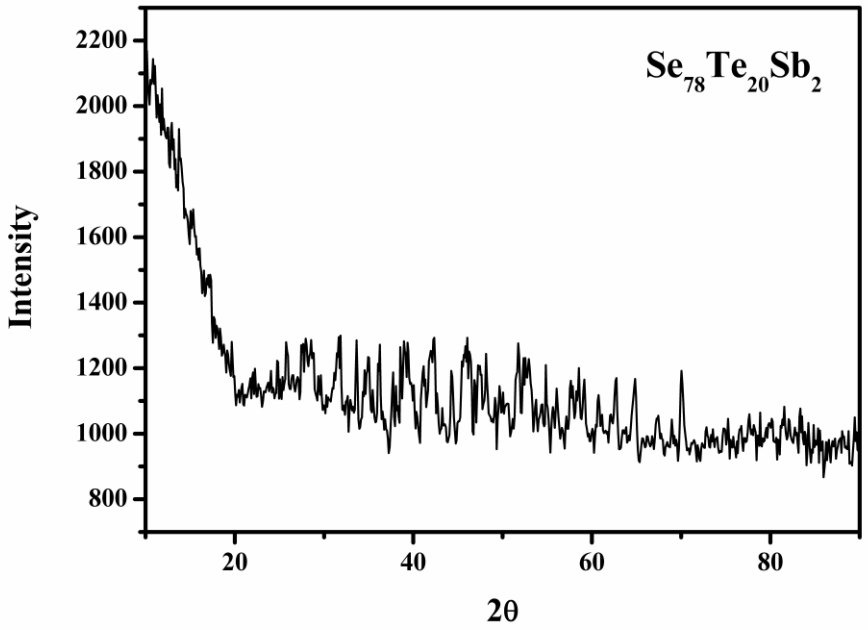

Figure 1. *XRD pattern for ternary chalcogenide $Se_{78}Te_{20}Sb_2$ bulk sample.*

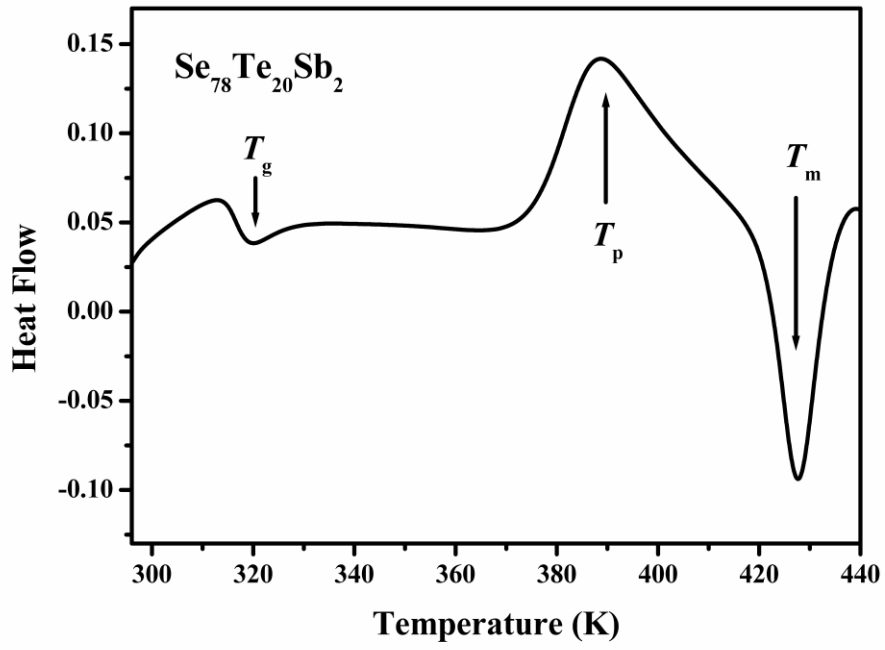

Figure 2. *DSC thermogram for ternary $Se_{78}Te_{20}Sb_2$ glass at the heating rate 10°C/min.*

X-ray diffraction pattern verified the amorphous nature of glassy alloys. Fig. 1 shows the XRD pattern for ternary $Se_{78}Te_{20}Sb_2$ bulk alloy and absence of any prominent peak in the spectrum confirmed the amorphous nature of the investigated chalcogenide alloy. Similar XRD patterns have been observed for the other investigated samples (not shown here).

The glasses thus prepared are ground to make fine powder for DSC studies. The thermal behaviour of the glasses is investigated using DSC. Approximately, 3-5 mg of sample in powder form is encapsulated in standard aluminum pan and heated at 10°C/min. The values of glass transition temperature are determined by using the microprocessor of the thermal analyzer. Fig. 2 shows a typical thermogram for ternary $Se_{78}Te_{20}Sb_2$ glassy alloy displaying characteristics glass transition temperature, crystallization temperature and melting temperature observed at the heating rate 10°C/min. similar thermograms are also observed for other investigated samples.

3. RESULTS AND DISCUSSION

3.1. Average Coordination Number and Constraints

The coordination number is the average atoms coordinated with its nearest neighbours of the constituents. It is useful in explaining the cross linking and testing the validity of topological concepts [13]. For the composition $Se_{80-x}Te_{20}Sb_x$ (x = 1, 2, 4, 6 and 10), the average coordination number is given by:

$$<r> = (\alpha Z_{Se}+\beta Z_{Te}+\gamma Z_{Sb})/ (\alpha+\beta+\gamma) \quad (1)$$

Where α, β and γ are the atomic percentages of Se, Te and Sb respectively and Z_{Se}, Z_{Te} and Z_{Sb} represent their respective coordination numbers. The calculated value of average coordination number <r> is given in the Table 1. From Table 1 it is observed that <r> increases with the increase in Sb content. It shows that the cross linking of chains between the atoms increases with increasing Sb content. Since the value of <r> obtained in our case is lie in between 2.01 to 2.10. Hence, we can say that the system under investigation is a good glass former. Covalent networks in a glassy system are mechanically constrained by interatomic valence forces such as bond stretching and bond bending. In optimal glass formation, the bond stretching constraints and bond bending constraints are given [14] as N_a= <r>/2 and N_b= (2<r>–3), respectively. The calculated values of average constraints i.e. N_C= N_a + N_b for $Se_{80-x}Te_{20}Sb_x$ system at different values of x are reported in Table 1. From Table 1, it is observed that the value of average constraints increases with the increase in Sb content.

Table 1. *Values of average coordination number <r> and average number of constraints for $Se_{80-x}Te_{20}Sb_x$ (x = 1, 2, 4, 6 and 10).*

Composition	<r>	N_a	N_b	N_c
$Se_{79}Te_{20}Sb_1$	2.01	1.005	1.02	2.03
$Se_{78}Te_{20}Sb_2$	2.02	1.01	1.04	2.05
$Se_{76}Te_{20}Sb_4$	2.04	1.02	1.08	2.10
$Se_{74}Te_{20}Sb_6$	2.06	1.03	1.12	2.15
$Se_{70}Te_{20}Sb_{10}$	2.10	1.05	1.20	2.25

3.2. Lone Pair Electrons and Glass Forming Ability

The number of lone pair electrons in a chalcogenide glass system has been calculated by using the method which is proposed by Phillips:

$$L = V – <r> \quad (2)$$

Here L and V are lone pair electrons and valance electrons respectively. The number of lone pair electrons is given in Table 2. The number of lone pair electrons decreases with the increase in Sb content. This result is caused by the interaction between the Sb ion and lone pair electron of the bridging Se atom. This interaction decreases the number of lone pair electrons in the investigated system. Zhenhua [15] proposed a simple criterion for a binary system and a ternary system i.e. for a binary system the number of lone-pair electrons must be greater than 2.6, while for a ternary system it must be greater than 1. In our system, the values of lone-pair of electrons are found to be greater than 1.

Table 2. *Values of the number of lone-pair electrons for $Se_{80-x}Te_{20}Sb_x$ (x = 1, 2, 4, 6 and 10).*

Composition	*V*	*L=V – <r>*
$Se_{79}Te_{20}Sb_1$	5.99	3.98
$Se_{78}Te_{20}Sb_2$	5.98	3.96
$Se_{76}Te_{20}Sb_4$	5.96	3.92
$Se_{74}Te_{20}Sb_6$	5.94	3.88
$Se_{70}Te_{20}Sb_{10}$	5.90	3.80

3.3. Deviation from the Stoichiometry of Composition

The parameter *R* which determines the deviation of stoichiometry is defined as the ratio of covalent bonding possibilities of chalcogen atom to that of non-chalcogen atom. The quantity *R* is given by [16, 17]:

$$R= (\alpha Z_{Se}+\beta Z_{Te})/\gamma Z_{Sb} \quad (3)$$

For $R > 1$, the system is chalcogen rich and for $R < 1$, the system is chalcogen poor. The threshold at $R = 1$ (the point of existence of only heteropolar bonds) is evident. For the present investigating system $Se_{80-x}Te_{20}Sb_x$, the value of *R* is greater than 1 leading the system to chalcogen-rich region (Table 4).

3.4. Cohesive Energy

The bond energy of heteropolar bonds can be calculated by the method suggested by Pauling:

$$E_{A-B} = [E_{A-A} \times E_{B-B}]^{0.5} + 30(\chi_A-\chi_B)^2 \quad (4)$$

Where E_{A-B} is the bond energy of heteropolar bonds, E_{A-A} and E_{B-B} are the bond energies of homopolar bonds. The bond energies of the homopolar bonds are taken as Se–Se = 44 kcal/mol, Te–Te = 33 kcal/mol and Sb–Sb = 30.2 kcal/mol. χ_A and χ_B are the electronegativities of A and B atoms respectively. The electronegativities for Se, Te, and Sb according to Pauling scale are 2.55, 2.10 and 2.05 respectively [19, 20].

The Cohesive energy of samples has been calculated by chemical bond approach [21]:

$$CE = \sum C_i D_i \quad (5)$$

Table 3. *The bond probabilities in chalcogenide $Se_{80-x}Te_{20}Sb_x$ glass and cohesive energy.*

Composition	Bonds formed			Cohesive energy (kcal/mol)
	Se–Te	Se–Sb	Se–Se	
$Se_{79}Te_{20}Sb_1$	0.2531645	0.0189873	0.7278482	44.0446
$Se_{78}Te_{20}Sb_2$	0.2564102	0.0384615	0.7051283	44.0442
$Se_{76}Te_{20}Sb_4$	0.2631578	0.0789473	0.6578949	44.0434
$Se_{74}Te_{20}Sb_6$	0.2702702	0.1216216	0.6081082	44.0425
$Se_{70}Te_{20}Sb_{10}$	0.2857142	0.2142857	0.5000001	44.0407

Where C_i and D_i are the number of expected chemical bond and the energy of each corresponding bond respectively. Calculated values of the *CE* along with the distribution of chemical bonds for all the compositions studied are given in Table 3. The results indicate that the cohesive energy of the investigated glassy system decreases with increasing Sb content. Values of electronegativity for $Se_{80-x}Te_{20}Sb_x$ semiconducting alloys are also calculated using Sanderson's principle [21]. According to this principle, electronegativity of the alloy is the geometric mean of electronegativity of its constituent elements. It is evident from the Table 4 that the value of electronegativity decreases with increasing Sb content.

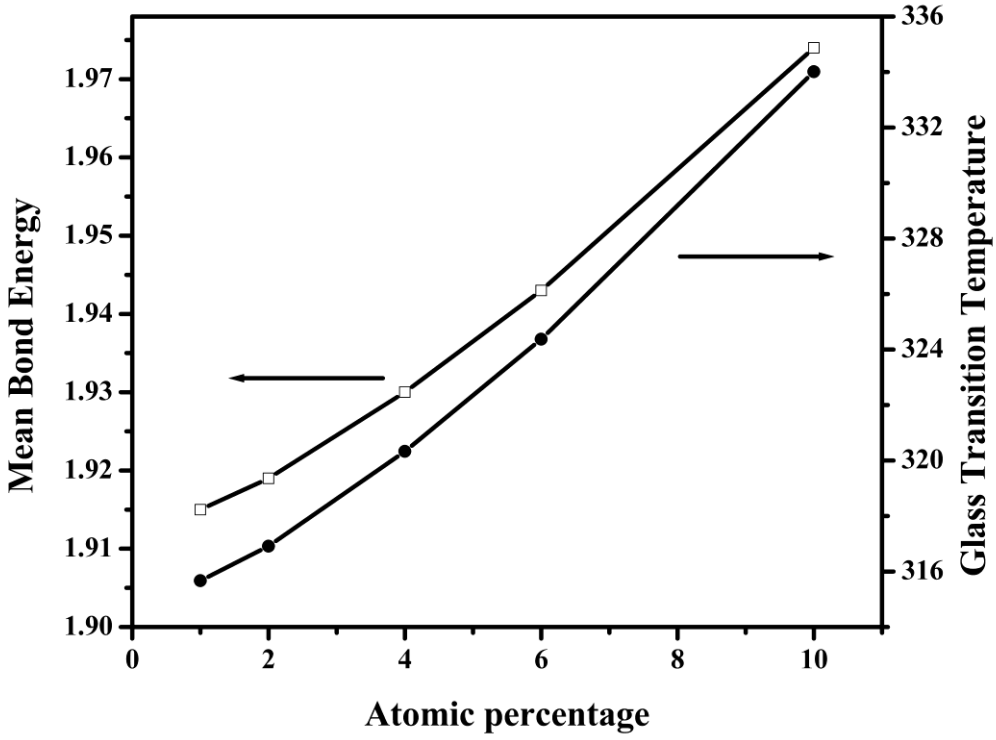

Figure 3. *Variation of Mean Bond Energy and Glass Transition Temperature with Sb at. %.*

3.5. Mean Bond Energy and Glass Transition Temperature

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 (chalcogenide rich system) we can determine the value of <*E*> [17] and is given by:

$$\langle E \rangle = E_c + E_{rm} \quad (6)$$

where E_c is the overall contribution to the bond energy arising from strong heteropolar bonds and is given by:

$$E_c = P_r D_{hb} \quad (7)$$

P_r is the degree of cross linking and given by:

$$P_r = (\alpha Z_{Te} + \gamma Z_{Sb})/(\alpha+\beta+\gamma) \quad (8)$$

and D_{hb} is the average heteropolar bond energy and given by:

$$D_{hb} = (\alpha Z_{Te} E_{Se\text{-}Te} + \gamma Z_{Sb} E_{Se\text{-}Sb})/(\alpha Z_{Te} + \gamma Z_{Sb}) \quad (9)$$

E_{rm} is the average bond energy per atom of the remaining matrix and given by:

$$E_{rm} = 2[0.5\langle r \rangle - P_r] E_{Se\text{-}Se}/\langle r \rangle \quad (10)$$

Tichy and Ticha illustrated a correlation of T_g and mean bond energy in the form:

$$T_g = 311[\langle E \rangle - 0.9]$$

The calculated value of T_g are given in Table 4 and is found to increase with increasing Sb content. The experimental values of T_g obtained from DSC thermograms and its theoretical values evaluated using Eq. (10) for each Sb additive alloy are given in Table 4. However, applying Tichy-Ticha approach to $Se_{80-x}Te_{20}Sb_x$ system, the estimated T_g is not consistent with

experimental values though there is an increase in T_g with increase in Sb content (Table 4).

Table 4. *Deviation of stoichiometry (R), mean bond energy<E>, electronegativity (χ) and glass transition temperature (T_g) for $Se_{80-x}Te_{20}Sb_x$ composition.*

Composition	*R*	<*E*> (eV)	χ	T_g	
				Experimental	Tichy-Ticha
$Se_{79}Te_{20}Sb_1$	66	1.915	2.455	315.61	315.67
$Se_{78}Te_{20}Sb_2$	32.67	1.919	2.45	316.33	316.91
$Se_{76}Te_{20}Sb_4$	16	1.930	2.44	316.53	320.33
$Se_{74}Te_{20}Sb_6$	10.44	1.943	2.43	315.60	324.37
$Se_{70}Te_{20}Sb_{10}$	6	1.974	2.41	316.82	334.01

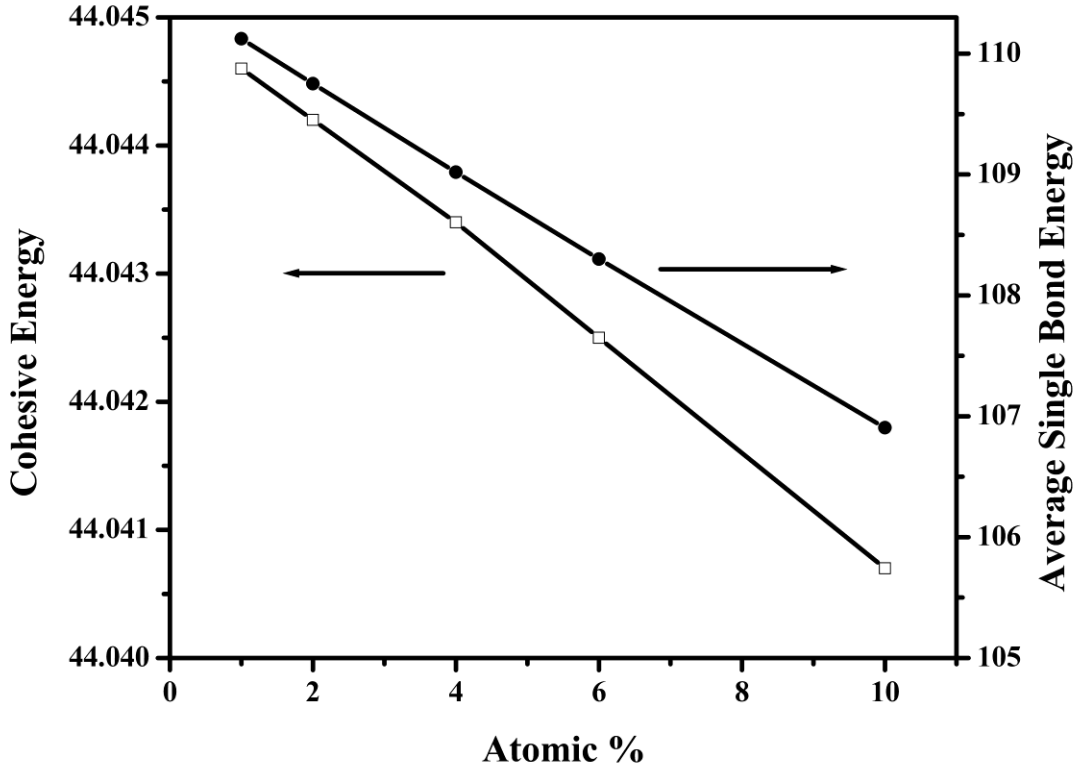

Figure 3. *Variation of Cohesive energy and average single bond energy with Sb at. %.*

3.6. Heat of Atomization

According to Pauling, 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 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 *A* and *B* respectively [22, 23]:

$$H_S\ (A–B) = \Delta\ H + 1/2(H_S^{\ A} + H_S^{\ B}) \quad (12)$$

The first term in the above equation is proportional to the square of the difference between the electronegativities *A* and *B* of the two atoms

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

In order to extend this idea to ternary and higher order semiconducting compounds, the average heat of atomization H_s is defined for a compound is given as:

$$H_S = (\alpha H_S^{Se} + \beta H_S^{Te} + \gamma H_S^{Sb})/(\alpha + \beta + \gamma) \quad (14)$$

H_S is the useful parameter for correlating the physical properties of semiconducting compounds. Heat of atomization of atoms are H_S (Te) = 197 kJ/mol, H_S (Se) = 227 kJ/mol, H_S (Sb) = 262 kJ/mol [24]. The calculated values of heat of atomization are given in Table 5.

Table 5. *Values of average heat of atomization (H_s) and average single bond energy ($H_s/<r>$) for $Se_{80-x}Te_{20}Sb_x$ composition.*

Composition	H_s (kJ/mol)	Hs/<r> (kJ/mol)
$Se_{79}Te_{20}Sb_1$	221.35	110.124
$Se_{78}Te_{20}Sb_2$	221.70	109.752
$Se_{76}Te_{20}Sb_4$	222.40	109.019
$Se_{74}Te_{20}Sb_6$	223.10	108.301
$Se_{70}Te_{20}Sb_{10}$	224.50	106.905

4. CONCLUSIONS

Different physical parameters like transition temperature, mean bond energy, cohesive energy, lone-pair electrons, coordination number and heat of atomization are calculated theoretically for $Se_{80-x}Te_{20}Sb_x$ (x = 1, 2, 4, 6 and 10) glassy alloys. It has been observed that Sb atom leads to the cross linking of chains and increases the coordination number of the system. Glass transition temperature, mean bond energy, constraints and heat of atomization increases with increasing Sb content in the investigated Se-Te-Sb system. The cohesive energy of the investigated samples has been calculated using chemical bond approach (*CBA*) method and has been found to decrease with the increase in Sb content. The number of lone pair electrons found to decrease with the addition of Sb content and has a minimum value 3.80 which is much more than 1 indicating that the compositions for present investigation has a good glass forming ability. Thus the addition of Sb content to $Se_{80-x}Te_{20}Sb_x$ glassy alloy leads to change in the physical properties.

REFERENCES

[1] Zakery A. and Elliot S. R., J. Non-Cryst. Solids 330, 1 (2003).

[2] Ovshinsky S. R., Reversible electrical switching phenomena in disordered Structures, Phys. Rev. Lett. 21(20), 1450 (1968).

[3] Ovshinsky S. R., Amorphous Material – The key to new Devices, "IEEE Proceedings of circuits and Systems, Vol. 1, 1998, pp.33

[4] Feinleib J., J. de Neufville, Moss S. C. and Ovshinsky S. R., "Rapid reversible light-induced crystallization of amorphous semiconductors," Applied Phys. Lett. 18(6), 254 (1971).

[5] Seddon A. B., "Chalcogenide Glasses:" A review of their preparation, properties and applications, J. Non – Cryst. Solids. 184, 44 (1995).

[6] Sugiyama Y, Chiba R, Fugimori S and Funakoski N, J. Non – Cryst. Solids. 83, 122 (1990).

[7] Gupta S., Agarwal A., Saxena M., Study of crystallization kinetics of some Tex(Bi2Se3)1-x glassy alloys", Adv. Appl. Sci. Res. 2(4), 49(2011).

[8] Chiba R. and Funakoshi N., Crystallization of vacuum deposited Te- Se- Cu alloy film, J. Non – Cryst. Solids. 105(1-2), 149(1988).

[9] Saxena M., J. Phys. D: Appl. Phys. 38, 460(2005).

[10] Mehta N., Agrahari S.K. and Kumar A., Phys. Scr. 74, 579 (2006).

[11] Saxena M. and Bhatnager P. K., Bull. Mater.Sci. 26, 547(2003).

[12] Suri N., Bindra K. S., Kumar P., Kamboj M. S. and Thagaraj R., J. Ovonic Res. 2, 111 (2006).

[13] Fayek S. A., Maged A. F. and Balboul M. R., Vacuum 53, 447 (1999).

[14] Fauad S. S., J. Phys. D 28, 2318 (1995).

[15] Zhenhua L., J. Non-Cryst. Solids. 127, 128 (1991).

[16] Tichy L. and Ticha H., Mater Lett. 21, 313 (1994).

[17] Tichy L. and Ticha H., J. Non-Cryst. Solids. 189, 141 (1995).

[18] Pauling L., The Nature of the Chemical Bond, "Cornell University Press, New York, 1960.

[19] Pattanaik A. K. and Srinivasan A., Electrical and optical studies on Pb – modified amorphous Ge-Se-Te Films", Semicond. Sci. Tech. 19(2), 157 (2004).

[20] Sanderson R. T., Inorganic Chemistry, East-West Press, New Delhi (1971).

[21] Cox J. D., Wagman D. D., Medvedev V. A., CO-DATA key values from thermodynamics, Hemisphere Publishing Corp., New York, 1989.

[22] Fayek S. A. and Fouad S. S., Vacuum. 52, 359 (1998).

[23] Brewer L., Electronic Structure and Alloy Chemistry of the Transition Element, edited by P. A Beck (Interscience, New York) 1963, 222.

[24] Sadagopan V. and Gatos H.C., Solid State Electron. 8, 529 (1965).

AUTHORS' BIOGRAPHY

Dr. Balbir Singh Patial,
Assistant Prof. in Physics
Department of Physics
Govt. College Sunni Shimla-171 301 H.P. India

Neha,
Research scholar (Ph.D. student)
Department of Physics
H.P. University Summerhill Shimla
H.P.-171 005 India.

Prof. Nagesh Thakur
Professor
Department of Physics
H.P. University Summerhill Shimla
H.P.-171 005 India.

Prof. S. K. Tripathi
Center of Advanced Study in Physics
Panjab University Chandigarh
Chandigarh 160 014 India.