Theoretical prediction of physical properties of 0.7Se-0.2Ge-(0.1-x)Te-xSb (x=0.01,0.02,0.03) chalcogenide and glassy composite system.

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Abstract:

This present communication is based on the theoretical prediction of different physical parameter of a novel quaternarymaterial 0.7Se-0.2Ge-(0.1-x)Te-xSb system. The effect of variation of introducing Sb atom by replacing Te atom in the glass matrix has been systematically studied in terms of average coordination number, different constraint parameter, lone pair electron, heat of atomization mean bond energy and the glass transition temperature. The investigation on lone pair electron confirms the glass forming ability of the sample. Chemical bond approach model has been used to calculate the mean bond energy of different system. Theoretically calculated mean bond energy shows a linearly increasing values with the increasing amount of Sb. Incorporation of Sb atom in to the glass matrix changes the transition temperature.

Keyword:

Quaternary chalcogenide glasses, Heat of atomization, Mean bond energy, Glass transition temperature.

1. Introduction:

In recent times the investigation on chalcogenide glasses becomes highly interesting because of its application in several areas like quasi-stability, photoconductivity, infrared transparency non-linear optical properties and ionic conduction it is also uses field of infrared optics, fiber optics, optical and electronic memory devices, biosensor application, memory devices, radiation shielding and antireflection coating[1-5]. The chalcogenide glasses are stable against crystallization and are chemically inanimate and its thermal stability is very good and comparatively easy to construct. The chalcogenide glasses are non-oxide amorphous semiconductors having high transmission in the IR region [6].Chalcogen glasses are normally less weakly bonded materials than oxide glasses. Understanding the relation between microscopic structures and macroscopic parameters has been a subject in solid-state physics. On the basis of the amorphous structure of covalent glasses, building components may be classified into two components; one of the bonding structure consisting of covalent bonds of densities on orders of 10^{22}-10^{23} cm^{-3}, which can be signified by chemical and topological natures, and the other one is defects, e.g., impurities, valence-alternation pairs, inclined and wrong bonds, i.e., the homopolar bonds in stoichiometric alloys [7,8].Selenium is the most important semiconductor that has an application in different technological areas, on the basis of its binary and ternary chalcogenide glasses[9-12].The Selenium has a drawback of high photosensitivity and crystallization temperature but also have low aging effect [13].The properties of chalcogenide glasses can be tuned by the incorporation of different doping materials. Doping of Sb with the Se atom introduces important changes in the compositional matrix. But the Sb-Se matrix has a poor stability which can be improved by adding some amount of Ge [14] which also improves material strength by increasing the cross linking in the glassy network. Due to the strong metallic character of Te, it has poor glass formation character as compared to Se. For improvement in glass formation and to increase the dimensionality of structure it is necessary to add trivalent and tetravalent atoms such as Ga, Ge, As, and I in Te based glasses for this reason generally Te have been used for its excellent glass forming ability[15].Te–based glasses are applied at longer wavelength in IR region[16]. To investigate on the structure property relationship with the compositional variation in Sb incorporated Se-Ge-Te glassy composite. In the present study the topological explanation of glass network has been discussed. Phillips and Thorp introduced this topological concept by considering the Lagrangian constraints[17,18]. According to this theory the value of average coordination number <r>=2.4, plays a vital role and it is used as a threshold point at which the glass network

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changes from a floppy to rigid type. The elements such as Sb causes the structural disorder which leading to tune the optical and thermal properties [19, 20] of material. The material structure also depends upon the mean coordination number variation. On other hand in the studies of Ge–Sb–Se–Te glassy composite system is the close of Sb and Te in the periodic table, which is the reason for Te and Sb to same each other.

In the present communication different physical properties of 0.7Se-0.2Ge-(0.1-x)Te-xSb, (x=0.01,0.02,0.03) system has been investigated. The aim of the study is to theoretically estimate the effect of Sb incorporation in Se-Ge-Te glass matrix on some parameters like total number of constraints, cross linking density, floppy modes, mean bond energy etc.

2. Result and Discussion:

Different physical properties e.g. average coordination number, lagrangian stretching force, bending force, total number of constraints, floppy mode, lone pair, heat of atomization, bond energy, chalcogen rich parameter and transition temperature theoretically calculated of Se-Ge-Te-Sb chalcogenide and glassy composite system.

2.1 Coordination Number and Constraints:

Calculation of coordination number is very important in order to understand the main features of the chalcogenide glassy system under study. The average coordination number has a great impact on the physical properties of the chalcogenide.

In our quaternary chalcogenide system 0.7Se-0.2Ge-(0.1-x)Te-xSb , the average coordination number <r> is given by the equation

$$\langle r\rangle = 0.7CN(Se) - 0.2CN(Ge) - (0.1-x)CN(Te) - xCN(Sb),\ (x=0.01,0.02,0.03) \quad (1)$$

Where, $CN_{Se}=2$, $CN_{Ge}=4$, $CN_{Te}=2$, $CN_{Sb}=3$ are the coordination numbers of Se, Ge, Te and Sb respectively. The value of average coordination numbers stay in the limit $2.41 \leq r \geq 2.43$ as listed in **table1**. The mechanical constraints or the total number of constraints (N_{CO}) arise for covalent bonded glassy networks i.e. bond stretching force (N_a) and bond bending force constraints (N_b). In this quaternary system bond stretching force constraints are calculated by the equation[21]

$$N_a = \langle r\rangle/2 \quad (2)$$

The bond bending force constraints in quaternary system is given by the equation[21]

$$N_b = 2\langle r\rangle - 3 \quad (3)$$

In quaternary system total number of constraints is given by the equation[21]

$$N_{CO} = N_a + N_b \quad (4)$$

The calculated values of different bonds stretching parameters are enlisted in **table1.**

Table1 The average coordination Number <r>, lagrangian stretching force(N_a), bending force(N_b), Total number of Constraints(N_{co})

Composition	<r>	N_a	N_b	N_{co}
$Se_{0.7}$-$Ge_{0.2}$-$Te_{0.09}$-$Sb_{0.01}$	2.41	1.205	1.82	3.025
$Se_{0.7}$-$Ge_{0.2}$-$Te_{0.08}$-$Sb_{0.02}$	2.42	1.210	1.84	3.050
$Se_{0.7}$-$Ge_{0.2}$-$Te_{0.07}$-$Sb_{0.03}$	2.43	1.215	1.86	3.075

It has been observed from **table1**, that the stretching force parameter, bending force parameter and the total number of constraints are gradually increasing with the increasing value of average coordination number.

2.2 Fraction of Floppy Modes and cross linking density:

The floppy modes(f) for quaternary chalcogenide glass system 0.7Se-0.2Ge-(0.1-x)Te-xSb; (x=0.01,0.02,0.03) are calculated using the relation[22]

$f=2-5/6<r>$ (5)

where, <r> is the average coordination number, the values of floppy modes are tabulated in table2. It has been noted from table2, that the value of 'f ' becomes more and more negative with the progressive amount of Sb.

Table2 the average coordination Number <r> and floppy mode (f)

Composition	<r>	f	D_{CL}
$Se_{0.7}$-$Ge_{0.2}$-$Te_{0.09}$-$Sb_{0.01}$	2.41	-0.008	1.025
$Se_{0.7}$-$Ge_{0.2}$-$Te_{0.08}$-$Sb_{0.02}$	2.42	-0.016	1.050
$Se_{0.7}$-$Ge_{0.2}$-$Te_{0.07}$-$Sb_{0.03}$	2.43	-0.025	1.075

The variation of floppy modes with the average coordination number is depicted in Fig.1. The linear relationship of floppy mode with the average coordination number has been observed.

The value of cross linking density has been calculated by using the equation[23].

$$D_{CL}=N_{CO}-2 \quad (6)$$

The calculated value of D_{CL} has been tabulated in **table2**. It has been observed that, the value degree of cross linking is gradually increasing with <r>. Floppy mode value becomes more negative therefore the rigidity increases in the network due to rise in the value degree of cross linking which makes system spongy. The graph has been plotted the floppy modes f vs the average coordination number <r> in **figure 1.**

2.3 Lone pair electrons:

The number of lone pair of electron(L) is calculated by using the expression[24],

$$L=0.7V_{Se}-0.2V_{Ge}-(0.1-x)V_{Te}-xV_{Sb},\ (x=0.01,0.02,0.03) \quad (7)$$

Where, $V_{Se}=6$, $V_{Ge}=4$, $V_{Te}=6$, $V_{Sb}=5$ are the valence electron of Se, Ge, Te and Sb respectively. The value of lone pair electron for the quaternary chalcogenide glass system 0.7Se-0.2Ge-(0.1-x)Te-xSb ;(x=0.01,0.02,0.03) are listed table3. A graphical representation of L and <r> composition is given in figure 2. The value of lone pair electrons are decreases with increase the amount of Sb. In this quaternary composition lone pair electrons are present which ensure the composition glassy nature. The interaction reduces the role of lone-pair electrons in the glass system.

Table3 the average coordination Number <r> and lone pair electron

Composition	<r>	L
$Se_{0.7}$-$Ge_{0.2}$-$Te_{0.09}$-$Sb_{0.01}$	2.41	5.59
$Se_{0.7}$-$Ge_{0.2}$-$Te_{0.08}$-$Sb_{0.02}$	2.42	5.58
$Se_{0.7}$-$Ge_{0.2}$-$Te_{0.07}$-$Sb_{0.03}$	2.43	5.57

The graph has been plotted the lone pair electron L vs the average coordination number <r> in **figure 2.**

2.4 Heat Atomization parameter:

Heat atomization H_S at standard temperature and pressure of binary semiconductor, it was proposed by Pauling [25]. In many cases the heat of creation of chalcogenide glasses is unknown. Also several glasses, the heat of creation is known, its value is not greater than 10%, so it can be disregarded[26]. The heat atomization parameter "H_s" is calculated by using the expression [25].

$$H_s=0.7H_{Se}-0.2H_{Ge}-(0.1-x)H_{Te}-xH_{Sb},\ (x=0.01,0.02,0.03) \quad (8)$$

Where, H_{Se}=227 KJ/mol, H_{Ge}=377 KJ/mol, H_{Te}=197 KJ/mol, H_{sb}=262 KJ/mol

Table4 the average coordination Number <r> and Heat Atomization parameter:

Composition	<r>	H_s(KJ/mol)	R
$Se_{0.7}$-$Ge_{0.2}$-$Te_{0.09}$-$Sb_{0.01}$	2.41	254.65	1.90
$Se_{0.7}$-$Ge_{0.2}$-$Te_{0.08}$-$Sb_{0.02}$	2.42	255.3	1.81
$Se_{0.7}$-$Ge_{0.2}$-$Te_{0.07}$-$Sb_{0.03}$	2.43	255.95	1.73

The graph has been plotted the heat atomization parameter H_S vs the average coordination number <r> in **figure 3**.

2.5 Deviation from Stoichiometry of composition:

The parameter R signifies the deviation of stoichiometry which can be expressed by the ratio of covalent bonding aspect of chalcogen atom to that of non-chalcogen atoms. This parameter plays a vital role for analysing different result. The system is consider to be a chalcogen-rich when the value of R becomes greater than 1.The system is called chalcogen-poor when the value of R becomes less than 1. The value of R can be calculated by the equation[27,28]

$$R=\frac{0.7CN(Se)+(0.1-x)CN(Te)}{0.2CN(Ge)+xCN(Sb)},\ (x=0.01,0.02,0.03) \quad (9)$$

Where CN_{Se}=2, CN_{Ge}=4, CN_{Te}=2, CN_{Sb}=3 are the coordination numbers of Se, Ge, Te and Sb respectively. The obtained value of R is tabulated in table4. From the calculated value of R it has been noted that all the samples are chalcogen rich sample. The value of R are found to decrease from 1.90 to 1.73 with an increase in the concentration of Sb content.

2.6 Bond Energy:

The heteropolar bond energy has been allotted by the equation introduced by Pauling[29]; Chemical bond approach (CBA)describe feasible bond distribution[30]. Presupposing that various type of atoms merge simply balance similar atoms and bonds made in the order of reducing bond energies. The bond energy is calculated by using the expression[31].

$$E_{a-b}=(E_{a-a}*E_{b-b})^{1/2}+30(X_a-X_b)^2 \quad (10)$$

Where, E_{a-a} and E_{b-b} are homonuclear bond energy and X_a and X_b are the electronegativity. The homopolar bond energy E_{Se-Se} ,E_{Te-Te} , E_{Sb-Sb} ,E_{Ge-Ge} are 44.04 Kcal/mol, 33 Kcal/mol, 30.22 Kcal/mol and 37.6 Kcal/mol respectively [32,33]. By applying the above relation, determined the heteropolar bond energy E_{Se-Ge}=49.440 Kcal/mol, E_{Se-Te}=44.197 Kcal/mol, E_{Se-Sb}=43.981 Kcal/mol.

2.7 Mean Bond Energy:

The characteristic of chalcogenide glasses are also connected to mean bond energy <E>, it is the function of average coordination number <r>, the type of bonds and the bond energy. The interrelation recommend by Tichy[34]. We are calculate the value of <E> for the chalcogenide system using the expiration[35].

$$<E>=P_rE_{hb} \quad (11)$$

Here P_r is the degree of cross linking given,

$$P_r = \frac{0.2CN(Ge)+(1-x)CN(Te)+xCN(Sb)}{1} \quad , (x=0.01,0.02,0.03) \qquad (12)$$

E_{hb} is the heteropolar bond energy is given by,

$$E_{hb} = \frac{0.2CN(Ge)*E_{Ge-Se}+0.09CN(Te)*E_{Te-Se}+0.01CN(Sb)*E_{Sb-Se}}{0.02CN(Ge)+0.09CN(Te)+0.01CN(Sb)} \quad , (x=0.01,0.02,0.03) \qquad (13)$$

Where CN_{Se}=2, CN_{Ge}=4, CN_{Te}=2, CN_{Sb}=3 are the coordination numbers of Se, Ge, Te and Sb respectively.

Table5 the average coordination Number <r> and mean bond energy <E>:

Composition	<r>	<E>(ev)
$Se_{0.7}$-$Ge_{0.2}$-$Te_{0.09}$-$Sb_{0.01}$	2.41	2.11
$Se_{0.7}$-$Ge_{0.2}$-$Te_{0.08}$-$Sb_{0.02}$	2.42	2.13
$Se_{0.7}$-$Ge_{0.2}$-$Te_{0.07}$-$Sb_{0.03}$	2.43	2.15

The graph has been plotted the mean bond energy <E> vs the average coordination number <r> in **figure 4.**

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2.8 Glass Transition Temperature:

The glass transition temperature is the most necessary part for the characteristic of chalcogenide glasses. According to Thorpe and Tichy in a chemically ordered system, there should be a relationship between the glass transition temperature (T_g) and mean bond energy. The glass transition temperature is proportional to the mean bond energy <E>, which is based on factors like average coordination number, degree of cross linking, bond energy and the nature of the bonds formed. We get the glass transition temperature theoretically for the composition 0.7Se-0.2Ge-(0.1-x)Te-xSb ,(x=0.01,0.02,0.03) by using Tichy-Ticha Approach [35]. The equation between the glass transition temperature (Tg) and overall mean bond energy <E> is given by,

$Tg = 311[<E> - 0.9]$ (14)

Where <E> is the average mean bond energy.

Table6 the average coordination Number <r> and Transition Temperature:

Composition	<r>	T_g(K)
$Se_{0.7}$-$Ge_{0.2}$-$Te_{0.09}$-$Sb_{0.01}$	2.41	376.31
$Se_{0.7}$-$Ge_{0.2}$-$Te_{0.08}$-$Sb_{0.02}$	2.42	382.53
$Se_{0.7}$-$Ge_{0.2}$-$Te_{0.07}$-$Sb_{0.03}$	2.43	388.75

The graph has been plotted the transition temperature T_g vs the average coordination number <r> in **figure 5.**

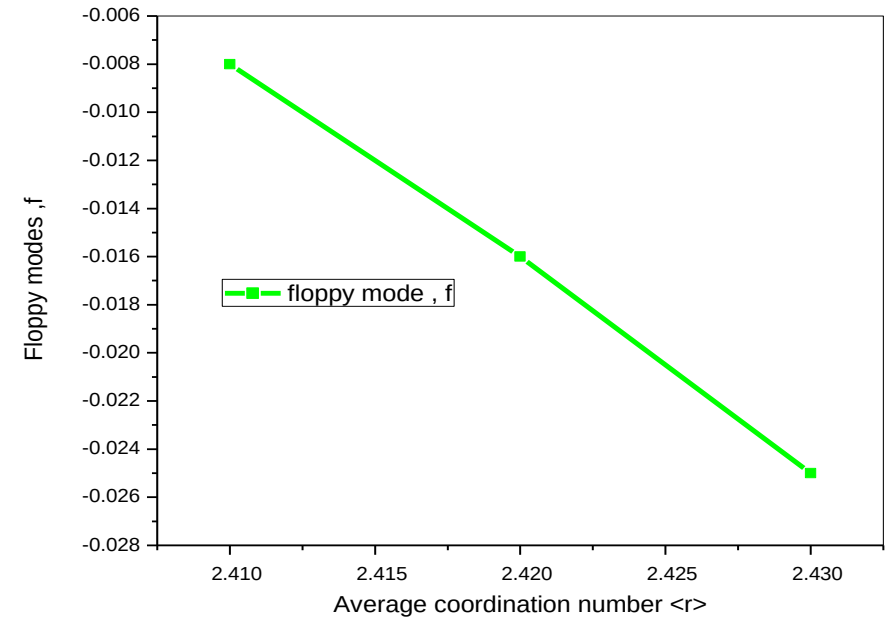

Fig. 1. The floppy modes vs the average coordination number <r> in the system.

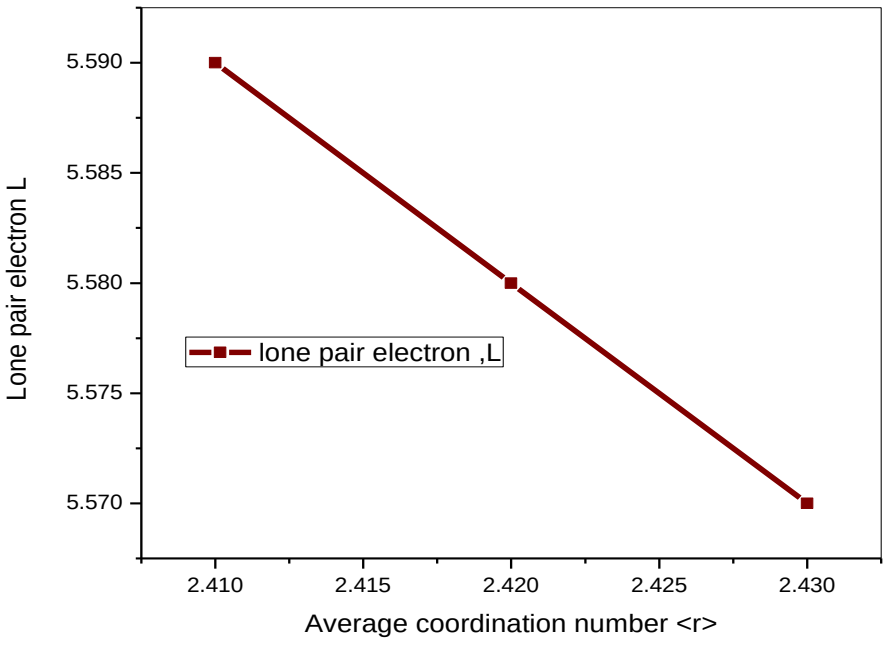

Fig. 2. The lone pair electron vs the average coordination number in the system.

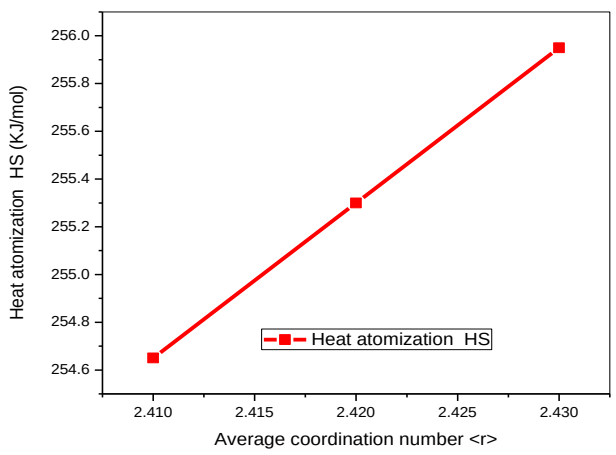

Fig. 3.The heat atomization parameter vs the average coordination number in the system.

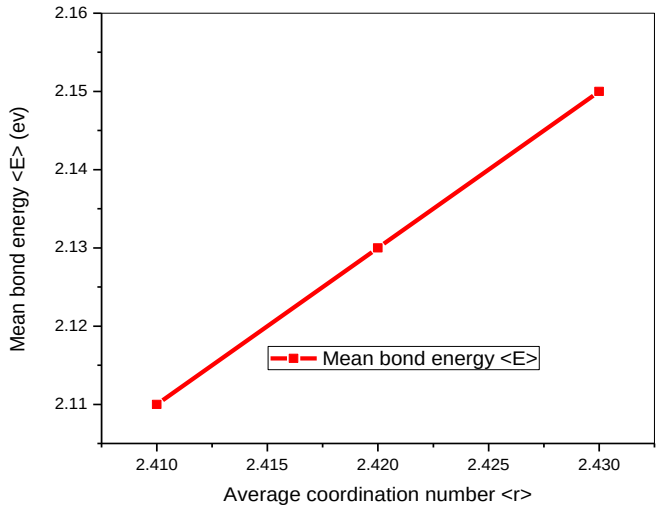

Fig.4.The mean bond energy<E> vs the average coordination number <r> in the system.

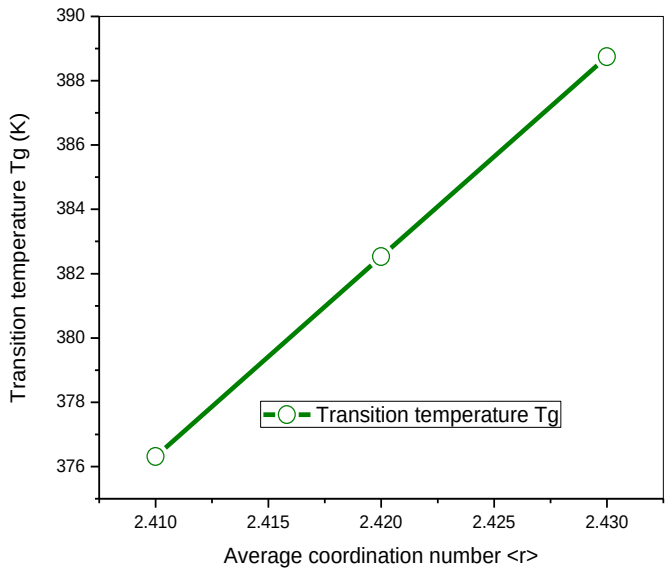

Fig.5.The Transition Temperature vs the average coordination number <r> in the system.

3. Conclusion:

The effect of Sb incorporation on the physical parameters are theoretically analyzed for the novel 0.7Se-0.2Ge-(0.1-x)Te-xSb (x=0.01,0.02,0.03) glassy system and we have come to the following conclusions. It has been observed that average coordination number, constraints and mean bond energy linearly increases with increasing quantity of Sb or decreasing quantity of Te in Se-Ge-Te-Sb composite system. It is found that the value of average coordination number is greater than 2.4 for each sample under study that means the glassy composite under study are in over coordinated mode. The increasing cross linking density value and decrease in value of floppy mode symbolizes the gradual increase in rigidity of the system. The deviation of stoichiometry parameter R decreases due to decrease in quantity of chalcogen Te and hence increases in quantity of Sb. It is noteworthy that the Floppy Modes(f) becomes more and more negative with the increases amount of Sb. The value of cross linking density(D_{CL}) increases due to increases content of Sb. The number of lone pair electrons are found to decrease with increasing Sb content. Its value are found to be greater than 2 for all samples which means all the samples are good glass formers. The glass transition temperature of the glassy system is found to increase with the minor increase of the Sb-content in the glassy 0.7Se-0.2Ge-(0.1-x)Te-xSb ,(x=0.01,0.02,0.03) matrix.

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