A study of Sn addition on bonding arrangement of Se-Te alloys using far infrared transmission spectroscopy

Rajneesh Kumar,[1] Parikshit Sharma,[2] S. C. Katyal,[3] Pankaj Sharma,[4,a] and V. S. Rangra[1]

[1]*Department of Physics, Himachal Pradesh University, Summer-Hill, Shimla, H.P. – 171005, India*
[2]*Department of Physics, Sri Sai University, Palampur, HP, India*
[3]*Department of Physics, Jaypee Institute of Information Technology, Noida, U.P., India*
[4]*Department of Physics, Jaypee University of Information Technology, Waknghat, Solan, H.P. 173215, India*

Far infrared transmission spectra of $Se_{92}Te_{8-x}Sn_x$ (x = 0, 1, 2, 3, 4, 5) glassy alloys are obtained in the spectral range 50–600 cm^{-1} at room temperature. The results are interpreted in terms of the vibrations of the isolated molecular units in such a way so as to preserve fourfold and twofold coordination for Sn and chalcogen atoms (Se,Te), respectively. With the addition of Sn, Far-IR spectra shift toward high frequency side and some new bands start appearing. Sn atoms appear to substitute for the selenium atoms in the outrigger sites due to large bond formation probability. Theoretical calculations of bond energy, relative probability of bond formation, force constant, and wave number were also made to justify the result. © *2011 American Institute of Physics*. [doi:10.1063/1.3603010]

I. INTRODUCTION

Chalcogenide glasses are characterized by two fold coordinated chalcogen atoms, which makes the local structure flexible. They are non-oxide, inorganic semiconducting materials having high transmittance in the IR spectral regions,[1,2] and they show a variety of phenomenon when exposed to light or other radiation having photon energy comparable to the bandgap.[3–6] Chalcogenide glasses have a lot of applications in infrared optics, reversible optical memory switching, inorganic photoresist, optoelectronics, antireflection coating, and holographics.[7–10]

Infrared spectroscopy is a useful tool for obtaining information about the structure of chalcogenide glasses. Talking about chalcogenide glasses brings, first, discussion about their transmittance. These glasses are transparent in the far-infrared region. Recently, several workers have reported vibrational spectroscopic studies of these glasses and have tried to assign the observed absorption to the different chemical bonds in the system.[11,12]

IR transparency of chalcogenide glasses have been generally reported in the wavelength region 1–14 μm.[1,11] The high IR transparency of such types of glassy materials offers a breath of technological utility, such as low material dispersion, long wavelength multiphonon edge, along with good chemical, thermal, and mechanical properties.[13,14] Amorphous solids display a characteristic extreme far-infrared and microwave absorption as a result of phonon coupling to modes which are not active in the corresponding crystalline counterpart material. The combination of infrared spectroscopy with the theory of reflection has made advances in surface analysis possible.[15,16] Recent advances in low frequency IR and Raman spectroscopy has given a great stimulus to study on vibrations in solids and liquids. Low frequencies are needed to complete the vibrational assignments and for calculating thermodynamic properties. Sometimes, the low frequencies cannot be obtained from Raman spectra, because selection rule forbids them. The only source of data may be the far-infrared. Structural properties of both amorphous and crystalline solids can be explained with topological model, chain crossing model, continuous random covalent network model approach (CRNM), and chemical bond approach.[17–20]

The glass network has either a mechanical threshold or critical composition at which the glass network changes from an elastically floppy mode to a rigid mode. To understand the structural, vibrational properties, the information of the medium range order is also important. The alloy substitution is a useful method to investigate the short and intermediate range structures and binding forces. Substituting Sn for selenium produces change in the nature of the chemical bond. It is expected that the difference of iconicity and metallicity in the chemical bond gives a large influence on the glass forming ability and vibrational properties. In the present work, far-infrared absorption studies have been carried out on $Se_{92}Te_{8-x}Sn_x$ (x = 0, 1, 2, 3, 4, 5) thin films. The results are discussed in terms of probabilities and bond energies of various chemical bonds possible in these glassy samples.

II. EXPERIMENTAL DETAIL

Glassy alloy of $Se_{92}Te_{8-x}Sn_x$ (x = 0, 1, 2, 3, 4, 5) system were prepared by melt quenching technique. Materials (99.999% purity) were weighed according to their atomic percentage and sealed in evacuated ($\sim 10^{-3}$ Pa) quartz ampoules. The sealed ampoules were kept in a furnace where temperature was increased up to 900 °C at a heating rate of 3–4 °C/min and then the ampoules were frequently rocked for 8 h at the highest temperature to make the melt homogeneous. Ice cold water was used for quenching of glassy

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a)Author to whom correspondence should be addressed. Electronic mail: pks_phy@yahoo.co.in.

samples. The bulk samples were characterized by x ray diffaraction (XRD) technique and found to be amorphous in nature, as no prominent peak was observed in the spectra. The far-infrared spectra of different glassy alloys were recorded in the spectral range of 50–600 cm^{-1} at room temperature using Perkin Elmer 1600 FT-IR Spectrometer with a resolution of 2 cm^{-1}. All the measurements were carried out using polythene pallet method. For the absorption of polythene, the spectrum of polythene was used as a reference spectrum. The spectrum of sample was divided by the reference spectrum to nullify the polythene absorptions.

III. RESULTS AND DISCUSSION

A. X ray diffraction

Figure 1 shows x ray diffraction spectra of the $Se_{92}Te_{8-x}Sn_x$ (x = 0, 1, 2, 3, 4,5) glassy system. As no sharp peak is observed in the spectrum, material under consideration is amorphous in nature. All the investigated samples show a big hallo at 25°–35° (2θ value), which implies polymeric nature of these glasses and short range order.[21] When Sn is introduced in Se-Te alloy, there is slight increase in 2θ maximum (26.05°–26.90°). As our decided composition is Se rich and Sn is in minute quantity, it results in slight change in 2θ maximum. A small peak at 2θ = 30° may be due to $SnSe_2$ phase.[22,23]

B. Bond energies and relative bond formation probabilities

The bond energy of various possible heteropolar bonds (Se-Sn, Se-Te, Sn-Te) have been calculated on the basis of the relation given by Pauling:[24]
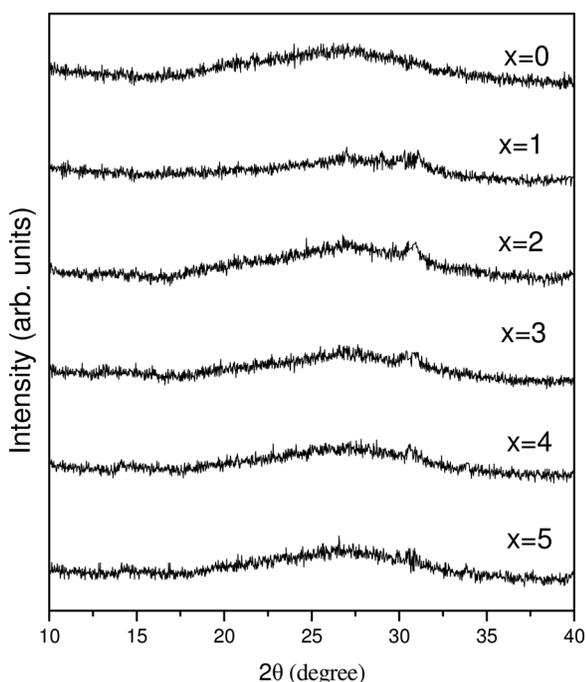
FIG. 1. X ray diffraction spectrum of $Se_{92}Te_{8-x}Sn_x$ (x = 0, 1, 2, 3, 4, 5) system.

$$D(A - B) = [D(A - A) \times D(B - B)]^{1/2} + 30(\chi_A - \chi_B)^2, \quad (1)$$

where χ_A and χ_B are the electronagativities of the atom A and B and D(A-A) and D(B-B) are the bond energies of A-A and B-B bonds. The relative probabilities of different bonds have also been calculated using the probability function $exp.(D/k_BT)$ at room temperature as well as at 900 °C, which is the sample preparation temperature. The results are shown in Table I. It is clear from Table I that Se atoms probably first saturate Sn atoms and then Se-Te and Se-Se bonds are formed. The bond formation probability of Sn-Sn, Te-Sn, and Te-Te are expected to be least because of low bond energies.

C. Theoretical calculations of possible absorption bands

The Far-IR transmission measurement of the Se-Te-Sn glassy material are discussed under the following assumptions: (i) the valence force field model (VFF) and (ii) the position of the intrinsic IR feature is influenced mainly by stretching force constants of corresponding chemical bonds. The wavenumber of the vibrational modes in IR spectra can be determined using the mass of the atoms and interatomic force within the groups of atoms composing the glass network. The wavenumber v is given by the following formula:

$$v = (1/2\pi c)(K/\mu)^{1/2}, \quad (2)$$

where K is the bending or stretching force constant, c is the speed of light, and μ is the reduced mass of the molecule, which is given by the following relation:

$$\mu = (M_1 \times M_2)/(M_1 + M_2), \quad (3)$$

where M_1 and M_2 are the atomic masses of two atoms. In order to determine the stretching force constant K, the following relation has been given by Gordy:[25]

$$K = aN(\chi_A\chi_B/d^2)^{3/4} + b. \quad (4)$$

This relation, in general, holds accurately for a large number of diatomic and simple polyatomic molecules in their ground states. It is not possible to check it for the different excited states of one and the same molecule because values for N and χ are available for ground states only. The constants a

TABLE I. Bond energies and their relative probabilities of formation at 27 °C and 900 °C of $Se_{92}Te_{8-x}Sn_x$ (x = 0, 1, **2**, 3, 4, 5) system.

Bond	Bond energy (kcal/mol)	Relative probability of bond formation	
		27 °C	900 °C
Se-Sn	49.41	1	1
Se-Te	44.14	1.46×10^{-4}	1.03×10^{-1}
Se-Se	44.00	1.15×10^{-4}	9.8×10^{-2}
Sn-Sn	34.20	8.45×10^{-12}	1.46×10^{-3}
Te-Sn	34.16	7.90×10^{-12}	1.43×10^{-3}
Te-Te	33.00	1.13×10^{-12}	8.7×10^{-4}

and *b* in the above equation have the same values for stable bonds of atoms exhibiting their normal covalencies, except those in which both atoms have a single electron in the valence shell.

Gordy equation may not be applied to those polyatomic molecules having appreciable interactions between non-bonded atoms, as it assumes a characteristic bond-stretching constant, which depends solely on the properties of the two atoms forming the bond. Polyatomic molecules for which the valence force field function is inadequate may not, in general, be expected to fit the rule.

In Eq. (4), *a* and *b* are constants which depend upon the structural unit type having values 1.67 and 0.30, respectively, *d* is bond length (nm), χ_A and χ_B are the electronagativities in the Pauling scale,[26] and *N* is the bond order, which can be determined from the expression

$$N = (d + 2r_1 - 3r_2)/(2d + r_1 - 3r_2), \qquad (5)$$

where r_1 and r_2 are the covalent radii for the single bond and double bond, respectively.

Somayayulu[27] has developed a method for predicting the polyatomic force constant by using elemental covalent force constants and electronagativities in the equation

$$K_{AB} = (K_{AA}K_{BB})^{1/2} + (\chi_A - \chi_B)^2, \qquad (6)$$

where K_{AB} is the force constant between the elements *A* and *B* and K_{AA} and K_{BB} are the force constants for the bonds *A-A* and *B-B*, respectively, the values of which are (10^5 dyne cm^{-1}) 1.91 eV for Se-Se, 1.25 eV for Te-Te, and 1.21 eV for Sn-Sn. The calculated values of ν (cm^{-1}) using the above equations are given in Table II. Reduced mass and force constants of probable bonds have also been given.

D. Far-IR study

The Far-Infrared spectra of $Se_{92}Te_{8-x}Sn_x$, where x = 0, 1, and 2 and x = 3, 4, and 5, glassy alloys are shown in Fig. 2 and Fig. 3, respectively. With the addition of Sn content, transmission spectra shifts toward high frequency side may be due to absorption coefficient or scattering of light by increased defect centers with the addition of Sn content. Many approaches have been proposed to explain the physical and structural properties of chalcogenide glasses. One of them is the chemical bond approach given by Bicerno and Ovshinsky,[20] in which formation of heteropolar bonds are favored over the formation of homopolar bond, and the
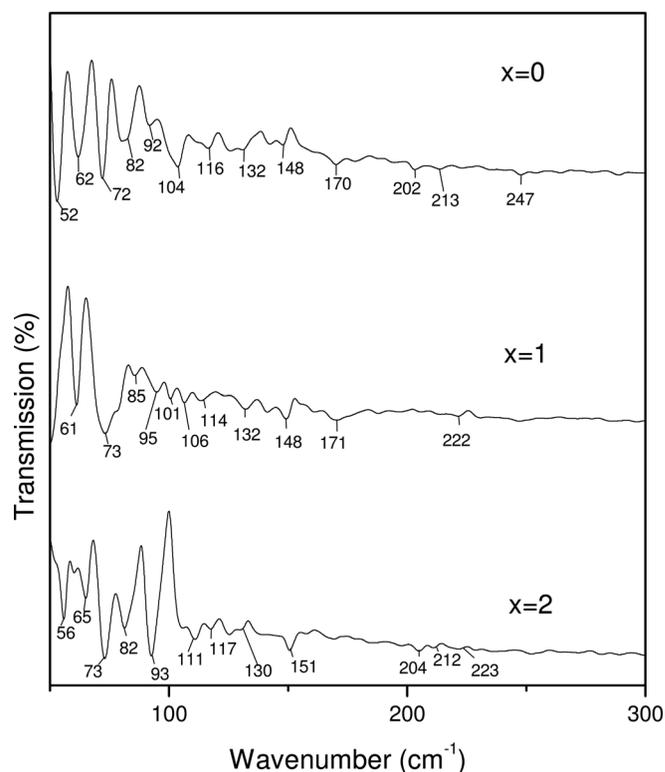
FIG. 2. Far-infrared transmission spectra of $Se_{92}Te_{8-x}Sn_x$ (x = 0, 1, 2) alloys.

bonds are formed in the order of decreasing bond energy until all available valences of atoms are saturated. Glass structure is assumed to be composed of cross linked structural units of heteropolar bonds.

In pure $Se_{92}Te_8$, i.e., x = 0 glassy sample, main absorption bands are at 52–92 cm^{-1}, 104 cm^{-1}, 116 cm^{-1}, 132 cm^{-1}, 148 cm^{-1}, 170 cm^{-1}, 202 cm^{-1}, 213 cm^{-1}, and 247 cm^{-1} along with shoulders at 58–88 cm^{-1}, 107 cm^{-1}, 121 cm^{-1}, 140 cm^{-1}, and 152 cm^{-1}. These bands are in good agreement with Ball *et al.*[28] The band at 52–92 cm^{-1}, 247 cm^{-1} has been assigned to Se_8 [E_2 mode],[28] while the band at 104 cm^{-1} has been assigned A_2 mode of trigonal selenium, which is infrared active. Oshaka has also reported infrared active fundamental mode in the spectra of Se containing Te at 102 cm^{-1} and assigned it A_2 mode of trigonal selenium. The band at 132 cm^{-1} is due to Se_n chain. The band at 170 cm^{-1} may be due to vibration of the Te-Te bond. The weak band at 213 cm^{-1} has been assigned to vibration of the Se-Te bond. Wang *et al.*[29] has also reported the vibration of Se-Te bond at

TABLE II. Theoretically calculated values of wave number (ν), reduced mass, bond length (*d*), and force constant of probable bonds.

Bond	Reduced mass (μ) $\times 10^{-26}$ (kgU^{-1})	Bond length (*d*) (nm)	Force constant (K_{AB}) (eV)	Theoretical wavenumber (ν) (cm^{-1})
Se-Se	6.559	0.234	1.91	270
Te-Te	10.622	0.286	1.25	172
Sn-Sn	9.882	0.280	1.21	175
Te-Sn	10.239	0.283	1.23	173
Se-Te	8.121	0.260	1.63	224
Se-Sn	7.884	0.257	1.52	220
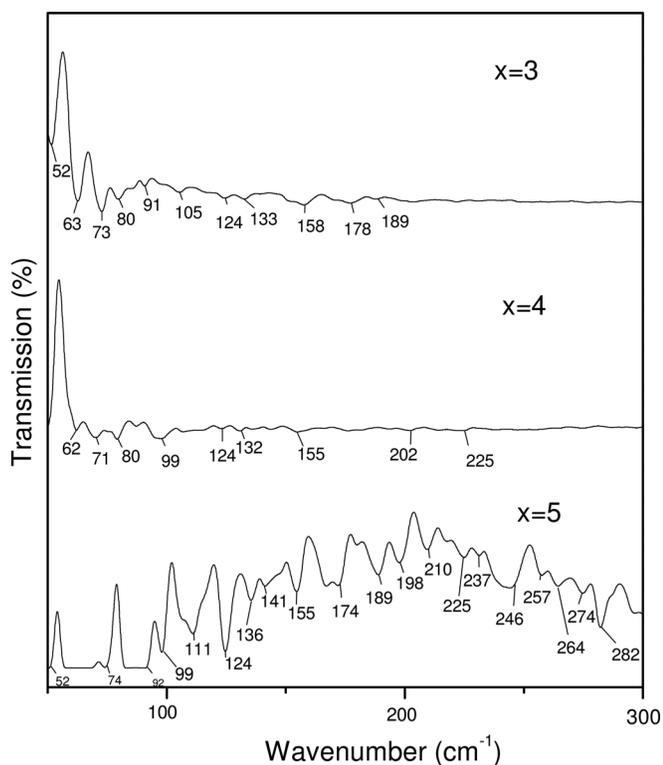
FIG. 3. Far-infrared transmission spectra of $Se_{92}Te_{8-x}Sn_x$ (x = 3, 4, 5) alloys.

TABLE III. Various absorption peak positions of $Se_{92}Te_{8-x}Sn_x$ (x = 0, 1, 2, 3, 4, 5) glassy system and their respective assignments.

x = 0	x = 1	x = 2	x = 3	x = 4	x = 5	Assignment
52	–	56	52	–	52	Se_8 (E_2 mode)
62	61	65	63	62	–	Se_8 (E_2 mode)
72	73	73	73	71	74	Se_8 (E_2 mode)
82	85	82	80	80	–	Se_8 (E_2 mode)
92	95	93	91	–	92	Se_8 (E_2 mode)
104	101, 106	–	105	99	99	Trigonal Se (A_2 mode)
116	114	111, 117	124	124	111, 124	$Sn(Se_{1/2})_4$
132	132	130	133	132	136	Se polymeric chain
148	148	151	158	155	155	$Sn(Se_{1/2})_4$
170	171	–				Te-Te bond
–	–	–	178	–	174	Te-Sn or Sn-Sn bond
–	–	–	189	–	189	$Sn(Se_{1/2})_4$ Raman mode
202	–	204	–	202	198	Se-Te bond
213	–	212	–	–	210	Se-Te bond
–	222	223	–	225	225	$Sn(Se_{1/2})_4$
247	–	–	–	–	246	Se_8 (A_1, E modes)
–	–	–	–	–	257	Se_8 (A_1, E modes)
–	–	–	–	–	264	Se-Se bond
–	–	–	–	–	274	Se-Se bond
–	–	–	–	–	282	Se-Se bond

210 cm^{-1} in $Ge_2Se_5Te_3$ alloy, while Oshaka has reported the vibration of Se-Te bond at 205 cm^{-1}.[30] The shoulders at 58–88 cm^{-1} and 121 cm^{-1} can be considered as Se_8 rings, while the shoulder at 140 cm^{-1} is assigned as Se polymeric chains. When Sn is introduced into Se-Te glass, it prefers to enter the outrigger tetrahedral site of Se, located at the edges of the molecular cluster, where it would cause the greatest reduction in stress.[31] This is because Sn has large covalent radius than Se and bond forming probability is maximum. In $Se_{92}Te_7Sn_1$, i.e., x = 1, main absorption bands are at 61–96 cm^{-1}, 106 cm^{-1}, 148 cm^{-1}, 171 cm^{-1}, and 222 cm^{-1}. On introducing Sn, some old bands from 58–88 cm^{-1} got merged in a single band of high intensity, which confirms the addition of Sn in Se-Te glass. In addition, a band is observed in the spectra at 148 cm^{-1} with a small sharp peak and large width in comparison to previous composition. This band may be assigned as $(SnSe_{1/2})_4$ tetrahedran, which is in agreement with Adam.[32] With further addition of Sn, this band (148 cm^{-1}) remains but becomes broader and shifts toward the high frequency side. The shift of peak in the spectrum is attributable to the presence of a $(SnSe_{1/2})_4$ tetrahedran unit; Sn and Se may form separate ribbon like clusters which are mixed together in the glass. When concentration of Sn increases, intercluster interaction results in softening of the breathing mode and shifting in the polarizability of the structure.[33] A weaker band at 222 cm^{-1} also appeared in the spectra of x = 1. This may be assigned as $Sn(Se_{1/2})_4$. Fayek[34] has also observed $Sn(Se_{1/2})_4$ band in the spectral range of 224–228 cm^{-1} in Ge-Se-Sn alloy. In x = 2, a band of high intensity at 93 cm^{-1} may be due to the Se_8 ring, and it seems to shift toward high frequency side. In x = 3, intensity of this band decreases, but

when x = 5, this band again appears along with other absorption band, which are at 52–99 cm^{-1}, 111–141 cm^{-1}, 155–210 cm^{-1}, and 225–282 cm^{-1}. Most of these bands are in good agreement with the theoretical wavenumber calculated in Table II. Although these bands are also present in previous compositions, i.e., x = 1–4, they are weak. The different IR behavior of x = 5 may be due to overlapping of bands or formations of voids in amorphous material, which reduces the density of available final states and results in increase in transmission intensity at certain wavelengths. Main absorption bands with their assignments are given in Table III. The study of bonding arrangement will help to explain the electrical and optical properties of these alloys. The relative probability of bond formation (Table I) shows the least existence of bonds like Sn-Sn, Sn-Te, and Te-Te, which is in good agreement with the Far-infrared spectra results, where only Te-Te and Sn-Te bonds are observed feebly.

IV. CONCLUSION

Bonding arrangements of Sn addition to Se-Te alloys have been studied. Addition of Sn confirms the appearance of Sn-Se bonds at 222–225 cm^{-1}, which is $Sn(Se_{1/2})_4$ mode. A comparison has been made between the bands obtained in the experimental Far - IR spectrum with the theoretically calculated values for the normal modes of various units. The experimental values are in good agreement with the theoretical values. The relative probability of bond formation indicates the least existence of bonds, like Sn-Sn, Sn-Te, and Te-Te. These results have been confirmed with the Far-IR results. The formation of different bonds will lead the researchers to understand the electrical and optical properties of Sn-Se-Te alloys.

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