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## Far-infrared transmission in $\text{Ge}_{1-x}\text{Sn}_x\text{Se}_{2.5}$ glassy alloys

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**Abstract.** Far-infrared transmission spectra of homogeneous compositions in the glassy alloy system  $\text{Ge}_{1-x}\text{Sn}_x\text{Se}_{2.5}$  ( $0 < x < 0.6$ ) have been observed in the spectral range  $50\text{--}650\text{ cm}^{-1}$  at room temperature. Tin atoms appear to substitute for the germanium atoms in the outrigger sites of  $\text{Ge}(\text{Se}_{1/2})_4$  tetrahedra up to  $x = 0.4$ . For  $x > 0.5$ , the glasses show a new vibrational band of an isolated  $\text{F}_2$  mode of the Ge-centred tetrahedra outside the clusters.

The system Ge–Se provides a rather wide range of concentrations for which it is possible to obtain bulk amorphous compounds. The system has been widely investigated using Raman and IR spectroscopy [1–7]. Alloys of the glassy system  $\text{Ge}_x\text{Se}_{1-x}$  in the Ge concentration range  $0 < x < 0.5$  are supposedly composed of Se chain,  $\text{Ge}(\text{Se}_{1/2})_4$  tetrahedral,  $\text{Ge}_2(\text{Se}_{1/2})_6$  ethane-like and  $\text{Ge}(\text{Se}_{1/2})_2$  structural units in proportions varying to comply with the actual  $x$ -values. Substitution of tin into  $\text{GeSe}_2$  makes the system of interest. The system  $\text{Ge}_{1-x}\text{Sn}_x\text{Se}_2$  ( $0 < x < 0.7$ ) has been studied with emphasis on the effect of tin on the tendency for the system to phase-separate into the constituent  $\text{GeSe}_2$  and  $\text{SnSe}_2$  binary components [8–10]. Related to the phase separation of the glasses during quenching of the melt is the difficulty in preparing completely homogeneous samples. By setting the composition on the selenium-rich side of the stoichiometric compound  $\text{GeSe}_2$  the tendency to crystallize is strongly reduced [11, 12]. In the present study, therefore, the sample compositions of interest,  $\text{Ge}_{1-x}\text{Sn}_x\text{Se}_{2.5}$  ( $0 < x < 0.6$ ), were chosen so that the compositions of these alloys are Se rich (related to  $\text{GeSe}_2$ ) in order to avoid crystallization of any significant fraction of the sample which might lead to phase separation and an unknown composition of the glass residue. Raman scattering [13] and optical absorption [14] studies in this system assure homogeneity for the melt-quenched samples. The present paper reports the far-infrared transmission through the glassy compositions with  $0 < x < 0.6$  in the system  $\text{Ge}_{1-x}\text{Sn}_x\text{Se}_{2.5}$ .

The glassy alloys of the system with  $x$ -values between zero and 0.6 were prepared by the conventional melt-quench technique. The high-purity (99.999%) elemental constituents were weighed and mixed in sealed evacuated ( $10^{-4}$  Torr) quartz ampoules followed by heat treatment in steps up to  $950^\circ\text{C}$  for about 24 h. In each case the reacting elements were first allowed to heat in a high-temperature electric furnace at  $210^\circ\text{C}$  for 2–3 h so that the element Se melted completely. The ampoules were kept rotating with a motor at about  $5\text{ rev min}^{-1}$ . The temperature of the furnace was then increased to  $400^\circ\text{C}$  and kept constant for 3–4 h. Subsequently the temperature was raised slowly and gradually to  $950^\circ\text{C}$ , keeping the ampoules at this temperature for 15–16 h whilst still rotating them. The melt in the quartz ampoules was then quenched into ice-cold water.

To check that the compositions made for study were amorphous, they were examined by the x-ray powder diffraction method. The lack of any sharp peaks indicates the glass state.

The observation of a single, very narrow crystallization transition in DSC scans for all the compositions assured homogeneity of the glasses. Far-infrared transmission measurements in the spectral range 50–650  $\text{cm}^{-1}$  were made at room temperature in vacuum with a Perkin-Elmer 1800 (FTIR) spectrophotometer. The resolution during measurements was 4  $\text{cm}^{-1}$ . Measurements were made using the polyethylene pellet method. The results of the transmission measurements are given in figures 1 and 2. The composition with  $x = 0$  ( $\text{GeSe}_{2.5}$ ) shows three bands at 170, 260 and 304  $\text{cm}^{-1}$ . The absorption band at 260  $\text{cm}^{-1}$  is very sharp whereas the other two bands are very weak. The existence of these bands is in good agreement with the results reported earlier [7]. On addition of Sn to  $\text{GeSe}_{2.5}$ , a new band appears at 231  $\text{cm}^{-1}$ . As the tin content is increased, the bands at 260 and 304  $\text{cm}^{-1}$  start to become weak and finally disappear at  $x = 0.5$  whereas the band at 231  $\text{cm}^{-1}$  becomes broad on increasing  $x$ . At  $x = 0.5$  (figure 2), a new band appears in the spectral range 258–278  $\text{cm}^{-1}$  which becomes very sharp at 278  $\text{cm}^{-1}$  for  $x = 0.6$ .

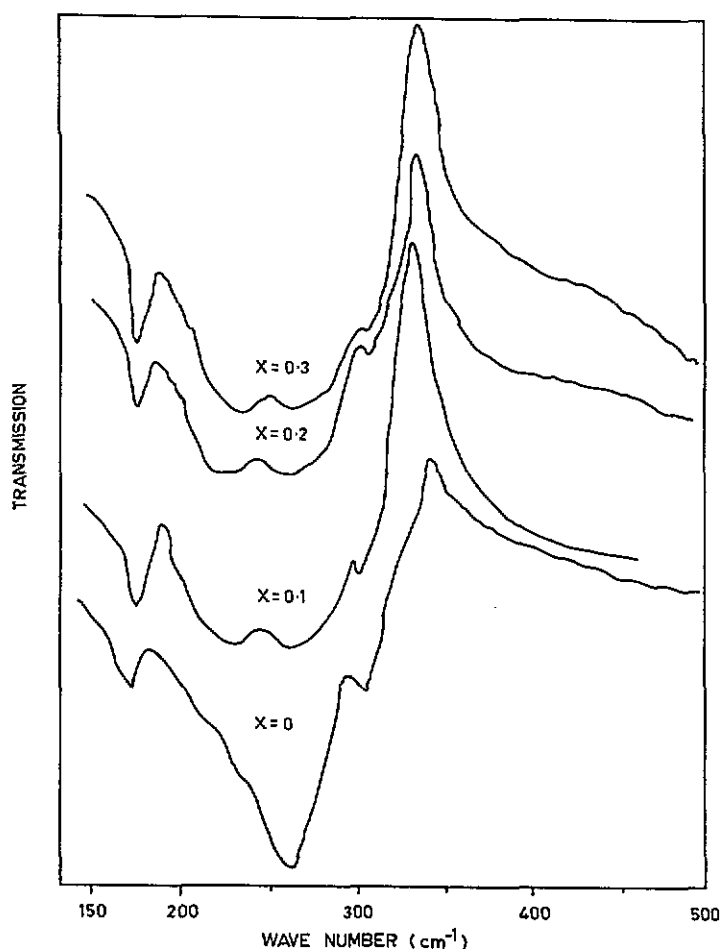


Figure 1. Far-IR transmission spectra of  $\text{Ge}_{1-x}\text{Sn}_x\text{Se}_{2.5}$  for  $x = 0, 0.1, 0.2$  and  $0.3$ . The ordinate scale for different  $x$ -values is shifted for clarity.

Two models have been proposed for the structure of Ge-Se glasses. In the first model [3, 15] called the chain-crossing model (CCM), the fourfold, tetrahedrally coordinated germanium atoms act as chain-crossing points in the selenium chain structure. In the second model [15], known as the random covalent model (RCM), the tetrahedrally coordinated

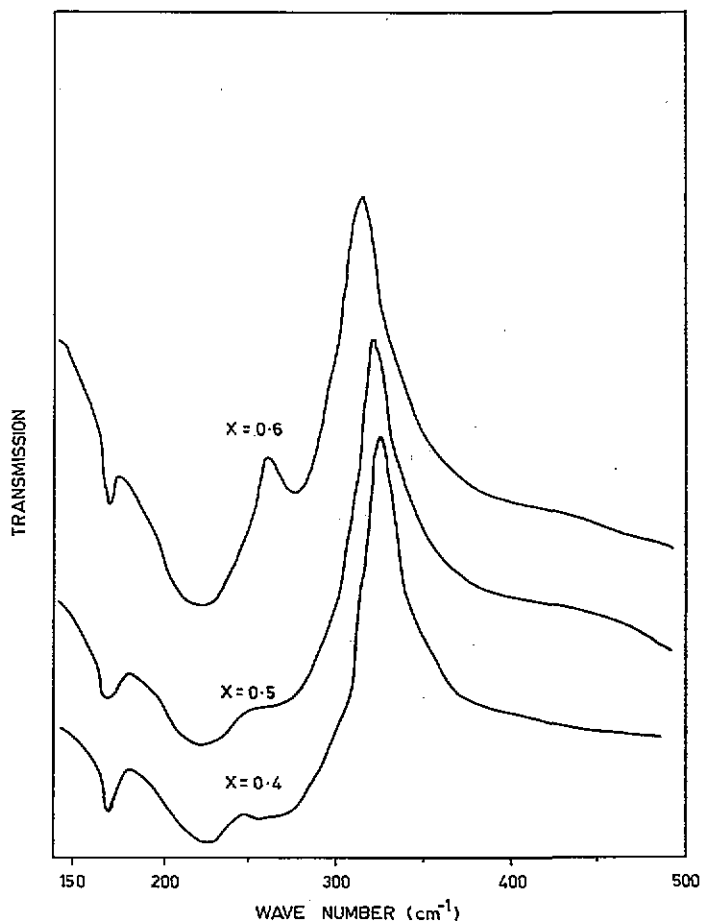


Figure 2. Far-IR transmission spectra of  $Ge_{1-x}Sn_xSe_{2.5}$  for  $x = 0.4, 0.5$  and  $0.6$ . The ordinate scale for different  $x$ -values is shifted for clarity.

germanium atoms bond to the other germanium atoms as readily as to the twofold-coordinated selenium atoms. The bond energies of the Ge-Se, Ge-Ge, Se-Se, Sn-Se, Ge-Sn and Sn-Sn bonds have been calculated on the basis [16] of the relation postulated by Pauling:

$$D(A-B) = [D(A-A) \times D(B-B)]^{1/2} + 30(X_A - X_B)^2$$

where  $X_A$  and  $X_B$  are the electronegativities of atoms A and B, and  $D(A-A)$  and  $D(B-B)$  are the bond energies of A-A and B-B bonds, respectively. The relative probabilities of the different bonds have also been calculated using the probability function  $\exp(D/k_B T)$  at room temperature as well as at the temperature of 950 °C at which the sample was prepared. The results are shown in table 1. From an energy point of view, heteronuclear bonds should be preferred. This is the case of bulk glasses prepared by quenching from the melt [2, 17]. The table also shows that there is the least probability of forming Ge-Ge, Ge-Sn and Sn-Sn bonds.

The characteristic vibration spectra of  $a-Ge_xSe_{1-x}$  have been explained in terms of its short-range order [2, 12, 15]. Chemical ordering is exhibited by these alloys at certain compositions ( $GeSe_2$  and  $Ge_2Se_3$ ). The vibration spectra in Se-rich alloy regimes ( $x < \frac{1}{3}$ ) are well described by the presence of two local molecular environments  $Ge(Se_{1/2})_4$  and  $(Se)_n$ . The Ge-rich alloy regime has a new local environment  $Se_{3/2}Ge-GeSe_{3/2}$ . Thus, in

**Table 1.** Bond energies and the relative probabilities of various bonds in  $\text{Ge}_{1-x}\text{Sn}_x\text{Se}_{2.5}$  alloys. The probability of the Ge-Se bond has been taken as unity.

Bond	Bond energy (kJ mol <sup>-1</sup> )	Relative probability at the following temperatures	
		27 °C	950 °C
Ge-Se	215.37	1	1
Sn-Se	207.49	$4.2 \times 10^{-2}$	$4.60 \times 10^{-1}$
Se-Se	184.10	$3.6 \times 10^{-6}$	$4.60 \times 10^{-2}$
Ge-Ge	157.32	$7.8 \times 10^{-11}$	$3.30 \times 10^{-3}$
Ge-Sn	150.04	$4.2 \times 10^{-12}$	$1.60 \times 10^{-3}$
Sn-Se	143.10	$2.6 \times 10^{-13}$	$8.20 \times 10^{-4}$

$\text{Ge}_x\text{Se}_{1-x}$ , the Se-rich composition would contain predominantly Ge-Se and Se-Se bonds, and the Ge-rich composition predominantly Ge-Se and Ge-Ge bonds in their networks.

In g-Se, the band near 275 cm<sup>-1</sup> has been assigned to the modes of Se ring fragments incorporated into an infinite chain [18]. For  $x = \frac{1}{3}$  in  $\text{Ge}_x\text{Se}_{1-x}$ , the 258 cm<sup>-1</sup> mode is known to come from the F<sub>2</sub> mode of the  $\text{GeSe}_{4/2}$  tetrahedron [4, 5]. The optical bands at 260 and 304 cm<sup>-1</sup> in our composition ( $\text{GeSe}_{2.5}$ ) may be attributed to the mutually interacting F<sub>2</sub> mode of the vibrations obtained by the model of Sen and Thorpe [19]. The origin of the other weak band at 170 cm<sup>-1</sup> is unknown. Izvekov *et al* [7] reported the band at 170 cm<sup>-1</sup> to be due to the vibrations of Ge-Ge bonds in the  $\text{Ge}_2(\text{Se}_{1/2})_6$  structural units. According to Tronc *et al* [3], for  $\text{Ge}_x\text{Se}_{1-x}$  with  $x < \frac{1}{3}$  the existence of the Ge-Ge bonds is forbidden. The IR absorption spectra of a-Ge obtained by Ball and Chamberlain [6] contain strong lines at 135, 183 and 275 cm<sup>-1</sup>, but they did not assign these values to Ge-Ge bonds in the  $\text{Ge}_x\text{Se}_{1-x}$  compositions. Again, Fukunaga *et al* [20] found a weak band at 220 cm<sup>-1</sup> for  $\text{GeSe}_2$  and attributed it to the vibrations of Ge-Ge bonds. This weak band at 170 cm<sup>-1</sup> in our composition may be assigned to the  $\text{GeSe}_2$  Raman mode [6].

$\text{SnSe}_2$  has a CdI<sub>2</sub> structure and does not form the glass state in contrast with  $\text{GeSe}_2$ . On substituting only a small amount of Ge atoms for Sn atoms, the glass is made easily within the range where the concentration of selenium atoms is three times that of group IV atoms. It is expected that the tin atoms have a fourfold coordination built of the sp<sup>3</sup> hybrid orbitals. On substitution of tin atoms into  $\text{GeSe}_{2.5}$ , a new band appears at 231 cm<sup>-1</sup>. Mikrut and McNeil [21] calculated the vibrational energies of the  $\text{Sn}(\text{Se}_{1/2})_4$  and  $\text{Ge}(\text{Se}_{1/2})_4$  modes and found that the energy of the breathing mode of the Sn-centred tetrahedron is 24 cm<sup>-1</sup> lower than that of the breathing mode of the Ge-centred tetrahedron. In our composition, a difference of  $27 \pm 1$  cm<sup>-1</sup> between the energies of the symmetric breathing mode (261 cm<sup>-1</sup>) of the  $\text{Ge}(\text{Se}_{1/2})_4$  tetrahedron and the new band at 231 cm<sup>-1</sup> is observed. This band at 231 cm<sup>-1</sup> is assigned, therefore, to the vibrational mode of the  $\text{Sn}(\text{Se}_{1/2})_4$  tetrahedron. Fukunaga *et al* [20] also observed a similar band at 228 cm<sup>-1</sup> for  $\text{Ge}_{1-x}\text{Sn}_x\text{Se}_2$  alloys which they assigned to the  $\text{Sn}(\text{Se}_{1/2})_4$  tetrahedron mode. As the Sn concentration is increased, the vibration mode of  $\text{Ge}(\text{Se}_{1/2})_4$  at 260 cm<sup>-1</sup> becomes broad and weak whereas the Sn-centred mode at 231 cm<sup>-1</sup> shifts towards a lower energy and broadens. At  $x = 0.5$  the F<sub>2</sub> mode of vibration (304 and 260 cm<sup>-1</sup>) disappears and a new band appears in the spectral range 258–278 cm<sup>-1</sup>. This band becomes very sharp at 278 cm<sup>-1</sup> for  $x = 0.6$ .

$\text{GeSe}_2$  according to Bridenbaugh *et al* [22] is composed of fragments of the layered crystal structure, consisting of corner-sharing  $\text{Ge}(\text{Se}_{1/2})_4$  tetrahedra (chains) connected by edge-sharing tetrahedra. The fragments, referred to as 'rafts', are terminated in the direction of edge-sharing tetrahedra with Se-Se bonds but can extend indefinitely in the direction of the corner-sharing tetrahedra. Each homopolar Se bond connects two neighbouring

corner-sharing tetrahedra so that the tetrahedra located on the edges of the clusters share one Se atom and one Se dimer. These tetrahedra are referred to as 'outrigger' sites. In  $\text{Ge}_{1-x}\text{Sn}_x\text{Se}_{2.5}$ , Sn atoms are supposed to substitute for Ge atoms in the 'outrigger' sites. As the Sn concentration is increased, the scarcity of these sites causes the 'rafts' to break up into smaller 'rafts', creating more 'outrigger' sites for the Sn atoms to occupy. In  $\text{Ge}_{1-x}\text{Sn}_x\text{Se}_{2.5}$  glasses, the substitution of Ge atoms by Sn atoms takes place up to  $x = 0.4$ . That is why the intensity of the  $\text{Ge}(\text{Se}_{1/2})_4$  band decreases with the increase in concentration  $x$  whereas the intensity of the  $\text{Sn}(\text{Se}_{1/2})_4$  band increases. At  $x = 0.5$ , the vibrational bands ( $260$  and  $304 \text{ cm}^{-1}$ ) disappear and a new band appears in the  $258\text{--}278 \text{ cm}^{-1}$  spectral range which becomes very sharp at  $278 \text{ cm}^{-1}$  at  $x = 0.6$ . DSC measurements in our samples also show that the glass transition temperature increases with increasing  $x$  up to  $x = 0.4$ ; thereafter it starts to decrease. This indicates that some structural changes are taking place at  $x = 0.5$ . Ksendzov *et al* [14] have reported that for  $x > 0.4$  the glasses have increasing ability to relax and optimize bent Se–Se–Se bonds because the large chemically ordered clusters become floppy [23]. So the band at  $278 \text{ cm}^{-1}$  for  $x > 0.5$  may be assigned to the vibrations of the nearly isolated  $\text{F}_2$  mode of  $\text{Ge}(\text{Se}_{1/2})_4$  tetrahedra which are connected with the selenium chains outside the clusters [20] because of lack of symmetry and the relaxation of selection rules.

In conclusion we have observed the far-infrared transmission spectra of various compositions in the glassy system  $\text{Ge}_{1-x}\text{Sn}_x\text{Se}_{2.5}$  ( $0 < x < 0.6$ ) in the spectral range  $50\text{--}650 \text{ cm}^{-1}$ . The present analysis of far-IR results and the bond energies indicates that the alloys of  $\text{Ge}_{1-x}\text{Sn}_x\text{Se}_{2.5}$  fit the CCM model. There is no evidence of bonds such as Ge–Ge, Sn–Ge, etc. Sn atoms substitute for the Ge atoms in the 'outrigger' sites of  $\text{Ge}(\text{Se}_{1/2})_4$  tetrahedra up to  $x = 0.4$ . For  $x > 0.5$ , the glasses have increasing ability to relax and optimize bent Se–Se–Se bonds. A new band appears which is assigned to the vibrations of an isolated  $\text{F}_2$  mode of the Ge-centred tetrahedra outside the clusters.

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