



**ISSN: 2454-9940**



**INTERNATIONAL JOURNAL OF APPLIED  
SCIENCE ENGINEERING AND MANAGEMENT**

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# Research on Sn<sub>x</sub>-Sb<sub>5</sub>-Se<sub>95x</sub> chalcogenide glasses using infrared and Raman spectroscopy

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## Abstract

Systems based on tin, antimony, and selenium (Sn-Sb-Se) are ternary chalcogenide compounds of the IV-V-VI family. Due of their high elemental weights, continuously varying band gap-energies and lattice constants, and electrical characteristics, they may find use in infrared regions. Using Fourier transform infrared (FTIR) and Raman spectroscopy, the structures of Sn<sub>x</sub>-Sb<sub>5</sub>-Se<sub>95x</sub> system samples synthesized through melt quench have been investigated; here,  $x = 0, 5, 10,$  and  $12.5$  mole percent. The FTIR spectrum shows that the intensity and breadth of the IR peak change from long to short wavelength when Sn-mole% is added to the system. These modifications include the appearance of the pyramidal SbSe<sub>3</sub> mode between 147 and 210 cm<sup>-1</sup> for Sn = 5 mole% and the asymmetrical tetrahedral SnSe<sub>4</sub> mode between 117 and 145 cm<sup>-1</sup> for Sn = 12.5 mole%, all the way up to 180 cm<sup>-1</sup> in spectra. A pyramidal SbSe<sub>3</sub> peak, seen in Raman spectra, is located at 190 cm<sup>-1</sup>. The addition of Sn-mole% raises the intensity of this peak to a wavelength of 183 cm<sup>-1</sup>. The average co-ordination number,  $\bar{r} = 2.4$ , and the percentage of Sn-Se bonds,  $f_{\text{Sn-Se}} = 44.3\%$ , define the amorphous area, confirming the appropriateness of utilizing 4, 3, and 2 as co-ordination numbers of Sn, Sb, and Se, respectively.

## Introduction

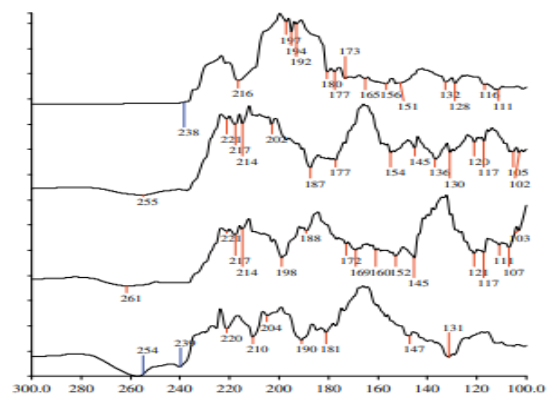
To produce novel materials with semiconducting characteristics, studying the amorphous and crystalline areas of chalcogenide glasses is of practical relevance. Theoretically, it's valuable because it helps distinguish between the effects of short- and long-range commands on material characteristics. Previous research has determined that in the glass area, the mole percent of Sn in Ge<sub>1x</sub>-Sn<sub>x</sub>-Se<sub>2</sub>, As<sub>33</sub>-Se<sub>67x</sub>-Sn<sub>x</sub>, and Ge-Sn-Sb-Se is 19.8%, 7.0%, and 12.5%, respectively (Jagtap and Zope, 1990; Mikurt and McNell, 1890; Kislitskaya et al., 1971). Solar cell materials, memory switching devices, holographic recording systems, thermal imaging systems, and infrared sensors are just some of the many uses for chalcogenide glasses that include selenium (Bureau, 2005; Padiyan et al., 2004; Kumar et al., 2006). In specifically, it was envisaged that Sn would be introduced into the Sb-Se system, with a co-ordination number of 4, prior to the creation of the stoichiometric compound, and that 12.5 mole percent of Sn would be incorporated

into the glass (Adam et al., 2005, 2006, 2002). Above this range, however, the pronounced metallic nature of Sn with co-ordination number 6 causes the problem in glass production. It is worth noting that in the binary stoichiometric compounds Sb<sub>2</sub>Se<sub>3</sub> and SnSe<sub>2</sub>, the atomic stoichiometry of Sb and Sn resulted in a change in the co-ordination number of Se from 2 to 3. Zhenhua (1991) and Philips (1979) determined that the average stoichiometric co-ordination number for these two elements was  $\bar{r} = 3.8$  and 4, respectively. Infrared and Raman spectra of the Sn<sub>x</sub>-Sb<sub>5</sub>-Se<sub>95x</sub> system are obtained and described in this study. 2. Methods used in experiments The Sn and Sb granules used had a purity of 99.999%, whereas the Se granules utilized had a purity of 99.99%. To prevent accidental contamination, the containers containing these items were opened in a carefully monitored procedure. Sn, Sb, and Se were batched utilizing sample

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percentage techniques and weighed on a closed scale balance to create a 5.00 g sample (Adam et al., 2005, 2002). Elements were mixed together and then put in a clean quartz ampoule. A vacuum pump was connected to the ampoule, and the space within was reduced to 66.5 Pa. After that, for the next half an hour, the pumps were fed a supply of inert argon gas. In the end, an oxygen-natural gas flame melt was used to close the ampoule by gently heating its wall and bending it. Selenium's high vapour pressure and propensity to react with oxygen are well-known facts. As a result, extreme caution was used while closing the tube to prevent an explosion. After that, we placed the ampoule into an orbital-shaking furnace. Six hours of heating at a pace of 5 C min<sup>-1</sup> got us to 700 C. To ensure that our samples were well mixed, we used a connected orbital shaker to agitate them at a rate of 100.0 rpm. In order to meet the urgent need for rapid chilling, the ampoule was submerged in liquid nitrogen. The spectra were collected using a Fourier transform infrared (FTIR) spectrophotometer (model 8000 from Shimadzu) at room temperature with a resolution of 2.0 cm<sup>-1</sup>. At room temperature, a disc manufactured using the KBr process was subjected to a polarized Raman spectrum recording (using a Magna-spectrometer 560 at the Rubber Research Center in Malaysia) in the range 400-100 cm<sup>-1</sup> with a 4 cm<sup>-1</sup> step. The computer kept track of how many photons were counted at each stage. Third, the findings and analysis Sn<sub>x</sub>Sb<sub>5</sub>Se<sub>95-x</sub> Infrared Spectra 3.1 Spectra of the Sn<sub>x</sub>-Sb<sub>5</sub>-Se<sub>95-x</sub> system at infrared wavelengths (where x = 0, 5, 10, and 12.5) are shown in Fig. 1. At the very least five or six distinct transmission bands may be seen in the infrared transmission (%) against the

wave number (cm<sup>-1</sup>) spectrum shown at the very bottom. In Ge-Se alloy, the band at 100-131 cm<sup>-1</sup> is associated with the Se<sub>8</sub>-ring bending mode, whereas the band at 115 cm<sup>-1</sup> is associated with the Se<sub>8</sub> chain (Goyal and Maan, 1995). According to Kato et al. (1983), the band between 131 and 190 cm<sup>-1</sup> is due to the SbSe<sub>3</sub> stretching mode, and its two shoulders may be found at 147 and 181 cm<sup>-1</sup>. The band between 190 and 210 cm<sup>-1</sup> is associated with the Se-Se stretching mode or the Sb-Se bending mode, while the band between 210 and 239 cm<sup>-1</sup> is related to the Sb-Se bending mode.



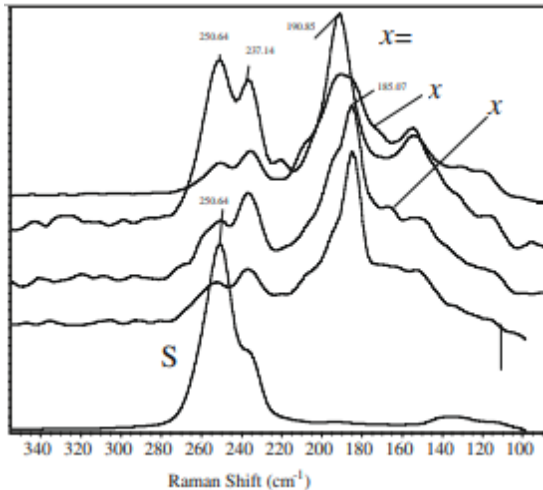
Transmission spectra in the infrared for the Sn<sub>x</sub>Sb<sub>5</sub>Se<sub>95-x</sub> system are shown in Figure 1.

with a sloping upper edge at 220 revealing SbSe<sub>3</sub> stretching mode and Se<sub>8</sub> chain mode. However, the Sb-Se bond in Sb-Ge-Se glass was attributed to the band between 177 and 210 cm<sup>-1</sup> (Sharma et al., 1989). Absorption peaks around 227 and 247 cm<sup>-1</sup> were attributed to the Se polymeric chain and the Se<sub>8</sub> ring modes, respectively (Zhenhua, 1991), establishing an unambiguous assignment of the transmission cutoff at 254 cm<sup>-1</sup> to the Se<sub>8</sub> chain ring. The Sn = 5% mole percentage in the sample is shown by the second spectrum. The tetrahedral mode of SnSe<sub>4</sub> has been designated a new band with a

frequency range of 117 to 145  $\text{cm}^{-1}$ . In the prior spectra, this band was not detected. In this composition, however, Adam et al. (2005) describe a first-chance formation of Sn-Se covalent bonds, as shown by the Sn-Se bond percentage. Raman study of binary Sn-Se, which reveals a strong intensity peak at 150  $\text{cm}^{-1}$  (Adam et al., 2002), further lends credence to this attribution. When the band in  $\text{Sb}_5\text{Se}_9$  between 147 and 181  $\text{cm}^{-1}$  has its intensity lowered, it moves to a new band between 169 and 198  $\text{cm}^{-1}$ , with a shoulder at 188  $\text{cm}^{-1}$ . Another pyramidal  $\text{SbSe}_3$  mode is responsible for this band. In contrast, the  $\text{SnSe}_4$  tetrahedral mode is associated with the shoulder at 188  $\text{cm}^{-1}$ .  $\text{SnSe}_4$  units were identified as the source of the Raman shift at 189  $\text{cm}^{-1}$  in  $\text{Ge}_1\text{Sn}_x\text{Se}_2$  glasses (Stevens et al., 1985). Se-Se or  $\text{SbSe}_3$  bending modes are responsible for the 198-238  $\text{cm}^{-1}$  third band, whereas the 214 and 221  $\text{cm}^{-1}$  shoulder regions are associated with  $\text{Se}_8$  chains. It's worth noting that IR analysis has trouble distinguishing the frequency vibrations of Sn and Sb due to their comparable atomic masses. If there is any overlap, it may be explained by comparing and supporting the IR analysis with Raman investigation.

The intensity of the band is seen to change from roughly 117-145  $\text{cm}^{-1}$  at  $x = 5$  to 154-187  $\text{cm}^{-1}$  in  $\text{Sn} = 10$ -mole% spectra.  $\text{SnSe}_4$  mode is responsible for this new frequency range. Between 187 and 237  $\text{cm}^{-1}$ , the  $\text{SbSe}_3$  pyramidal band stretches, with shoulders at 202, 214, 217, and 221. The Se-chain mode, which may alternatively be ascribed to the pyramidal  $\text{SbSe}_3$  mode, is responsible for the shoulders about 217 and 237  $\text{cm}^{-1}$ . When analyzing the spectrum at  $\text{Sn} = 12.5$  mole%, a change in band position and a decrease in band intensity are seen. A

tetrahedral  $\text{SnSe}_4$  bending mode is seen in the band at 132–151  $\text{cm}^{-1}$ . A tetrahedral  $\text{SnSe}_4$  stretching mode is attributed to the 180-194  $\text{cm}^{-1}$  band, whereas a pyramidal  $\text{SbSe}_3$  stretching mode is responsible for the 194-216  $\text{cm}^{-1}$  band. The last band, located between 216 and 238  $\text{cm}^{-1}$ , has been variously attributed to a  $\text{Se}_8$ -chain mode or a pyramidal  $\text{SbSe}_3$  bending mode.  $\text{Sn}_x\text{Sb}_5\text{Se}_9$  Raman vibration spectrum, section 3.2 Fig. 2 shows the Raman spectra of amorphous Se and the  $\text{Sn}_x\text{-Sb}_5\text{-Se}_9$  combination. In the Raman spectrum of amorphous Se, the peak at 250.64  $\text{cm}^{-1}$  is the most prominent feature. As noted by Mort (1973), this peak is also seen in monoclinic selenium. Based on this evidence and the polarization dependence of this line, the 250  $\text{cm}^{-1}$  Raman peak is attributed to a fully symmetric vibration mode of the  $\text{Se}_8$ -ring. The prominent peak of crystalline trigonal Se was found to correspond with a weak shoulder in amorphous Se at 239  $\text{cm}^{-1}$  (Mort, 1973).  $\text{Se}_8$ -bending mode therefore occupies the low frequency range at 239  $\text{cm}^{-1}$ . However, in  $\text{Ge}_x\text{Se}_1$  glasses, Raman vibrations at 235 and 255  $\text{cm}^{-1}$  are attributed to Se-Se chains (Wong et al., 1998). Many bands can be seen in the Raman spectra of the  $\text{Sn}_x\text{-Sb}_5\text{-Se}_9$  system at wavelengths of 250, 239, 190, 183, and 150  $\text{cm}^{-1}$  (see Fig. 2 for an example). For the  $\text{Sb}_5\text{Se}_9$  spectrum ( $x = 0$ ), the peak at 190  $\text{cm}^{-1}$  is associated with the symmetrical stretching mode of the  $\text{SbSe}_3$  pyramidal vibration. We identify the two brief peaks at 250 and 239  $\text{cm}^{-1}$  as the stretching and bending modes of  $\text{Se}_8$ . The symmetrical bending pyramidal of  $\text{SbSe}_3$  is responsible for the fourth peak at 150  $\text{cm}^{-1}$ . It can't be ignored



*Raman spectra of amorphous Se (Figure 2) and the Sn<sub>x</sub>-Sb<sub>5</sub>-Se<sub>95x</sub> system for x = 0, 5, 10, and 12.5 are shown.*

Raman peak intensity and breadth are sensitive to changes in Sn, Sb, and Se mole percent. The peak at 190 cm<sup>-1</sup> in the spectra of Sn = 5 mole%, which is attributed to the stretching mode of pyramidal SbSe<sub>3</sub>, is shifted and attenuated. This modification denotes the possibility that Sn, rather than Se, shares the bonds in Sn-Se-SbSe<sub>3</sub> net. The symmetric bending mode of SnSe<sub>4</sub> tetrahedral is attributed to the 150 cm<sup>-1</sup> peak, which is somewhat higher than that of Sb<sub>5</sub>Se<sub>95</sub>. The presence of Se chains is suggested by the enhancement of the peak intensities at 250 and 239 cm<sup>-1</sup>. The Raman peak shifts dramatically in the spectrum at Sn = 10 mole%. At 185 cm<sup>-1</sup>, the tetrahedral mode of SnSe<sub>4</sub> is extending symmetrically, but the pyramidal SbSe<sub>3</sub> stretching is still dominating. According to reports (Mikurt and McNell, 1890), the bending mode of SnSe<sub>4</sub> has a peak at 184 cm<sup>-1</sup>. This pattern persists in the Sn = 12.5 mol% spectra, where the peak at 184 cm<sup>-1</sup> may be ascribed more credibly to the symmetric stretching of the SnSe<sub>4</sub> tetrahedral mode than to the stretching of the SbSe<sub>3</sub> pyramidal mode. We can better describe the structure of the

Sn-Sb-Se system thanks to the results of IR and Raman spectrometers. The Sb-Se structure is modified by the incorporation of coordination number 4 in the glass transition region upon addition of Sn mole% to the system. The creation of glass in a Se-rich area, where the concentrations of Sn and Sb are below the levels required to form their stoichiometric binary compounds with Se, is supported by the observation of a Se stretching bond. The 8-N rule of classical valence bond theory may be used to conceptualize the local coordination in Sn-Se and Sb-Se glasses' structure (Lucovsky et al., 1977). Long chains of selenium atoms with a coordination number of 2 were thought to make up the structure of Se glasses (Aronovitz et al., 1983). Cross-linking atoms, such as Sn and Sb, were introduced in trace quantities to these selenium chains. These numbers should be less than those needed to make stoichiometric quantities of SnSe<sub>2</sub> and Sb<sub>2</sub>Se<sub>3</sub>. As a result, the glass framework may expand. When covalently bound, the Sn atoms are four-coordinated, with each Sn atom forming a connection to a Se atom, while the Sb atoms are three-coordinate, with each Sb forming a bond to a Se atom. The tetrahedral unit of SnSe<sub>2</sub> glass is derived to be SnSe<sub>4</sub>, whereas the pyramidal unit of Sb<sub>2</sub>Se<sub>3</sub> glass is SbSe<sub>3</sub>. These units branch out among Se chains and create a web-like structure of Se<sub>3</sub>-Sn-Se-Se-Sb-Se<sub>2</sub> in the glass. Strong evidences corroborate the creation of this net structure, including the appearance of a new IR transmission band in the range of 125-145 cm<sup>-1</sup> and the shift of the Raman peak from 190 to 183 cm<sup>-1</sup> as a result of raising Sn-mole% while keeping Sb-mole% constant at 5.

**4. Final Thoughts** The asymmetrical stretching of the pyramidal

SbSe<sub>3</sub> mode is prominent at 147 and 210 cm<sup>-1</sup> in the IR-transmission data for the Sn<sub>x</sub>-Sb<sub>5</sub>-Se<sub>95-x</sub> system, and the Se-chain mode appears in the binary system at 210-254 cm<sup>-1</sup>. The peak moves and additional transmission bands appear for different Sn concentrations, beginning at 117-145 cm<sup>-1</sup> for spectra with Sn = 5 mole% and ending at 180 cm<sup>-1</sup> for those with Sn = 12.5 mole%, all of which may be explained by the asymmetric infrared active of the tetrahedral SnSe<sub>4</sub> mode. The Raman peak for pyramidal SbSe<sub>3</sub> is located at 190 cm<sup>-1</sup>, but increasing the Sn mole percentage induces a shift in the Raman spectrum to 183 cm<sup>-1</sup>, showing the presence of Sn-Se bonds. According to the findings, the optimal coordination numbers for promoting glass formation in the Sn-Sb-Se system are 4, 3, and 2, which correspond to the co-ordination numbers of Sn, Sb, and Se, respectively. Acknowledgements The author acknowledges the financial backing of University of Kordofan in Sudan and University of Technology in Malaysia.

## References

- Asa B. Adam. 2002. Malaysian Institute of Technology Doctoral Dissertation. Citation: Adam, A.B., S. Sakrani, and Y. Wahab, 2005. *J. Materials Science*, 40(7), 1571. Reference: Adam AB, Sakrani S, Wahab Y (2006). 41, 5797 (*J. Materials Science*). It was published in 1983 by Aronovitz, J.A., Bonavar, J.R., Marcus, M.A., and Phillips, J.C. *Review of Physics B* 28(8):4454. Report by Bureau et al. 345, 346, 276 *J. Non-Cryst. Solids*. Reference: Goyal DR, Maan AS (1995). 183, 182 *J. Non-Cryst. Solids*. R. Jagtap and J. K. Zope, 1990. *Non-Crystalline Solids* 127 (19). Kato, M., S. Onari, and T. Arai. *Japan Journal of Applied Physics* 22.9:1382. 1971 publication by E.A. Kislitskaya and V.F. Kokorina. *A. I. Prikladnoi Khimii*, 44-3, 646 Z. Thangaraj, R., Kumar, P., K.S. Bindra, N. Suri, and P. Kumar, 2006. *Journal of Physics: Applied Physics* 39, 642. It was published in 1977 by Lucovsky, G., F.L. Galeener, R.H. Geils, and R.C. Keezer. The use of infrared and Raman spectroscopy to investigate chemical ordering in binary chalcogenide glasses. This article is in Gaskell, P.H. (Ed. ), *The Structure of Non-Crystalline Materials*. London: Taylor and Francis Ltd., page 127. 1890 citation: Mikurt, J.M., and McNell, L.E. *Journal of Non-Crystalline Solids* 114:127. Mort, J., 1973. Infrared spectroscopy through the Raman effect. *Electronic and Structural Properties of Amorphous Semiconductors*, edited by P.G. Le Comber and J. Mort. p. 475 in Academic Press, London and New York. 2004 - Padiyan, D.P., A. Marikani, and K.R. Murali. *Physical Review Materials* 88, 250. 1979 John C. Philips. 153 *J. Non-Cryst. Solids*. Published in 1989 by Sharma, A.K., K.L. Bhatia, V.K. Bhatnagar, and S.K. Malik. *Journal of Non-Crystalline Solids* 108:309. Authors: Stevens, M., P. Boolchand, and J.G. Hernandez. 31(2&#971;981 of the *Physical Review B*. Y. Wong, O. Matsuda, K. Inove, O. Yamamuro, T. Matsuo, and K. Murose published their findings in 1998. *Journal of Non-Crystalline Solids* 702(232-234). 1991 L. Zhenhua. *Non-Crystalline Solids* 127, 298 (JNCS).