

Far-infrared absorption in $\text{Sb}_{15}\text{Ge}_{10}\text{Se}_{75}$

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The study of the IR spectra of chalcogenide glasses is very important because it leads to an insight into the molecular structure of these glasses. Recently several workers have reported [1-4] vibrational spectroscopic studies of these glasses and have tried to assign the observed absorptions to the different chemical bonds in the system. In the present work far-IR absorption studies have been carried out on $\text{Sb}_{15}\text{Ge}_{10}\text{Se}_{75}$ glass. The results are discussed in the light of probabilities and the bond energies of various chemical bonds possible in this glass.

High-purity (99.999%) elements (antimony, germanium and selenium) in the desired proportion were heated at 1000°C for 10 h in an evacuated quartz tube with continuous rocking. The material was then quenched in ice-cold water. Differential thermal analysis and scanning electron microscopy confirmed the glassy nature of the alloy and the absence of any phase separation, etc. The far-IR spectrum was recorded on a Fourier Transform Spectrograph Polytec 30 from 50 to 500 cm^{-1} . A very fine layer of powdered sample was dispersed on the polyethylene sheet using a polyethylene finger. The spectrum of polyethylene was used as the reference spectrum to provide correct information of the sample.

Fig. 1 shows the far-IR absorption spectrum of the $\text{Sb}_{15}\text{Ge}_{10}\text{Se}_{75}$ sample. There are three absorption bands at 205, 280 and 383 cm^{-1} , and two shoulders centred around 310 and 347 cm^{-1} . There also seems to be a very weak band around 110 cm^{-1} . No other band was observed in the 4000 to 50 cm^{-1} region.

Two models have been proposed for the structure of Ge-Se glasses. In the first model [5, 6], called the "Chain Crossing Model" (CCM), the fourfold, tetrahedrally co-ordinated germanium atoms act as chain crossing points in the selenium chain structure. In the second model [6], known as the "random covalent model" (RCM), the tetrahedrally co-ordinated germanium atoms bond to the other germanium atoms as readily as to the twofold co-ordinated selenium atoms.

The energies of Ge-Se, Sb-Se, Se-Se, Ge-Ge and Sb-Ge bonds have been calculated on the basis [7, 8] of the relation postulated by Pauling:

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

where x_{A} is the electronegativity of atom A and $D(\text{A-A})$ is the energy of the bond A-A. The relative probabilities of the different bonds have also been calculated using the probability function $e^{D/KT}$ at room temperature as well as at the temperature (1000°C) at which the sample was prepared. The results are shown in Table I. The order of bond energies and the

probability functions indicate that the selenium atoms will preferentially first saturate germanium atoms and thereafter Sb-Se and Se-Se bonds will be formed. The results also show that there is least probability of forming Ge-Ge, Sb-Sb and Ge-Sb bonds. In the present composition where the germanium content is only 10% the CCM model is followed. The total number of selenium atoms required to saturate the tetrahedrally co-ordinated germanium and trivalent antimony atoms is 42.5. The rest of the selenium atoms will go to form the chain-like structure, and these chains will be interlinked by germanium and antimony atoms. The bond energy results exclude the random covalent model structure where the germanium atoms can be linked to other germanium atoms. Bonds like Sb-Ge and Sb-Sb are also ruled out because their bond energies are low.

Ball and Chamberlain [1] and Izvekov *et al.* [2] have reported far-IR measurements on Ge-Se glasses, but the transmission results reported by the two groups are quite different. In the present sample, $\text{Sb}_{15}\text{Ge}_{10}\text{Se}_{75}$, in which GeSe_4 tetrahedra are expected to exist isolated from other germanium and antimony atoms, the different absorption should correspond to the Ge-Se systems. Our results match the far-IR reflection data for the Ge-Se system reported in [1]. The Ge-Se alloy with 15% germanium atoms show the bonds at 275 and 287 cm^{-1} assigned to the GeSe_2 Raman mode and ν_1 mode, respectively, of Ge-Se-Ge. We also observed a strong band at 280 cm^{-1} in the Sb-Ge-Se alloy, which seems to be the ν_1 mode of Ge-Se-Ge. It can also have the Raman contribution of GeSe_2 . The shoulders centred around 310 and 347 cm^{-1} , in agreement with [1; 307 and 339 cm^{-1}], are also GeSe_2 and GeSe_4 Raman modes, respectively, which become active in the IR due to lack of symmetry and the relaxation of selection rules. Another strong absorption at

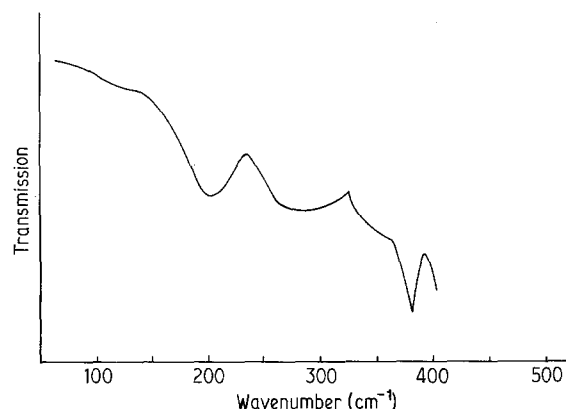


Figure 1 Far-IR transmission spectrum of $\text{Sb}_{15}\text{Ge}_{10}\text{Se}_{75}$.

TABLE I Bond energies and the relative value of probabilities of various bonds at 27 and 1000°C in Sb-Ge-Se alloy. The probability of the Ge-Se bond has been taken as unity

Bond	Bond energy (kJ mol ⁻¹)	Relative probability at	
		27° C	1000° C
Ge-Se	206.77	1	1
Sb-Se	183.89	1.0×10^{-4}	1.1×10^{-1}
Se-Se	184.10	1.1×10^{-4}	1.2×10^{-1}
Ge-Ge	157.32	2.4×10^{-9}	9.3×10^{-3}
Ge-Sb	141.17	3.7×10^{-12}	2.0×10^{-3}
Sb-Sb	126.36	9.9×10^{-14}	5.0×10^{-4}

205 cm⁻¹ is probably due to the ν_1 mode in GeSe₄. The absorptions due to asymmetric stretching of Sb-Se bonds are also expected in this region. The weak band at 110 cm⁻¹ is the ν_4 mode in GeSe₄ are accepted by Izvekov *et al.* [2] and Ball and Chamberlain [1] who have observed a band around 103 and 107 cm⁻¹, respectively, in the Ge-Se alloy. No band has been observed around 170 cm⁻¹, which is the region of the Ge-Ge bond, confirming that Ge-Ge bonds are absent in Sb₁₅Ge₁₀Se₇₅ as supported by the bond energy analysis. The results of the absorption bands in the present ternary alloy lie in the range of experimentally observed results in GeSe₄ tetrahedra in the Ge-Se system and calculated [1] ones on the basis of the GeBr₄ molecule.

The present analysis of far-IR results and the bond energies indicate that Sb₁₅Ge₁₀Se₇₅ alloy fits in the CCM model [5].

In conclusion, the structure of the Sb₁₅Ge₁₀Se₇₅ is based on the chain structure of selenium atoms inter-linked by the tetrahedrally co-ordinated germanium and perhaps trivalent antimony atoms. There is no evidence of bonds like Ge-Ge, Sb-Ge, etc.

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