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Journal of Non-Crystalline Solids 196 (1996) 183–186

JOURNAL OF
NON-CRYSTALLINE SOLIDS

Infrared studies of a $Ge_{0.20}Sb_{0.05}Se_{0.75}$ glassy semiconductor

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Abstract

Bulk samples of the glassy alloy $Ge_{0.20}Sb_{0.05}Se_{0.75}$ were fabricated by quenching the melt at 1000°C in ice water. The samples were obtained as polyethylene disks. The infrared transmission spectrum was measured in the wavenumber region 500–90 cm^{-1} at 4 cm^{-1} resolution, at room temperature and in a continuously purged sample compartment. The infrared features are assigned to Ge–Se bonds in $GeSe_4$ tetrahedral units and Sb–Se bonds in pyramidal molecules. The band at 95 cm^{-1} is considered as being due to Se_8 rings. On the other hand, from X-ray diffraction data it was found that a structural model, based on the random covalent network model assuming tetra-coordinated Ge, tri-coordinated Sb and di-coordinated Se, confirms the information obtained from infrared spectroscopy.

1. Introduction

The structure of $Ge_{0.20}Sb_{0.05}Se_{0.75}$ chalcogenide glass was investigated by means of infrared spectroscopy (IR) and X-ray diffraction. In this paper, we discuss the infrared transmission measurements of this material, under the following assumptions: (i) we assume the 'valence force field model' (VFF) [1], and (ii) the position of the intrinsic infrared features is influenced mainly by stretching force constants of the corresponding chemical bonds.

The VFF allows the determination of the vibrational frequencies, ω_i, of the possible structural units of the alloy under study [2]. Thus, ω can be expressed as a combined function

$$\omega = f(k_r, k_\theta, m_i, \theta), \tag{1}$$

where k_r and k_θ are force constants, m_i is the mass of the atoms which constitute the glass, and d and θ are the distance and bond angle between atoms, respectively. The magnitude of k_θ is about 10% of k_r [3] and was assumed to be this value in all calculations.

In order to determine the stretching force constant, k_r, the following methods have been used.

(i) A relation, obtained by Gordy [4], of the form

$$k_r = aN\left(x_A x_B/d^2\right)^{3/4} + b \tag{2}$$

has been found to hold accurately for a large number of diatomic and simple polyatomic molecules in their ground states. Here, a and b are constants which depend on the structural unit type, x_A and x_B are the electronegativities in the Pauling scale [5] (Ge 1.8; Sb 1.9; Se 2.4), d is the bond length and N is the bond order, which can be determined [6] from the expression

$$N = \frac{d + 2r_1 - 3r_2}{2d + r_1 - 3r_2}, \tag{3}$$

where r_1 and r_2 are the covalent radii for the single bond and the double bond, respectively. The covalent radii of the atoms [6] are listed in Table 1.

(ii) Somayayulu [7] has developed a method for predicting the polyatomic force constants by using

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SSDI 0022-3093(95)00583-8

Table 1
Covalent radii of the atoms

	Ge	Sb	Se
r_1 (Å)	1.22	1.41	1.17
r_2 (Å)	1.11	1.31	1.07

the elemental covalent force constants and electronegativities as follows:

$$k_{AB} = (k_{AA} k_{BB})^{1/2} + (x_A - x_B)^2, \quad (4)$$

where k_{AB} is the force constant between the elements A and B, and k_{AA} and k_{BB} are the force constants for bonds A–A and B–B, respectively, the values of which are (10^5 dyn cm^{-1}) 1.29 for Ge–Ge, 0.87 for Sb–Sb and 1.91 for Se–Se.

(iii) A third method owing to Siebert [8] suggests the following expression:

$$k = N k_{AB}, \quad (5)$$

where k_{AB} is the force constant of the bond in sp^3 hybridization, defined as [8]

$$k_{AB} = 7.2\left(Z_A Z_B / n_A^3 n_B^3\right), \quad (6)$$

where Z_A and Z_B are the atomic numbers of the atoms, and n_A and n_B are the principal quantum numbers of the valence electrons of the atoms bonded.

The distance values which appear in the above expressions were obtained through the realization of a model structure by the Metropolis–Monte Carlo method using structural data obtained from the radial distribution function. The latter was calculated through X-ray diffraction experiments, by assigning coordinations 4, 3 and 2 for Ge, Sb and Se, respectively. Such a model allowed the determination of the different structural units appearing in the alloy [9].

By using the expressions derived by Herzberg [2], the vibrational frequencies are calculated with the tetrahedral and pyramidal units which appear in the structural model.

2. Experimental procedure

The glass under study was prepared by direct synthesis from germanium, antimony and selenium. The total elemental weight of 8 g was placed in a quartz ampoule and submitted to an iterative process of filling and emptying with inert gas (He) to avoid possible oxidation of the sample. The resulting ampoule was maintained at 1000°C for 5 days in a rotary furnace and was quenched in ice water. The glassy state of the sample was confirmed by X-ray diffraction.

The transmission spectrum was obtained at room temperature in the spectral range 500–90 cm^{-1} in a spectrophotometer (Perkin–Elmer, Model 2000) following the polyethylene pellet method [10]. The resolution of the measurements was 4 cm^{-1}.

3. Results and discussion

Fig. 1 shows the infrared spectrum of $Ge_{0.20}Sb_{0.05}Se_{0.75}$ glass. Analysis of the spectrum reveals numerous small-scale features.

3.1. Tetrahedral structural units

The tetrahedral structural units obtained using the structure model are formed by one germanium atom in the centre of the tetrahedron, while the vertices are usually occupied by selenium atoms. The relative abundance of these units in the structure can allow consideration of the influence that its normal frequencies could have on the infrared spectrum.

The stretching force constants corresponding to the Ge–Ge bond of the tetrahedral units are calculated using the three mentioned methods. In the case

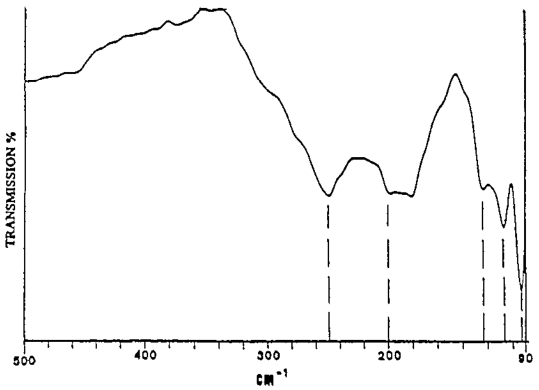

Fig. 1. Infrared transmission spectrum of $Ge_{0.20}Sb_{0.05}Se_{0.75}$ glass.

Table 2
Force constants and frequencies of normal modes calculated for $GeSe_4$ tetrahedra units

	$\langle k_r \rangle$ (10^5 dyn cm^{-1})	$\langle \omega_1 \rangle$ (cm^{-1})	$\langle \omega_2 \rangle$ (cm^{-1})	$\langle \omega_3 \rangle$ (cm^{-1})	$\langle \omega_4 \rangle$ (cm^{-1})
Gordy	2.5141	212	85	358	100
Somayayulu	2.0221	174	67	283	79
Siebert	2.4495	199	77	326	91
Reference		195 [12]	78 [3]	266 [14]	104 [13]

of the Gordy method, the values of a and b in Eq. (2) are, according to Herzberg [2] and Silver [11], 3.29 and 0.40, respectively. The mean value calculated for the bond order, N, in the tetrahedrons considered is 0.98. Thus, let us use, according to Hilton et al. [3], the value $N = 1$ in Eq. (2).

The force constants calculated using the different methods proposed, as well as the values of the normal frequencies obtained, are shown in Table 2.

The values of 212 and 199 cm^{-1} are very near the band observed at 200 cm^{-1} in the experimental spectrum. Ohsaka [12] found a band at 195 cm^{-1} for Ge_5Se_{95} glass, which was assigned to one fundamental mode of the $GeSe_4$ tetrahedral unit. On the other hand, the value of 100 cm^{-1} obtained using $k_r = 2.5141$ (Gordy) is close to the band observed at 105 cm^{-1} in the present spectrum and to the values 104 and 107 cm^{-1} data reported in the literature [13].

The calculated frequencies, ω_3, are 358, 283 and 326 cm^{-1} (Table 2). The value 283 cm^{-1} is in agreement with 266–267 cm^{-1} (< 7% error) assigned by Goyal and Maan [14] to the $GeSe_4$ structural unit in $Sb_{15}Ge_xSe_{85-x}$ alloy ($x = 5$, 10, 15, 20). So, we can assign the nearest strong band at 250 cm^{-1} observed in the experimental spectrum to $GeSe_4$ units.

3.2. Pyramidal structural units

Through Eq. (2) (with $a = 1.67$ and $b = 0.30$) [4] and Eq. (4), we calculated the force constants of the Sb–Se bonds. Using these values, we obtained the vibrational frequencies for the pyramidal units (Table 3). Comparison between these results and the experimental spectrum allowed assignment of the bands to $SbSe_3$ structural units. So, clearly the band situated at 250 cm^{-1} in the spectra corresponds well with the value of 250 cm^{-1} calculated by the Somayayulu method. The proximity of 240 cm^{-1} (< 5% error) obtained by the Gordy method allows the assumption that this value is included in the mentioned band. This band has already been assigned to $GeSe_4$ units. The major abundance of these units, with respect to pyramidal units, has only a small contribution from $SbSe_3$ in this band. On the other hand, the calculated values of 127 and 134 cm^{-1} are near to the band at 122 cm^{-1} (< 10% error), which appears in the experimental spectrum.

The other two calculated frequencies are found in the interval 90–95 cm^{-1}. In the experimental spectrum, there is a broad band at 94 cm^{-1}. However, Ohsaka [15] assigned a band at 95 cm^{-1} to Se_8 rings. Therefore, the assignment in this region of the spectrum is not clear, because both structural units could contribute to absorption in this region.

4. Conclusions

Comparison between the bands obtained in the experimental infrared spectrum and the values calculated for the normal modes of various units suggest the following assignments.

Table 3
Force constants and normal frequencies calculated for pyramidal $SbSe_3$ units

	$\langle k_r \rangle$ (10^5 dyn cm^{-1})	$\langle \omega_1 \rangle$ (cm^{-1})	$\langle \omega_2 \rangle$ (cm^{-1})	$\langle \omega_3 \rangle$ (cm^{-1})	$\langle \omega_4 \rangle$ (cm^{-1})
Gordy	1.2359	240	91	127	90
Somayayulu	1.1525	251	95	134	94

(1) The bands at 250, 200 and 105 cm^{-1} are assigned to vibrations of $GeSe_4$ tetrahedral units. The corresponding values calculated by the Siebert and Gordy methods are 212 and 100 cm^{-1} and 199 and 91 cm^{-1}, respectively. The frequencies obtained using the Somayayulu method are different from the values observed, except for ω_3. In this case, good agreement exists [14].

(2) The pyramidal $SbSe_3$ units are associated with the bands at 250 and 122 cm^{-1}. In this case, the value calculated by the Gordy and Somayayulu method is close to the experimental data. The contribution of these units to the 250 cm^{-1} band is small by comparison with the contribution of $GeSe_4$.

(3) According to Ohsaka [15], the band at 94 cm^{-1} is associated with Se_8 rings.

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