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Structural interpretation of the infrared spectrum of a $Sb_{0.05}As_{0.45}Se_{0.50}$ glassy semiconductor

C. Corredor [a], I. Quiroga [b,*], J. Vázquez [c], J. Galdón [c], P. Villares [b], R. Jiménez-Garay [c]

[a] *Dpto. de I.S.A., Universidad de Cádiz. Apdo. 40. 11510. Puerto Real, Cadiz, Spain*
[b] *Dpto. de Física Aplicada, Universidad de Cádiz. Apdo. 40. 11510. Puerto Real, Cadiz, Spain*
[c] *Dpto. de Física de la Materia Condensada, Universidad de Cádiz. Apdo. 40. 11510. Puerto Real, Cadiz, Spain*

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Abstract

The infrared (IR) absorption spectrum for glassy $Sb_{0.05}As_{0.45}Se_{0.50}$ was measured in the wave number region 500–90 cm^{-1} at room temperature and in a continuously purged sample compartment, following the polyethylene pellet method. Main structural units in the glassy are considered to be $AsSe_3$ and $SbSe_3$ pyramids, Se_8 rings and Se_n chains. By using X-ray diffraction data it was found a structural model with the assumption of tricoordinated As, tricoordinated Sb and dicoordinated Se [C. Corredor, J. Vazquez, R.A. Ligero, P. Villares, R. Jimenez-Garay, Materials Letters 36, 1998, 271; I. Quiroga, J. Vázquez, P. Villares, R. Jiménez-Garay, Materials Letters 17, 1993, 333.] which confirms the information obtained by means of far-infrared transmission (FIT). From the ''Valence Force Field'' (VFF) we can determine the vibrational frequencies, ω_i, of possible structural units of alloy in this study by using the expressions derived by Herzberg. The results for this alloy are the following: 85, 110 and 230 cm^{-1}, for $AsSe_3$, and 112, 215 and 315 cm^{-1}, for $SbSe_3$. The comparison between the frequencies obtained in the far-IR spectrum and the values calculated of the normal frequencies let us assign bands to structural units.

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Keywords: Chalcogenide; Glasses; Structure

1. Introduction

The structure of $Sb_{0.05}As_{0.45}Se_{0.50}$ chalcogenide glass was investigated by means of X-ray diffraction and infrared (IR) spectroscopy [1,2].

In this work, we discuss the IR transmission measurements of this alloy, assuming the valence force field (VFF) [3]. This model assumed that there is a strong restoring force in the line of every valence bond if the distance of the two atoms bound by this bond is changed. In addition he assumed that there is a restoring force opposing a change of the angle between two valence bonds connecting one atom with two others.

From the VFF we can determine the vibrational frequencies, ω_i, of possible structural units of alloy in this study, by using the expressions derived by Herzberg [4]. Several relations between force con-

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[*] Corresponding author. Tel.: +34-56-470850; fax: +34-56-470806.
E-mail address: quiroga@czv1.uca.es (I. Quiroga).

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stants or vibrational frequencies and bond distances have been found to hold approximately for a limited number of molecules. They, in general, have two or more parameters that depend on the atoms forming the bond or their position in the periodic table. The most widely of these seems to be that of Gordy [5]

$$k_r = aN\left(\frac{x_A x_B}{d^2}\right)^{3/4} + b \qquad (1)$$

where a and b are constants for certain broad classes of molecules; N, k_r, and d are the bond order, bond stretching force constant and bond distance, respectively; and x_A and x_B are the electronegativities of the atoms A and B, in the Pauling scale [6].

The bond distances which appear in Eq. (1) were obtained through the realization of a structural model using a random covalent network model (RCNM) with the assumption of tricoordinated As, tricoordinated Sb and dicoordinated Se. Such a model allowed the determination of the different structural units appearing in the alloy [7].

The vibrational frequencies are calculated with the pyramidal units which appear in the structural model.

2. Experimental procedure

Glassy alloy $Sb_{0.05}As_{0.45}Se_{0.50}$ was prepared by quenching technique. Materials (99.99% pure) were weighed according to their atomic percentage and were sealed in quartz ampoule with a vacuum of $\sim 10^{-4}$ Torr. The ampoule was kept in a furnace and heated up to 1000°C. After that, ampoule was rocked for 24 h at the maximum temperature to make the melt homogeneous. After taking out the sample from the furnace, quenching was done by blowing air on that at room temperature. X-ray diffraction was used to determine if the quenched products were glassy or crystalline. The thin plates for IR absorption measurements were also made by the same method as in Ref. [8]. The IR transmission spectrum of the glass was obtained with a Perkin-Elmer SYSTEM 2000 Fourier spectrometer. The resolution during measurements was 4 cm^{-1}.

Table 1
Averaged bonding distances

Bond	$\langle d \rangle$ (Å)	Squared deviation
As–Se	2.44	0.21
Sb–Se	2.51	0.18
Se–Se	2.45	0.22

Table 2
Averaged bonding angles

Type	$\langle \alpha \rangle$ (deg.)	Squared deviation
Sb	110.32	18.15
Se	108.45	11.34
As	108.76	12.62

3. Results and discussion

The generated structural model is constituted by pyramidal structural units, a vertex of which is occupied with an atom of As or Sb, and the remainder is usually occupied with atoms of Se. These units are joined together directly or by chains of Se atoms. The average values of the distances and bond angles are shown in Tables 1 and 2, respectively [1].

These values have used to determine the force constants through Eq. (1), as well as the normal vibration frequencies of the pyramidal units found in the model, Table 3, from the expressions developed by Herzberg, in which the value of the force constant associated to the bond angle distortion, k_α,has been considered a 10% of the k_r value, in accordance with the literature [9,10].

Fig. 1 shows the transmission spectrum in the IR of the analyzed sample.

From an analysis of the spectrum, it can be observed the existence of sharp bands of absorption

Table 3
Force constants and frequencies of normal modes (cm^{-1}) calculated for $AsSe_3$ and $SbSe_3$ pyramidal units

Structural unit	$\langle k_r \rangle$ (10^5 dyn cm^{-1})	$\langle w_1 \rangle$	$\langle w_2 \rangle$	$\langle w_3 \rangle$	$\langle w_4 \rangle$
$AsSe_3$	1.89	110	367	230	85
$SbSe_3$	1.75	112	315	215	78

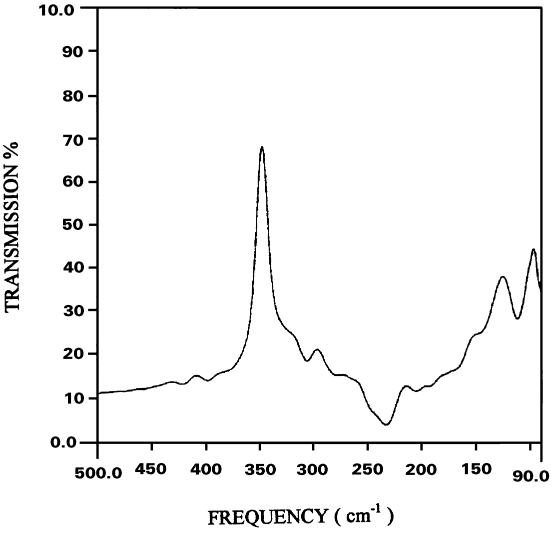

Fig. 1. Infrared transmission spectrum of $Sb_{0.05}As_{0.45}Se_{0.50}$.

in proximity to the frequencies 90, 110, 230, and 310 cm^{-1}.

The similar values of the frequencies of 110 and 230 cm^{-1} and the calculated frequencies ω_1 and ω_3 for the structural unit $AsSe_3$, allow us to assign the aforementioned bands to that structural unit, and which is in accordance with the allocation made by Hilton et al. [9] and Lucovsky and Martin [11].

In connection with remainder calculated frequencies (ω_2, ω_4) for the unit $AsSe_3$, it should be noted that ω_4 is out of the experimental range, whereas regarding ω_2, a weak band near 400 cm^{-1} can be seen in the experimental spectrum, which do not allow us to clearly assign the same.

Due to the low content of antimony in this alloy, the theoretical data obtained for the structural unit $SbSe_3$ are not statistically representative and therefore the allocation of experimental bands cannot be determined, although we can consider that the frequency ω_1 can contribute to the appearance of the experimental band located around 110 cm^{-1}.

The absorption peak which can be observed near 90 cm^{-1} has been assigned by various authors, like Ohsaka [12,13] and Lucovsky et al. [14], to Se chains present in the material.

4. Conclusions

In the theoretical aspect of the model of valence force field, a detailed analysis of the generated structural model has been carried out, which has permitted to calculate the force constants and the normal frequencies of vibration which appear on the same. The distributions of the aforementioned frequencies reproduce, in most case, the bands of absorption which appear in the experimental spectrum of IR.

Through the analysis of the transmission spectrum in the IR, some bands of absorption have been identified located around absorption values of 90, 110 and 230 cm^{-1}.

The data obtained from the calculated theoretical frequencies, together with the data given by the bibliography, have allowed to establish the general hypothesis of the existence in the material of pyramidal units $AsSe_3$, $SbSe_3$ and chains of Se atoms.

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