Raman spectra of the $(GeS_2)_{1-x}(Sb_2S_3)_x$ system glasses

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A study of the Raman spectra has been made on $(GeS_2)_{1-x}(Sb_2S_3)_x$ system glasses in the composition region of $0 \leqslant x \leqslant 0.60$. The dominant features of the obtained spectra were discussed using a molecular model with GeS_4 and SbS_3 structural units interconnected through bridging S atoms. For the SbS_3 structural group the Raman frequencies were estimated.

В работе были изучены рамановские спектры стекла системы $(GeS_2)_{1-x}(Sb_2S_3)_x$ в диапазоне состава $0 \leqslant x \leqslant 0,60$. Объяснение основных полос полученных спектров было сделано, исходя из молекулярной модели структуры стекла, образованного из конгломератов GeS_4 и SbS_3, связанных мостиковым атомом серы. Для структурного конгломерата SbS_3 были найдены рамановские частоты колебаний.

Raman spectra have been shown to be a useful technique for the determination of the short range order in solids. The analysis of the Raman spectra in disordered materials is more difficult than in the materials with a periodic structure due to a disorder-induced breakdown of crystalline selection rules. In the last years some approaches have been suggested for the dealing of the vibrations in random networks. In tetrahedrally bonded elemental amorphous semiconductors like amorphous Si and Ge, the Raman spectra reflect in gross features the density of phonon states and their explanation was made either by comparison with crystalline density of states [1] or by calculation of the vibrational states and the Raman and infrared spectra using a finite cluster of atoms [2].

The Raman and infrared spectra of amorphous chalcogenides show a distinct molecular-like character and their dominant features were explained mostly using a molecular model of *Lucovsky* and *Martin* [3]. The more fundamental approach, called the decoupled-network method, was proposed recently by *DeFonzo* and *Tauc* [4] for the explanation of the vibrational spectra of As_2X_3 ($X = O, S, Se$) glassy compounds or the cluster-Bethe-lattice methods used by *Laughlin* and *Joannopoulos* [5] for the glassy SiO_2. Nevertheless, the molecular model is useful

for the first approach in some complex glassy systems, *e.g.* in ternary chalcogenide alloy glasses. The utility of this model especially for the GeS_2 glass was proved also by *Sen* and *Thorpe* [6] who estimated that in AX_2 glasses it is justified to consider an amorphous network to be an assembly of weakly interacting molecular units when the A—X—A bond angle is close to 90° and the angular forces are weak, which is the case of glassy GeS_2. We used here the molecular model also for the explanation of the Raman spectra of $(GeS_2)_{1-x}(Sb_2S_3)_x$ system glasses.

Experimental

The samples of the $(GeS_2)_{1-x}(Sb_2S_3)_x$ glasses have been prepared in the bulk form in the composition region of $0 \leqslant x \leqslant 0.60$ from high-purity germanium, antimony, and sulfur. The mixtures of appropriate amounts of the elements were melted in vacuum-sealed fused silica tubes for 20 h at 900°C and then aircooled to room temperature. All the prepared glasses were homogeneous. Raman spectra were measured at room temperature on the Jeol Raman spectrometer JRS-S1 with a coherent 632.8 nm He—Ne laser radiation operated at about 16 mW at the sample. We have also prepared glassy samples of $(GeS_2)_{1-x}(Sb_2S_3)_x$ system with $0.60 < x < 0.75$, but we have not been successful in measuring their Raman spectra due to a destruction of the samples caused by the high absorption of the exciting He—Ne laser radiation by the samples.

Results and discussion

The Raman spectra of the $(GeS_2)_{1-x}(Sb_2S_3)_x$ glasses with $x = 0.12$, 0.33, and 0.60 are shown in Fig. 1. The spectra have one dominant band at 300—350 cm^{-1} which becomes broader with increasing Sb_2S_3 content and its maximum shifts to lower frequencies. In the Raman spectra of the samples with a higher GeS_2 content there is also a shoulder in the region of ~ 400 cm^{-1} which decreases with increasing Sb_2S_3 content.

The so-called "reduced" Raman spectra shown in Fig. 2 for glasses with $x = 0.25$, 0.33, and 0.50 have the same character. These spectra, obtained by the reduction method of *Shuker* and *Gammon* [7] as modified by *Kobliska* and *Solin* [8], correspond to an approximate density of vibrational states $\varrho(v)$ and were calculated using the equation

$$\varrho(v) = v(v_i - v)^{-4} [1 - \exp(-hv/kT)] I(v, T)$$

where v_i is the frequency of the incident laser radiation (in cm^{-1}), v is the frequency shift, *i.e.* $v_i - v_s$ where v_s is the frequency of the scattered light, T is the temperature which enters through the Bose—Einstein occupation number for
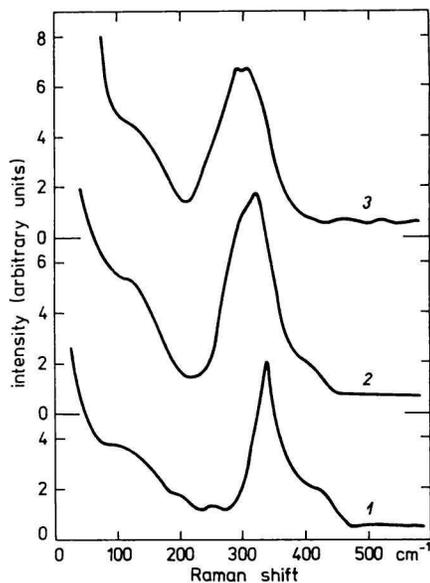
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Fig. 1. Raman spectra of $(GeS_2)_{1-x}(Sb_2S_3)_x$ glasses.
1. $x = 0.12$; 2. $x = 0.33$; 3. $x = 0.60$.
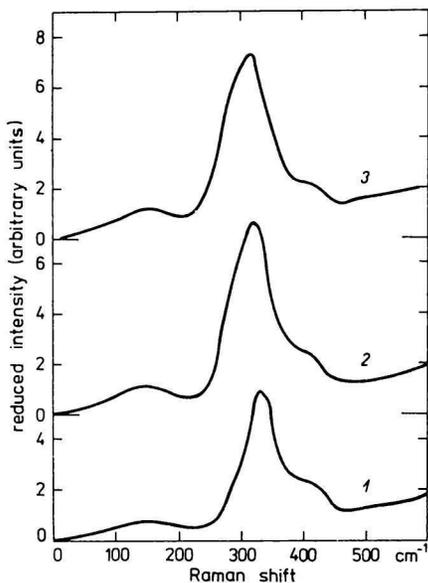
Fig. 2. Reduced Raman spectra of $(GeS_2)_{1-x}(Sb_2S_3)_x$ glasses.
1. $x = 0.25$; 2. $x = 0.33$; 3. $x = 0.50$.

a phonon of energy hv, and $I(v, T)$ is the scattered light intensity at a frequency shift v.

For the explanation of the obtained Raman spectra of $(GeS_2)_{1-x}(Sb_2S_3)_x$ glasses was applied the molecular model [3]. Bonding in such chalcogenide glasses according to previous studies [9] follows the 8-N rule. This rule determines the number of covalent bonds shared by an atom from the Nth group of the periodic table, *i.e.* in the glasses under study according to 8-N rule Ge is fourfold-, Sb threefold-, and S is twofold-coordinated. With consideration of relative bond energies we assume a strong tendency to form heteropolar bonds rather than homopolar ones like Ge—Ge, Sb—Sb or S—S. The glasses studied here are formed between compounds GeS_2 and Sb_2S_3 and thus, we assume Ge—S and Sb—S bonds to be present in the glasses but not S—S or Ge—Sb bonds. We expect that the basic structural units in these glasses are GeS_4 tetrahedron with the Ge atom at the centre and SbS_3 pyramid with the threefold-coordinated Sb atom at the apex like in the GeS_2—As_2S_3 system glasses [10]. The basic structural units GeS_4 and SbS_3 are interconnected through bridging S atoms and like in the other chalcogenide glasses [10—12] the coupling between the basic structural groups *via* S atoms is assumed to be weak and thus, the vibrational modes in this approximation can be separated into GeS_4- and SbS_3-like modes.

Vibrational frequencies of the GeS$_4$ tetrahedron were estimated by *Lucovsky et al.* [12]. They calculated the vibrational frequencies of the GeS$_4$ structural unit from the Raman frequencies of the GeCl$_4$ molecule by using a scale factor obtained from the comparison of the frequencies of dominant bands of corresponding vibrational modes of Raman spectra of GeCl$_4$ and glassy GeS$_2$. For the A_1 and F_2 stretching modes of the GeS$_4$ structural unit the authors [12] found the vibrational frequencies of 342 and 388 cm^{-1}, respectively. The frequencies of bending E (114 cm^{-1}) and F_2 (147 cm^{-1}) modes lie in a low-frequency region and in the measured Raman spectrum are not clearly resolved.

The vibrational frequencies of the SbS$_3$ structural units, which we assume to be formed in the (GeS$_2$)$_{1-x}$(Sb$_2$S$_3$)$_x$ glasses, have not been reported yet. We tried to estimate these frequencies by scaling the Raman frequencies of a real AB$_3$ molecule with similar structure and mass ratio like SbS$_3$. For this calculation we used the reported Raman frequencies of SbCl$_3$ [13]. For the scaling the same factor was used as for the estimation of Raman frequencies of structural units AsS$_3$ in glassy As$_2$S$_3$ from those of AsCl$_3$ [3], because the relations SbS$_3$—SbCl$_3$ and AsS$_3$—AsCl$_3$ in the first approximation are similar. The scaling factor $f = v_i(\text{AsS}_3)/v_i(\text{AsCl}_3) = 0.84$. In this way we estimated the vibrational frequencies of the SbS$_3$ structural unit shown in Table 1.

According to group theoretical consideration, the $v_1(A_1)$ stretching vibration should correspond with the dominant band in the Raman spectrum of pyramidal AB$_3$-type molecule. In the (GeS$_2$)$_{1-x}$(Sb$_2$S$_3$)$_x$ system glasses the role of this mode of the SbS$_3$ structural unit should increase with increasing Sb$_2$S$_3$ content.

The obtained Raman spectra are in good agreement with these predictions, because the dominant vibrational band of the GeS$_2$ glass is getting broader with increasing Sb$_2$S$_3$ content in the alloy glass and its maximum shifts from the value of 340 cm^{-1} at GeS$_2$ to lower values down to 300 cm^{-1} at $x = 0.50$ and 0.60. The experimental results indicate that the dominant vibrational band in the Raman spectra of (GeS$_2$)$_{1-x}$(Sb$_2$S$_3$)$_x$ glasses is composed of two bands: the 342 cm^{-1} band associated with the $v_1(A_1)$ vibrational mode of the GeS$_4$ tetrahedral unit and the

Table 1

Raman frequencies of SbS$_3$ structural unit

Mode	$\tilde{v}$/cm^{-1}	
	SbCl$_3$ (Ref. [13])	SbS$_3$
$v_1(A_1)$	360	302
$v_2(A_1)$	165	138
$v_3(E)$	320	269
$v_4(E)$	134	112

302 cm^{-1} band associated with the $v_1(A_1)$ vibrational mode of the SbS$_3$ pyramidal unit. Both the bands correspond to the symmetrical stretching modes and should be polarized [14]. A low value of the depolarization ratio $\varrho = I_\perp/I_\parallel$ in the region of 300—340 cm^{-1} found experimentally in our measurements for all the glasses with a higher Sb$_2$S$_3$ content and shown in Fig. 3 for the sample of (GeS$_2$)$_{0.5}$(Sb$_2$S$_3$)$_{0.5}$, is in agreement with the above predictions and supports the suggested interpretation of the Raman spectra of (GeS$_2$)$_{1-x}$(Sb$_2$S$_3$)$_x$ glasses. The nonmonotonous course of the depolarization spectra according to *Kobliska* and *Solin* [15] gives evidence also for the molecular character of the glasses. The failure of the depolarization spectra in achieving the theoretical maximum value of 3/4 is a manifestation of the effect of intermolecular coupling between the basic structural units which is, nevertheless, very weak in the molecular chalcogenide glasses in comparison with nonmolecular amorphous solids like amorphous Si.

The other calculated frequencies of the vibrational modes of the SbS$_3$ structural unit were not resolved in the measured Raman spectra. The $v_3(E)$ antisymmetric stretching mode (269 cm^{-1}) should be active especially in the infrared spectra. The frequencies of the bending modes $v_2(A_1)$ and $v_4(E)$ lie in the region <200 cm^{-1} where the molecular model is not so reliable as in the region of higher frequencies due to the coupling of basic structural units at the bridging S atoms.

We have reported here the two-mode behaviour of the (GeS$_2$)$_{1-x}$(Sb$_2$S$_3$)$_x$ glasses studied in the composition region of $0 \leqslant x \leqslant 0.6$. We estimated the pseudobinary
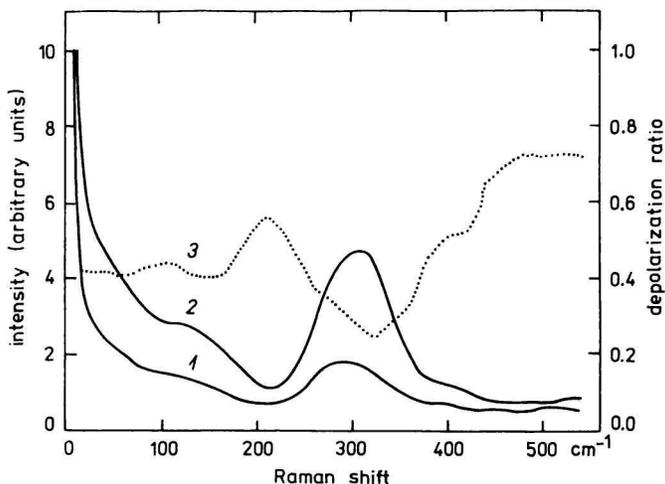

Fig. 3. Polarized Raman spectra and the depolarization spectrum of the (GeS$_2$)$_{0.5}$(Sb$_2$S$_3$)$_{0.5}$ glass.
1. $I_\perp$; *2*. $I_\parallel$; *3*. $\varrho = I_\perp/I_\parallel$.
Parallel and perpendicular polarization configurations are denoted by ‖ and $\perp$, respectively.
The depolarization spectrum is shown as a dashed line.

character of these glasses which we assume to be composed of GeS_4 and SbS_3 basic structural units interconnected through bridging S atoms into disordered network structure. Different local coordinations of the Ge and Sb atoms result in different stretching modes of GeS_4 tetrahedron and SbS_3 pyramid. In the Raman spectra of these glasses the symmetrical stretching modes of the both structural groups $v_1(A_1)$ of GeS_4 with frequency of 342 cm^{-1} and $v_1(A_1)$ of SbS_3 with frequency of 302 cm^{-1} play the most important role. The contribution from each structural group to the resulting Raman spectrum is weighted according to the glass composition. Additional weaker features of the Raman spectra are not explained by the model we are employing in this study, and can only be accounted for by the analysis which explicitly considers the coupling of the basic structural groups. The obtained results are compatible also with the chemically ordered network model because in the Raman spectra of the $(GeS_2)_{1-x}(Sb_2S_3)_x$ glasses we have not found the vibrational bands of Ge—Ge or S—S bonds, which should be present in the glasses according to the randomly ordered network model.

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Translated by L. Koudelka