

## INVESTIGATION OF NANOPHASE SEPARATION IN GLASSY $As_{40}Se_{60}$ USING RAMAN SCATTERING AND AB INITIO CALCULATIONS

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Raman spectra of stoichiometric glass (g)  $g-As_{40}Se_{60}$  have been investigated. It was observed that the increasing of excitation radiation energy  $h\nu > E_0$  ( $E_0$  is pseudogap width) changes a shape and position of Raman peaks of  $g-As_{40}Se_{60}$ . The structure and vibration spectra of some As-Se clusters were calculated applying Hartree-Fock (HF) and density functional theory (DFT). In order to elucidate structural features of  $g-As_{40}Se_{60}$ , we combined the experimental Raman data and theoretical calculations.

### 1. Introduction

Photo-induced effects in amorphous chalcogenide semiconductors are widely investigated as both fundamental processes of structural transformations in amorphous solids and promising applications in optoelectronics due to the related changes of optical parameters [1]. Among chalcogenide glasses, As-S and As-Se systems are model materials for studying the structure and photoinduced phenomena in non-crystalline semiconductors. Much efforts have been devoted to study these materials by various techniques, for instance, Raman spectroscopy. A usage of excitation radiation of different energies causes some changes in the Raman peak position and their shape. Phenomena of resonant behavior of Raman bands at energies less than pseudogap width in As-S system glasses can be explained by creation of As-As and S-S bonds in the matrix structure [2]. Theoretical calculations [3] and X-ray photoelectron spectroscopy (XPS) experiments [4] suggest that even in stoichiometric  $As_{40}Se_{60}$  glasses, there are wrong As-As and Se-Se bonds. So, it is interesting to investigate resonant Raman spectra of  $g-As_{40}Se_{60}$  at excitation energies  $h\nu < E_0$  and  $h\nu > E_0$ .

### 2. Experimental technique and calculations

The technique of glass synthesis is described in [5].

Raman spectra of  $As_{40}Se_{60}$  glasses were measured by RENISHAW SYSTEM 1000 Raman spectrometer with CCD (Charge Coupling Device) detecting cell. Raman scattering was excited by a diode laser with the wavelength 785 nm and output power 25 mW and a Spectra Physics Model 168 (Ar) laser with the wavelength 488 nm and output power 1W. The spectra were measured in a back scattering geometry. An output power was restricted by filters to avoid a photoinduced structural changes.

Raman spectrum excited by 1060 nm wavelength were taken by Fourier Transformation (FT) BRUKER IFS55 IR spectrophotometer with FRA-106 accessory, output power 90 mW [6].

Geometrical parameters and vibrational spectra of  $As_2Se_5$ ,  $As_4Se_6$ , and  $As_6Se_9$  (Fig. 1) clusters were calculated by the ab initio Hartree-Fock method with LANL2DZ basis set,

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GAUSSIAN-94 program packages [7]. The vibrational spectra for  $\text{As}_4\text{Se}_{4(3)}$  (geometries of this clusters shown on Fig. 2) clusters were calculated using the DFT (B3LYP)/Stuttgart RLC ECP method, GAMESS (US) software [8]. The vibrational spectra of molecular clusters  $\text{As}_4\text{Se(S)}_{4(3)}$  calculated by this method are in the best accordance with experimental data.

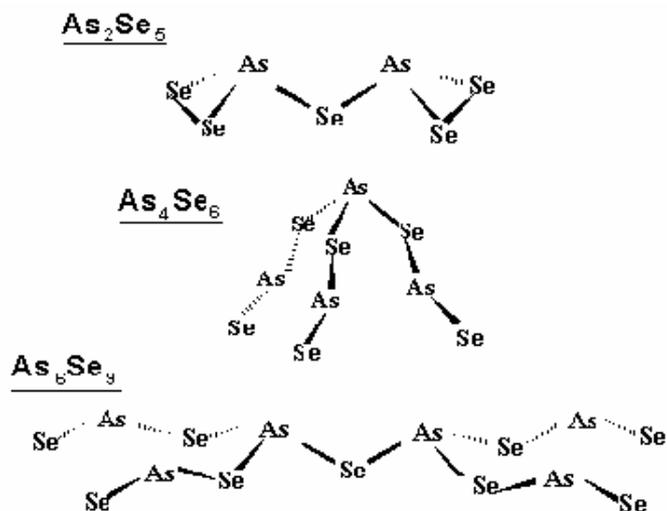


Fig. 1. The geometry of  $\text{As}_2\text{Se}_5$ ,  $\text{As}_4\text{Se}_6$ ,  $\text{As}_6\text{Se}_9$  clusters.

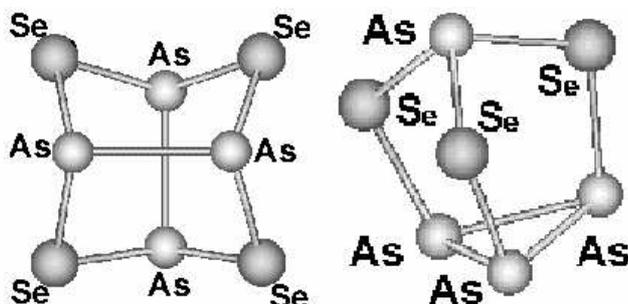


Fig. 2. The geometry of  $\text{As}_4\text{Se}_4$ ,  $\text{As}_4\text{Se}_3$  clusters.

### 3. Results and discussions

Recent investigations have shown that shape and position of Raman peaks in  $g\text{-As}_2\text{S}_3$  depends on excitation wavelength [9]. The energy of excitation radiation can be greater or lesser than the pseudogap width that causes a shift of maxima positions [9] by electronic processes influence. Fig. 3 shows Raman spectra inherent to  $\text{As}_2\text{Se}_3$  glass excited with light of different energies. The wavelengths are 1060, 785, and 488 nm with energies 1.17, 1.58, and 2.54, respectively. The latter energy value exceeds the pseudobandgap energy of  $g\text{-As}_2\text{Se}_3$  ( $E_0=1.9$  eV [10]). Raman spectra obtained using lasers with wavelengths 1060 and 785nm,  $h\nu < E_0$ , comprise one broad band peaking at  $227$   $\text{cm}^{-1}$ . Raman spectra of crystalline (c) c-Se and amorphous (a) a-As (Fig. 4) have intensive bands at 235, 250 and 227, 252  $\text{cm}^{-1}$ , respectively. So, it is impossible to give an exact identification of structural units (s.u.) of  $g\text{-As}_{40}\text{Se}_{60}$  by comparing the Raman spectra of  $g\text{-As}_2\text{Se}_3$ , c-Se, and a-As only. Some authors [11] suppose that it is enough to coincide the calculated vibration frequency of  $\text{AsSe}_3$  molecule with experimental position of the Raman spectra band for assignment of maxima at  $230$   $\text{cm}^{-1}$  to  $\text{AsSe}_{3/2}$  s.u. vibration. But Raman scattering by bulk  $\text{As}_x\text{S}_{1-x}$

glasses shows that the vibrational modes of  $\text{As}_4\text{S}_4$  monomers appear first near  $x=0.38$ , and their concentration sharply increases with increasing  $x$ , suggesting that the stoichiometric glass ( $x=0.40$ ) is intrinsically phase separated into small As-rich ( $\text{As}_4\text{S}_4$ ) and large S-rich clusters [12]. Since synthesis procedures of  $g\text{-As}_2\text{S}_3$  and  $g\text{-As}_2\text{Se}_3$  are similar, it is possible that the latter may contain not only  $\text{AsSe}_{3/2}$  s.u. but  $\text{As}_2\text{Se}_{4/2}$  and Se-Se inclusions. Really, for a laser with  $h\nu < E_0$  sensitive to the structural fragments of small sizes, Raman spectra of  $g\text{-As}_2\text{Se}_3$ , if using  $\lambda = 488$  nm, differ from the spectra taken at  $\lambda = 1060, 785$  nm (Fig. 3). For the photon energy 2,54 eV the Raman spectrum (Fig. 3) is superimposed on a broad photoluminescence background which complicates the precise determination of the peak position. It is necessary to note, that the penetration depth of the laser radiation with  $E = 2,54$  eV consists  $\sim 1 \mu\text{m}$ .

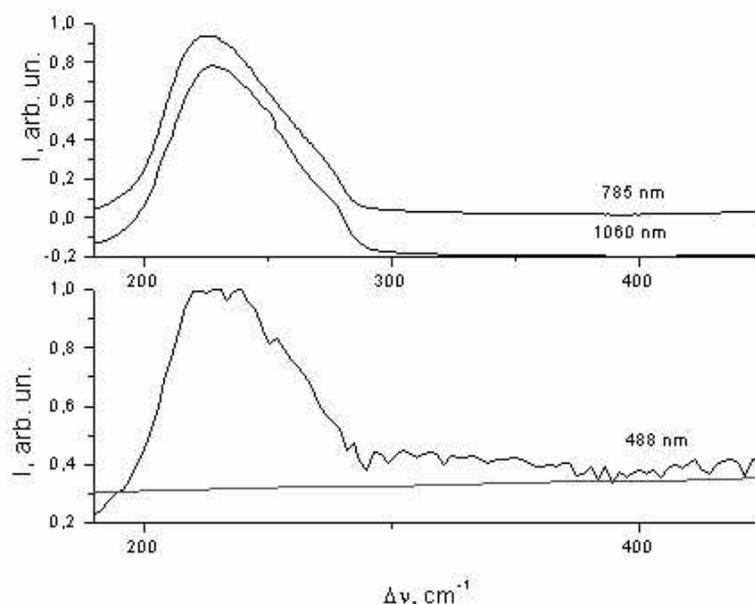


Fig. 3. Raman spectra for  $g\text{-As}_{40}\text{Se}_{60}$  excited with light of different wavelengths indicated. The drawn line indicates the underlying luminescence background.

In [13] it was assumed that the changes in the Raman spectra upon variation of the excitation energy are difficult to understand within a homogeneous structural model [14]. This implies that for a change in the photon energy used to excite the Raman spectrum also the relative intensities of the contributions from the two phases change [13]. Similar circumstances may cause changes in case of  $g\text{-As}_{40}\text{Se}_{60}$ . As can be seen from Fig. 3 Raman line of  $g\text{-As}_{40}\text{Se}_{60}$  excited with  $\lambda = 488$  nm has distinct shoulders at both sides of spectral curve. A frequency position of these shoulders coincides with Raman bands of crystalline  $\text{As}_4\text{Se}_4$  and  $\text{As}_4\text{Se}_3$  [15,16] and calculated frequencies of free molecules  $\text{As}_4\text{Se}_4$  and  $\text{As}_4\text{Se}_3$  (Table 1). The shoulders that appear on the low frequency side of main band of  $g\text{-As}_{40}\text{Se}_{60}$  at irradiation with wave energy 2,54 eV may be due to the exciting of homopolar As-As bonds. Indeed it is impossible to give an exact assignment of these bonds to molecules  $\text{As}_4\text{Se}_{4(3)}$  on Raman data. Such indefiniteness exists at interpretation of high frequency side of main Raman band of  $g\text{-As}_{40}\text{Se}_{60}$ . Existence of shoulder at  $254 \text{ cm}^{-1}$  may be related to the presence both of Se-Se bonds in free Se (Fig. 4) and As-Se bond vibrations of  $\text{As}_4\text{Se}_3$  molecule. The bend at  $245 \text{ cm}^{-1}$  may exist due to As-Se bonds of  $\text{As}_4\text{Se}_4$  molecule. If chalcogenides are exposed by laser radiation from the region of edge intrinsic absorption, incident photons are absorbed by the glass. That is, at exposure with photons with energy bigger than band gap width the activation of the photoinduced phenomena on the surface and in subsurface layers occur [17]. So the photodecomposition reactions also may cause an increasing of inclusions in form of  $\text{As}_{3/3}$ ,  $\text{As}_4\text{Se}_{4(3)}$  clusters.

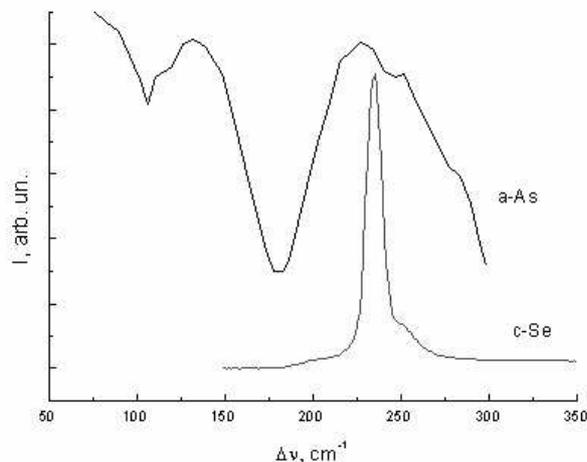


Fig. 4. Raman spectra of crystalline Se and amorphous As.

Table 1. Band positions in experimental Raman spectra of crystalline  $\text{As}_4\text{Se}_4$  [15],  $\text{As}_4\text{Se}_3$  [16] and calculated Raman frequencies of free molecules  $\text{As}_4\text{Se}_4$ ,  $\text{As}_4\text{Se}_3$ .

| Raman frequencies of c- $\text{As}_4\text{Se}_4$ [15] | Raman frequencies of molecule $\text{As}_4\text{Se}_4$ , calculations | Raman frequencies of $\text{As}_4\text{Se}_3$ [16] | Raman frequencies of molecule $\text{As}_4\text{Se}_3$ , calculations |
|---|---|--|---|
| 136 (m)   | 136 (m)   | 140 (w)  |   |
| 144 (m)   | 149 (s)   | 166 (w)  | 152 (m)   |
| 152 (w)   | 170 (w)   | 188 (w)  | 179 (m)   |
|   | 180 (w)   | 196 (s)  | 192 (m)   |
| 190 (s)   | 198 (s)   |  | 195 (m)   |
| 207 (s)   |   | 236 (w)  | 238 (w)   |
| 216 (m)   |   |  |   |
| 235 (m)   | 242 (w)   | 242 (s)  | 241 (s)   |
| 248 (s)   | 258 (s)   | 256 (s)  | 246 (m)   |
| 275 (w)   | 260 (w)   | 266 (m)  |   |
|   |   | 280 (m)  | 277 (m)   |

For  $g\text{-As}_2\text{S}_3$  Kawazoe et al. [18] have reported resonance enhancement of Raman peaks stemming from As-As and S-S homopolar bonds, which are assumed to provide band tail states of the valence band.

So, we can make a conclusion that structural study needs methods which may give exact information about bond types. For example we used [19] x-ray photoelectron spectroscopy for  $\text{As-GeS}_2$  system. Using short wavelength laser radiation to excite the Raman signal gives a series of low intensity bands in the range above  $300\text{ cm}^{-1}$  (Fig. 5). An assignment of these bands can be made using quantum-chemical calculations. Schematic geometry of the clusters are shown in Fig. 1. An important feature of  $\text{As}_2\text{Se}_5$  cluster is Se-Se bonds at the ends of clusters. The ends of  $\text{As}_4\text{Se}_6$ ,  $\text{As}_6\text{Se}_9$  clusters were closed by the double Se bond. A calculated frequencies at  $300\text{ cm}^{-1}$  may be assigned to

vibrations of Se-Se bonds at the cluster ends (Fig. 5). The vibrations of Se atoms at the ends of  $\text{As}_2\text{Se}_3$ ,  $\text{As}_4\text{Se}_6$ , and  $\text{As}_6\text{Se}_9$  clusters have frequency at  $360\text{ cm}^{-1}$  (Fig. 5). So, the low intensive bands at  $300$  and  $350\text{ cm}^{-1}$  in the Raman spectra of  $g\text{-As}_{40}\text{Se}_{60}$  (Fig. 3) may be related to the vibrations of Se-Se and As-Se ends, respectively. The same situation was observed by us for another cluster types Ge-S and As-S [20, 21]. So, excitation of the Raman signal by energy  $h\nu > E_0$  makes spectra more informative, which allows to reveal s.u.  $\text{As}_{3/3}$ ,  $\text{As}_2\text{Se}_{4/2}$ ,  $\text{Se}_{2/2}$  in  $g\text{-As}_{40}\text{Se}_{60}$  structure.

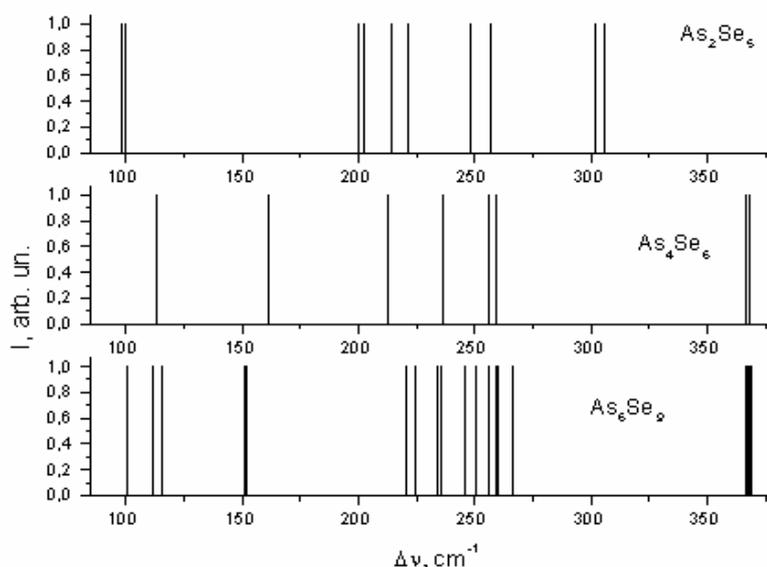


Fig. 5. Vibration spectra of clusters.

### Acknowledgements

Authors wish to acknowledge Prof. F. Billes for calculations of chain clusters and P-G. S. R. Holomb for calculations of molecular clusters. N. Mateleshko would like to thank R. Holomb for discussions. Special thanks to Prof. A. Stronski and Prof. M. Vlcek for Raman measurement with  $\lambda=1060\text{ nm}$ .

This work was supported by the Grant No. M/467-2003 and Grant No. 29/48-2001 (Ministry of education and science of Ukraine and Hungarian Science and Technology Foundation).

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