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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 the 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.

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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. The use 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 the 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 the photoinduced structural changes.

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Raman spectrum excited by 1060 nm wavelength were obtained 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, GAUSSIAN-94 program packages [7]. The vibrational spectra for $As_4Se_{4(3)}$ clusters (geometries of these clusters are shown on Fig. 2) were calculated using the DFT (B3LYP)/Stuttgart RLC ECP method, GAMESS (US) software [8]. The vibrational spectra of molecular clusters $As_4Se(S)_{4(3)}$ calculated by this method are in the best agreement with the experimental data.

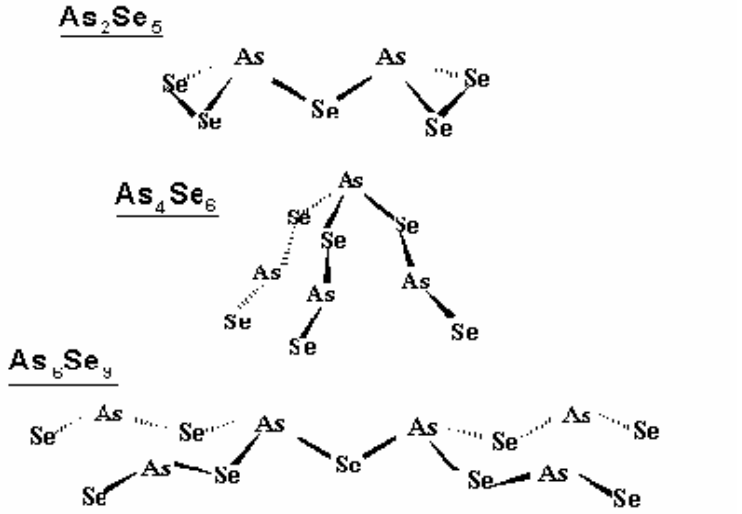

Fig. 1. The geometry of As_2Se_5, As_4Se_6, As_6Se_9 clusters.

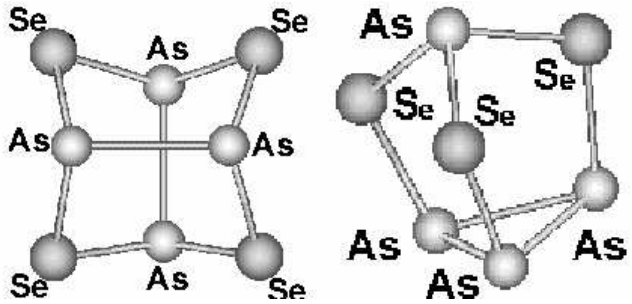

Fig. 2. The geometry of As_4Se_4, As_4Se_3 clusters.

3. Results and discussions

Recent investigations have shown that the shape and position of Raman peaks in g-As_2S_3 depend 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] due to electronic processes. Fig. 3 shows the Raman spectra inherent to As_2Se_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-As_2Se_3 (E_0 = 1.9 eV [10]). Raman spectra obtained using lasers with wavelengths 1060 and 785 nm, $h\nu<E_0$, comprise one broad band peaking at 227 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 cm^{-1}, respectively. So, it is impossible to give an exact identification of structural units (s.u.) of g-$As_{40}Se_{60}$ by comparing the Raman spectra of g-As_2Se_3, c-Se, and a-As

only. Some authors [11] suppose that it is enough to fit the calculated vibration frequency of $AsSe_3$ molecule with experimental position of the Raman spectra band for assignment of maxima at 230 cm^{-1} to $AsSe_{3/2}$ s.u. vibration. But Raman scattering by bulk As_xS_{1-x} glasses shows that the vibrational modes of As_4S_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 (As_4S_4) and large S-rich clusters [12]. Since synthesis procedures of g-As_2S_3 and g-As_2Se_3 are similar, it is possible that the latter may contain not only $AsSe_{3/2}$ s.u. but $As_2Se_{4/2}$ 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-As_2Se_3, if using λ = 488 nm, differ from the spectra taken at λ = 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 is ~ 1 μm.

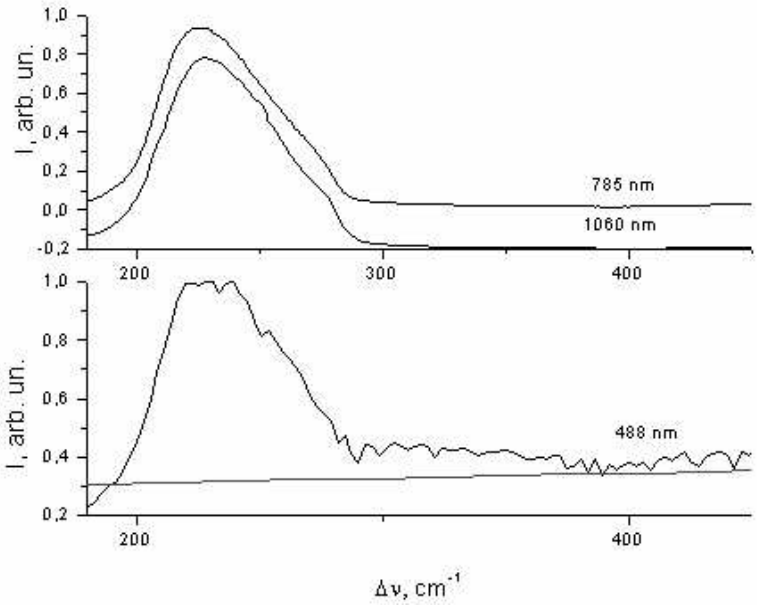

Fig. 3. Raman spectra for g-$As_{40}Se_{60}$ excited with light of different wavelengths indicated. The drawn line indicates the underlying luminescence background.

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 causes changes in case of g-$As_{40}Se_{60}$. As can be seen from Fig. 3 Raman line of g-$As_{40}Se_{60}$ excited with λ=488 nm has distinct shoulders at both sides of spectral curve. A frequency positions of these shoulders coincide with Raman bands of crystalline As_4Se_4 and As_4Se_3 [15,16] and calculated frequencies of free molecules As_4Se_4 and As_4Se_3 (Table 1). The shoulders that appear on the low frequency side of main band of g-$As_{40}Se_{60}$ 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 $As_4Se_{4(3)}$ on the base of Raman data. Such doubt exists at interpretation of high frequency side of main Raman band of g-$As_{40}Se_{60}$. Existence of shoulder at 254 cm^{-1} may be related to the presence both of Se-Se bonds in free Se (Fig. 4) and As-Se bond vibrations of As_4Se_3 molecule. The bend at 245 cm^{-1} may exist due to As-Se bonds of As_4Se_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 higher 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 $As_{3/3}$, $As_4Se_{4(3)}$ clusters.

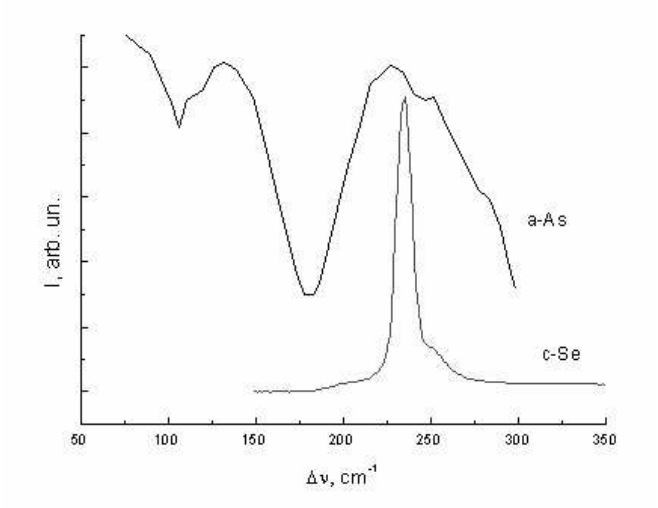

Fig. 4. Raman spectra of crystalline Se and amorphous As.

Table 1. Band positions in experimental Raman spectra of crystalline As_4Se_4 [15], As_4Se_3 [16] and calculated Raman frequencies of free molecules As_4Se_4, As_4Se_3.

Raman frequencies of c-As_4Se_4 [15]	Raman frequencies of the molecule As_4Se_4, (calculated)	Raman frequencies of As_4Se_3 [16]	Raman frequencies of molecule As_4Se_3, (calculated)
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-As_2S_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 conclude that the structural study needs methods which can give exact information about bond types. For example, we used [19] x-ray photoelectron spectroscopy for 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 cm^{-1} (Fig. 5). An assignment of these bands can be made using quantum-chemical calculations. The geometry of the clusters is shown in Fig. 1. An important feature of As_2Se_5 cluster is Se-Se bonds at the ends of clusters. The ends of As_4Se_6, As_6Se_9 clusters

were closed by the double Se bond. A calculated frequency at 300 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 As_2Se_3, As_4Se_6, and As_6Se_9 clusters have frequency at 360 cm^{-1} (Fig. 5). So, the low intense bands at 300 and 350 cm^{-1} in the Raman spectra of g-$As_{40}Se_{60}$ (Fig. 3) may be related to the vibrations of Se-Se and As-Se ends, respectively. The same situation was observed for another clusters of Ge-S and As-S [20, 21]. So, excitation of the Raman signal by the energy $h\nu > E_0$ makes spectra more informative, which allows to reveal the s.u. $As_{3/3}$, $As_2Se_{4/2}$, $Se_{2/2}$ in g-$As_{40}Se_{60}$ structure.

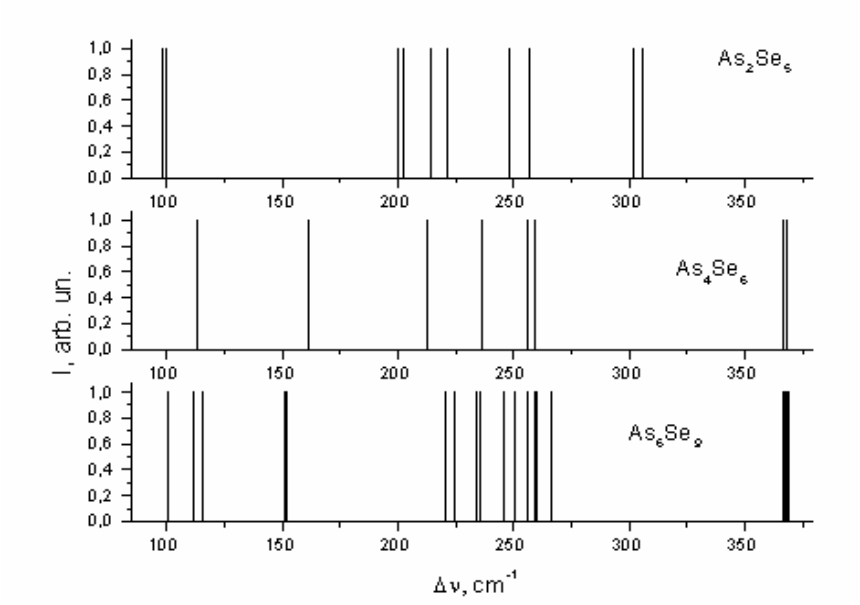

Fig. 5. Vibration spectra of clusters.

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