Ring-, branchy-, and cage-like As_nS_m nanoclusters in the structure of amorphous semiconductors: ab initio and Raman study

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Ab initio calculations were performed on ring-, branchy-, and cage-like As_nS_m nanoclusters being the building blocks of cluster model are generally found in As_xS_{100-x} glasses and of different crystals known in the As-S system. The optimal geometry, total energy, formation energy and Raman spectra of the As_nS_m nanoclusters were calculated using density functional theory (DFT). The formation probability of different types of As_nS_m nanoclusters in the glassy matrix were analyzed by calculating their energy components and the relative stabilities were revealed. The contribution of such structures to the experimental Raman spectra of As-S glasses, implications and some possible induced effects are also discussed.

1. Introduction

After first preparing of chalcogenide glassy semiconductors [1] the results of probabilistic thermochemical, diffraction and spectroscopic structural investigations of glassy materials like g-As_2S_3 at different stages of their formation (see [2,3-16] and references summarized there) testified a non-random character of the interaction of components in the melt and retention of a short-range ordering (SRO) in the glass similar to their crystalline analogues. Therefore the first attempts in the understanding of the features of the Raman spectra of amorphous or glassy As_2S_3 were based on the Raman spectrum of the crystalline counterpart (c-As_2S_3) [4] in molecular approximation. The similarity of the averaged vibrational spectra of c-As_2S_3 measured along the three crystallographic axes with the spectrum of the glass of the same composition was interpreted [5] within the frames of the microcrystalline hypothesis proceeding from the layered-chain structure. It is still considered that AsS_3 and GeS_4 type polyhedrons are connected by As(Ge)-S-As(Ge) flexible bridge bonds, which allow structural units to change their orientation relative to each other easily [11,12]. So just the variation of bridging bonds itself leads to the absence of the long-range ordering (LRO) during the formation of an ideal glassy structural matrix in classical continuous random network model (CRN) [22] where the SRO was explained by the correlations in bonding configuration of neighbouring atoms. However, the results of electron, X-ray and neutron diffraction studies indicated that the mutually correlated displacement of atoms in chalcogenide glasses extends to ~2.0 nm [23-31] which exceeds the sizes of one structural unit (about 0.4-0.5 nm). This was interpreted by the majority of researchers as demonstration of the presence of clusters (medium-range ordering) in glasses, where the topology of atoms is similar to that observed in truncated fragments of crystalline compounds-analogues [24-32].

The main band with maximum at 340 cm^{-1} in the Raman spectrum of As_2S_3 was assigned to valence vibrations of AsS_3 pyramids. However, the decomposition of the peak and the analysis of the Raman spectra of non-stoichiometric As-S glasses soon lead to the conclusion that not the AsS_3 pyramids the only structural units forming the glass [4]. The existence of more complex structural units within the frames of the cluster model was shown earlier [33-34]. The calculated Raman peaks of different clusters covered a broad spectral region from 260 to 450 cm^{-1} [33].

These observations raised new issues related to the formation probability, stability and ratio of the different clusters as well as their contribution to the measured Raman spectra. The knowledge about topology, concentration, stability and other physico-chemical properties of these structural blocks also helps the better understanding not only of the structure of As-S glasses, but in general the non-crystalline state at the nanoscale, and opens the way for detailed study of the effects related to induced structural changes in amorphous semiconductors.

This work focuses on ab initio study of optimal geometry, energy of formation and stability, as well as vibrational properties of different (branchy-, ring-, and cage-like) types of As_nS_m nanoclusters and their

contribution to the experimental Raman spectra of glassy arsenic sulphides.

2. Experimental and calculation details

Arsenic sulfide glasses were prepared by melting of elemental arsenic and sulfur in evacuated and sealed quartz vials, placed in a rocking furnace at 800 °C for 24 h. The samples were then cooled in air with cooling rate of ~1 K/s.

Raman spectra of As_xS_{100-x} glasses and polycrystalline As_2S_3 were measured using Renishaw 1000 Raman spectrometer equipped with a CCD detector. A diode laser (785 nm) was used as excitation source during the measurements. Optical filters limiting the output power were used in order to avoid photostructural changes in the

glass. The spectra were measured in micro-Raman configuration using back-scattering geometry.

Self-consistent DFT field calculations were performed using the BLYP [35,36] functional. The Stuttgart RLC ECP [37] basis set was used for the As and S atoms, which was modified by the addition of one polarization d-function (nd) identical to that in Pople's 6-31G* basis set. All calculations were done using the GAMESS (US) quantum-chemical program package [38].

Formation energy, stability and vibrational spectra of different finite As_nS_m clusters (and S_8 ring) were studied. The clusters belong to three categories that are expected to be important in As-S glasses: ring-, branchy-, and cage-like (Fig. 1) structural blocks. In order to improve the model of chemical environment within the clusters, the dangling bonds were saturated by hydrogen atoms.
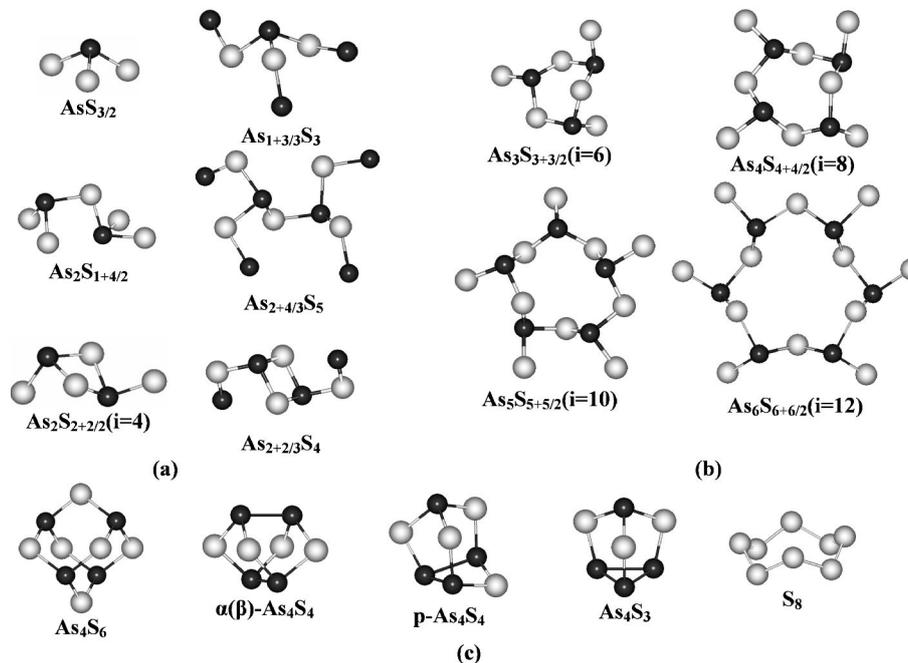
Fig. 1. Geometrical structure of the modeled branchy (a), ring- (b), and cage-like (c) As_nS_m nanoclusters (i – number of atoms in the ring).

To allow atomic relaxation all cluster geometries were fully optimized using augmented Hessian technique [38] and quadratic approximation (QA) method. The geometry optimizations were followed by second derivative calculations using the same method and basis set in order to verify that the structures found are true global minima. The Raman spectra of As_nS_m clusters were computed using standard techniques. To completely eliminate the influence of saturating hydrogen atoms on the vibrations the masses of these atoms are assigned a very large value (1024 a.u.) and the Raman modes were recalculated using modified zero dipole derivative and polarizability tensors as described in [32].

3. Results

3.1 Total energy, formation energy and stability of As_nS_m clusters

The formation energy of a cluster can be determined as:

$$E_{form} = E_{tot} - E_{at}, \qquad (1)$$

where E_{form} being the clusters formation energy, E_{tot} is the total energy of the cluster, and E_{at} is the sum of the energies of the free atoms that constitute the cluster. This way the influence of the H atoms can be excluded in whatever position they are. The following equations were used to calculate the cluster formation energies:

i) for clusters with S end-atoms:

$$E_{form.(As_nS_m)} = E_{tot.(As_nS_mH_k)} - [nE_{As} + mE_S + kE_H + \sum_{i=1}^{m} E_{b.(S-H)_i}]$$

ii) for clusters with As end-atoms:

$$E_{form.(As_nS_m)} = E_{tot.(As_nS_mH_k)} - [nE_{As} + mE_S + kE_H + \sum_{i=1}^{n} E_{b.(As\langle^H_H)_i}]$$

where E_S, E_{As} and E_H are the energies of S, As and H atoms respectively,

$$E_{b.(S-H)} = \frac{1}{2}[E_{tot.(H-S-H)} - E_s - 2E_H]$$

is the S-H bond energy, and finally

$$E_{b.(As\langle^H_H)} = \frac{2}{3}[E_{tot.(H-As\langle^H_H)} - E_{As} - 3E_H]$$

is the energy contribution of $As\langle^H_H$ bonds. All energy values (E_S, E_{As}, E_H, $E_{b.(S-H)}$ and $E_{b.(As\langle^H_H)}$) were calculated with the same method as $E_{tot.}$.

Table 1. Total energy (E_{tot}), energy of formation (E_{form}) and relative bond energy ($E_{form}/j_{(As-S/S-S)}$, where j is a number of bonds in the cluster) of As_nS_m clusters calculated by DFT/BLYP/Stuttgart_nd method..

Clusters	E_{tot}, Hartree	E_{form}, Hartree	E_{form}/j, Hartree/bond
Branchy:			
$AsS_{3/2}$	-36.53555	-0.40230	-0.13410 (As-S)
$As_{1+3/3}S_3$	-55.13828	-0.80473	-0.13462 (As-S)
$As_2S_{1+4/2}$	-63.05274	-0.80840	-0.13473 (As-S)
$As_{2+4/3}S_5$	-87.85450	-1.34313	-0.13431 (As-S)
$As_2S_{2+2/2}$	-53.02018	-0.79884	-0.13314 (As-S)
$As_{2+2/3}S_4$	-65.42611	-1.07040	-0.13380 (As-S)
$AsS_{1+3/2}(AsS_4)$	-46.69127	-0.53586	-0.13397 (As-S)
Ring:			
$As_2S_{2+2/2}(n=4)$	-53.02018	-0.79884	-0.13314 (As-S)
$As_3S_{3+3/2}(n=6)$	-79.54427	-1.21192	-0.13466 (As-S)
$As_4S_{4+4/2}(n=8)$	-106.05936	-1.61512	-0.13459 (As-S)
$As_5S_{5+5/2}(n=10)$	-132.57745	-2.02299	-0.13487 (As-S)
$As_6S_{6+6/2}(n=12)$	-159.08854	-2.42240	-0.13458 (As-S)
Cage:			
As_4S_6	-86.01424	-1.61421	-0.13452 (As-S)
$\alpha(\beta)-As_4S_4$	-65.65189	-1.29618	
$p-As_4S_4$	-65.64729	-1.29158	
As_4S_3	-55.46360	-1.13005	
S_8	-81.38861	-1.21131	-0.15141 (S-S)

The formation energy depends also on the number of bonds present in the cluster (*j*). For all clusters with only regular As-S (or S-S for S_8) bonds the ratio of $E_{form.}/j$ is proposed to be a good value for characterization of clusters relative stability. The results of calculations are summarized in Table 1 and Fig. 2.
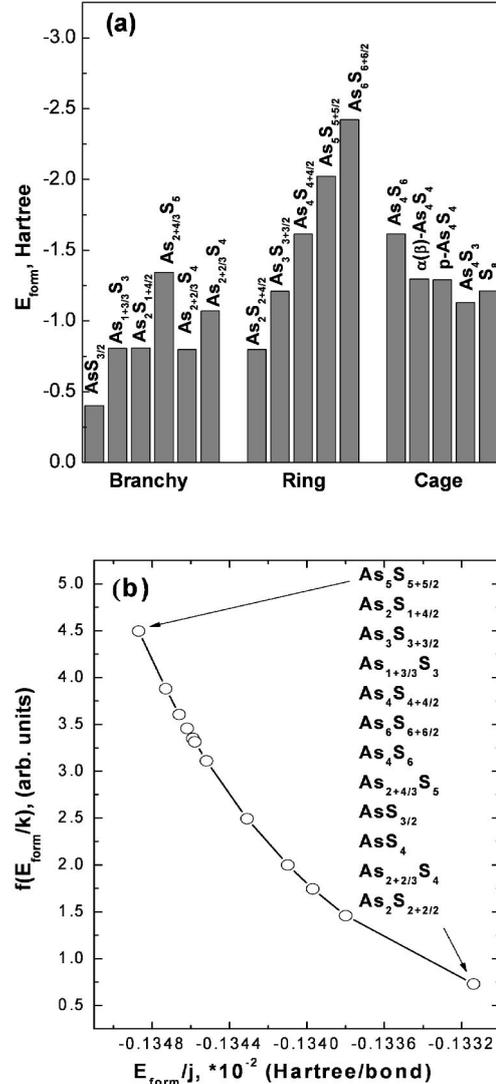
Fig. 2. (a) Formation energy (E_{form}) and (b) Boltzmann distribution of E_{form}/j values of $As_nS_m(S_8)$ clusters.

3.2 Raman Spectra of arsenic sulphides

The measured Raman spectra of As_xS_{100-x} glasses of different composition are shown in Fig. 3. The main band in the spectrum of the sample with stoichiometric glass composition (curve *b*) has a maximum at 340 cm^{-1} and two shoulders at ~310 and ~380 cm^{-1}. First two vibrational modes in the Raman spectra of As_2S_3 are commonly interpreted as symmetric and asymmetric As-S stretching vibrations of AsS_3 pyramidal structural units, respectively. The third mode at ~380 cm^{-1} is interpreted as "water like" S-As-S vibrations. Also, there are other features in the

spectrum at 187, 219, 233 and 490 cm^{-1} caused, first of all, by the non-ideality of the glassy network.
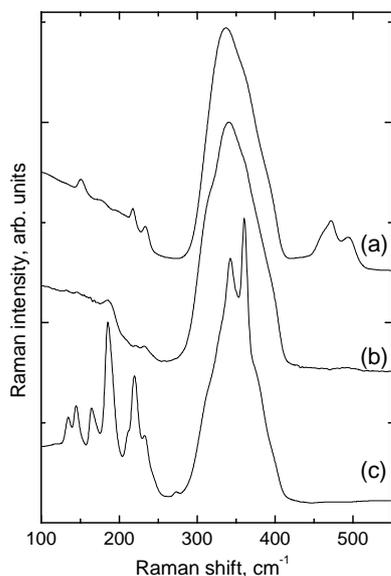
Fig. 3. Raman spectra of As_xS_{100-x} glasses: x=28.6 (a), x=40 (b), x=45 (c).

Additional vibrational modes can be observed also in the spectra of As-S glasses with excess sulphur (at 151 and 472 cm^{-1}, curve *a* in Fig. 3) or arsenic (135, 145, 165, and 360 cm^{-1}, curve *c*) compare to the stoichiometric sample. These peaks indicate the presence of extra S-S or As-As bonds in the structural matrix and/or in different molecular species.

While the calculated spectra of clusters with cage-like geometry and their correlations with the experimental Raman spectra of As_xS_{100-x} glasses were published elsewhere [39], the calculated Raman spectra of the different glass forming branchy- and ring-like As_nS_m nanoclusters are shown in Fig. 4a and 4b, respectively. It can be seen that the number of peaks and their position vary in a wide range depending on the geometrical configuration of the cluster. However, in most cases a number of bands are located in the 300-400 cm^{-1} region, where the maximum of the main band in the experimentally recorded spectra can be found.
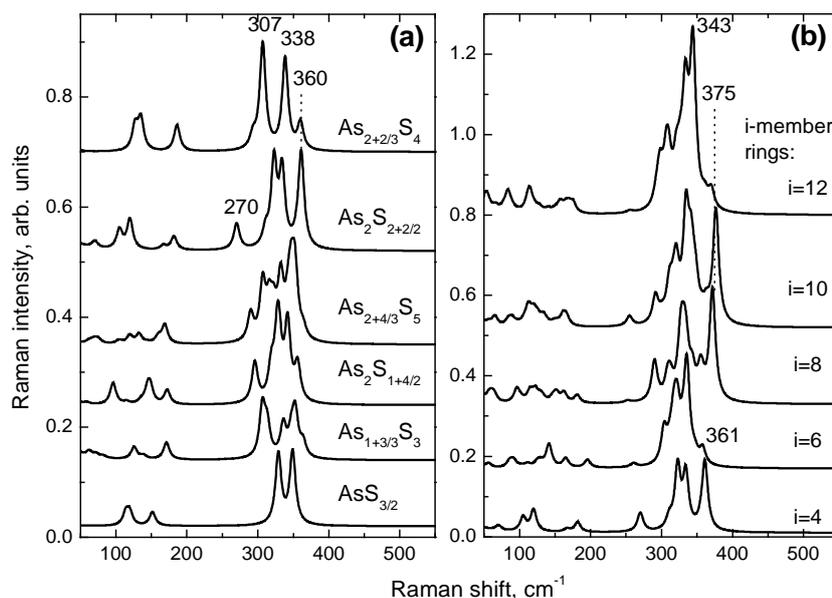
Fig. 4. Calculated Raman spectra of most stable glass forming (branchy- and ring-like) As_nS_m nanoclusters (DFT/BLYP/Stuttgart_nd).

4. Discussion

The comparison of the Raman spectra of polycrystalline and glassy As_2S_3 is shown in Fig. 5 together with the calculated Raman spectra of the 12-member ring (cluster $As_6S_{6+6/2}$). The spectrum of polycrystalline *c*-As_2S_3 consists of four vibrational modes at 292, 310, 355, and 382 cm^{-1}. The peaks obtained during peak-fitting of the spectrum of *g*-As_2S_3 (306, 340 and 385 cm^{-1}) can be compared with the Raman modes of *c*-As_2S_3,

however, there will be a relatively large difference in the case of the band having highest intensity.

On the other hand, the calculated Raman modes of $As_6S_{6+6/2}$ is grouped in the spectral region from 290 to 370 cm^{-1} what is the spectral region of the main band in the Raman spectra of As_2S_3 glass (Fig. 5). The curve obtained by superimposing Lorentzian functions generated from the parameters of the calculated Raman modes of the 12-member ring reveals well the features of the experimentally determined Raman spectrum of *g*-As_2S_3. Therefore, in this sense the cluster approximation

describes better the structure of the glass than the approach based on the analogy of the crystal and the glass.
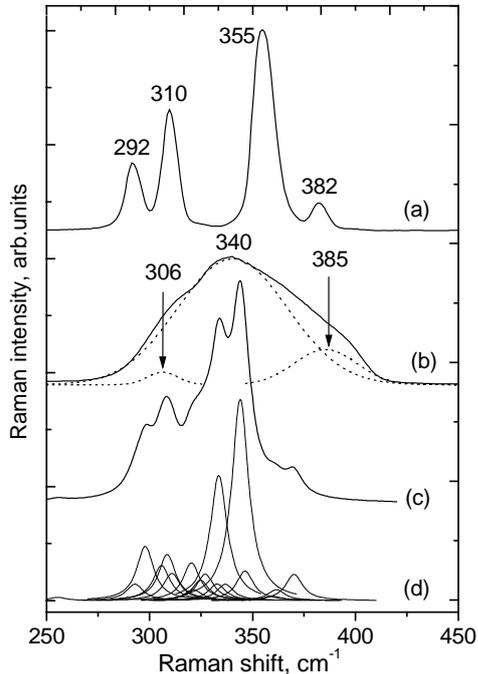
Fig. 5. Raman spectra of non-oriented polycrystalline (a) and glassy (b) As$_2$S$_3$ together with calculated Raman spectra of 12-member ring As$_6$S$_{6+6/2}$ cluster visualized as integrate spectra (c) and independent Lorentzian functions (d).

The analysis of the calculated values for different clusters (Table 1) leads to interesting observations regarding their contribution to the formation of the glassy matrix. The formation energies of the clusters vary from -2.4 to -0.4 Hartrees. Comparison of different cluster types shows that ring-like units have the lowest formation energy, and they followed by cage- and branchy-like clusters (Fig. 2a). The mean As-S energy values (per bond) of the As$_2$S$_{2+2/2}$ cluster composed of edge-shared AsS$_3$ pyramids forming 4-member ring ($E_{form.}/j$=-0.13314 Hartree/bond), the As$_{2+2/3}$S$_4$ branchy cluster ($E_{form.}/j$=-0.13380 Hartree/bond) and the hypothetic quasi-tetrahedral AsS$_{1+3/2}$(AsS$_4$) structural unit indicate their lower stability compared to other As$_n$S$_m$ formations. It is interesting to note that the most stable nanocluster is a 10-member ring (As$_5$S$_{5+5/2}$, -0.13487 Hartree/bond) and not the 12-member ring, which is the main building block of crystalline As$_2$S$_3$. Two branchy-like clusters come next in the stability order, namely the As$_2$S$_{1+4/2}$ and As$_{1+3/3}$S$_3$ units.

The relative formation probability of clusters in the amorphous structure can be estimated by plotting the Boltzmann distribution of $E_{form.}/j$ values (Fig. 2b). It can be concluded that the formation probability of branchy clusters is lower compared with ring-like ones. This becomes not surprising since according to the literature, the B$_3$O$_6$ rings are thought to be formed during slow cooling of vitreous *v*-B$_2$O$_3$ [40]. There is also an

investigation showing the polyamorphic transitions in *v*-B$_2$O$_3$ under pressure [41].

The formation probability values determine which nanoclusters will have the highest content in the matrix and, therefore, the highest contribution to the Raman spectrum. They can be used as some weighting function to determine the contribution of the vibrational modes of different clusters in the Raman spectra and this will be a task for further detailed investigations.

The formation probabilities will certainly be different if changing the initial conditions. The excess of arsenic or sulfur in the melt will increase the number of As- or S-rich clusters in the synthesized glasses. Therefore, the new bands appearing in the spectra of non-stoichiometric glass compositions can also be assigned based on the calculated Raman spectra of clusters.

The above results can effectively be used to interpret and analyze structural changes in As-S glasses induced by external factors, assuming that they affect on the stability of the nanoclusters forming the glass. Earlier it was shown that even the stoichiometric As$_2$S$_3$ composition could contain small amounts of different clusters, and their concentration in the matrix is affected by synthesis conditions [42]. The physico-chemical properties of these structural units differ from those of the main network and these centres can be very sensitive to the external influence. External factors will change the formation probabilities, and will lead to structural transformations, which can be detected by Raman spectroscopy for instance. Combining the measured and calculated data the type of newly formed clusters can be estimated. Using this approach we have found earlier, that due to laser illumination of the As-S glasses the As$_4$S$_4$ cluster with realgar-like geometry transforms into pararealgar-like As$_4$S$_4$ structural unit [43-45].

5. Conclusions

The microstructure of arsenic glassy chalcogenides was analysed in detail by modelling different As$_n$S$_m$ nanoclusters. A DFT method was used to optimize geometry and to calculate the energies of formation and stabilities as well as vibrational properties of the clusters. The results show that the formation energy of the clusters (E_{form}) and mean bond formation energy (E_{form}/j) characterize well the cluster stability, and the Boltzmann distribution of E_{form}/j is a good indicator for the formation probability of a given cluster in the glass structure. It was found that AsS$_3$ pyramids form the stable ring structures, the most stable of which is a 10-member ring. There is another possibility, where the network is formed by branchy-like structures, from which the most stable ones are the As$_2$S$_{1+4/2}$ and As$_{1+3/3}$S$_3$ clusters. The cage-like clusters involved in photostructural changes. The superposition of Raman spectra of a number of most stable As$_n$S$_m$ nanoclusters describe very well the Raman spectra of different As$_x$S$_{100-x}$ glasses.

Acknowledgements

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