

Comparing nature of low frequency vibration of As_nS_m nanoclusters in bulk glasses and clusters incorporated in dielectric matrixes

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Abstract - The position of calculated low frequency (LF) modes of i -member rings decreases with increasing cluster sizes. They are torsional and out of plane bending vibrations involving group of atoms and even extend to 3-5 bonds. The atomic motions for some of these vibrations have a “wave-like” character. Torsional LF vibration also have free elastic sphere oscillations transposed earlier to free or embedded nanoparticles acoustic modes.

I. INTRODUCTION

Earlier in [1] recall how Lamb's theoretical description of free elastic sphere oscillations, the so-called spheroid and torsional modes, and later transposed to nanoparticles low frequency (LF) acoustic modes so that they could be used for grain size determination. In general the Boson peak (BP) in the LF Raman spectra of bulk glasses has been related to the existence of intermediate range ordering (clusters) [2]. Our studies showed that the chain-like cluster sizes for the As-S system exceeds one structural unit (s.u.) in order to obtain vibrational modes in the (LF) region, and values of 6-8 Å were determined from the size distribution functions [2]. In this work we combined LF Raman scattering measurements on different As_xS_{100-x} glasses with *ab initio* DFT calculations on arsenic sulphide ring-, branchy-like and cage-like nanoclusters, the main building blocks of this glassy network.

II. METHODS

LF Raman spectra were measured using a triple grating Dilor-XY800 spectrometer equipped with a CCD detector. Finite size atomic As_nS_m nanoclusters containing structural units expected to be important for glassy As-S system were used to study the Raman active LF modes (Fig. 1). The 632.8 nm line of He and series of line of Ar/Kr-ion lasers was used as excitation source. The spectra were measured in macro-Raman configuration using back-scattering geometry. *Ab initio* DFT calculations were performed using the quantum-chemical package GAMESS (US) [4]. The DFT method with the pure corrected exchange functional by Becke [5] and the gradient-corrected correlation functional by Lee *et al.* [6] was applied for geometry optimizations and calculation of the Raman spectra. The Stuttgart RLC ECP [7] basis set modified by the addition of one polarization d-function (nd) identical to that in Pople's 6-31G* [8] basis set was used for the As and S atoms.

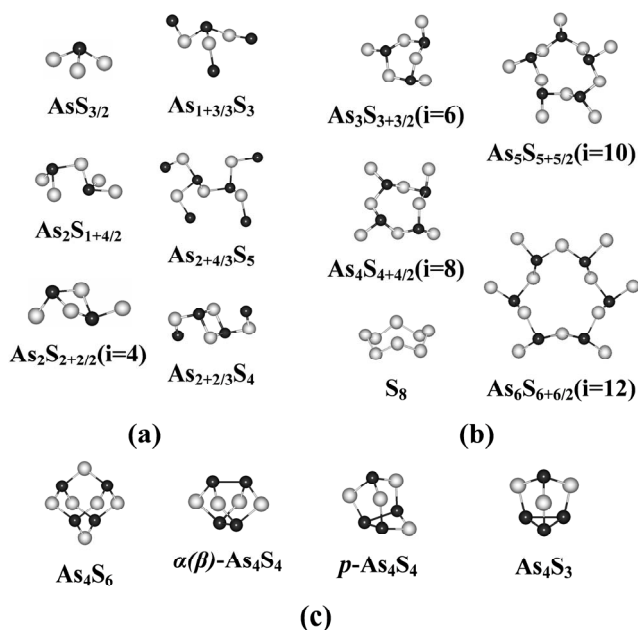


Fig.1 Branchy- (a), ring- (b), and cage-like (c) As_nS_m and S_8 nanoclusters used for calculations.

III. RESULTS AND DISCUSSION

The observed BP positions (Fig. 2) and coordination numbers (z) for As_xS_{100-x} glasses are summarized in Table 1. Three types of atomic As_nS_m nanoclusters were used to calculate the LF Raman active modes, namely branchy-, ring-, and cage-like ones (Fig.1). Only the glass-network forming branchy- and ring-like clusters have LF vibrational modes (Fig.3). No LF vibrations were calculated for the cage-like clusters. On the other hand, two clearly resolved bands can be seen at 33 and 41 cm^{-1} in the Raman spectra of glasses with excess sulphur ($x=6$), located in the high frequency part of the BP region.

Table 1
Compositional dependence of BP position in As_xS_{100-x} glasses.

X (at. %)	ω_B (cm^{-1})	Z	x (at. %)	ω_B (cm^{-1})	z
22.0	21.5	2.22	40.0	26.5	2.40
28.6	25.0	2.29	45.0	22.5	2.45

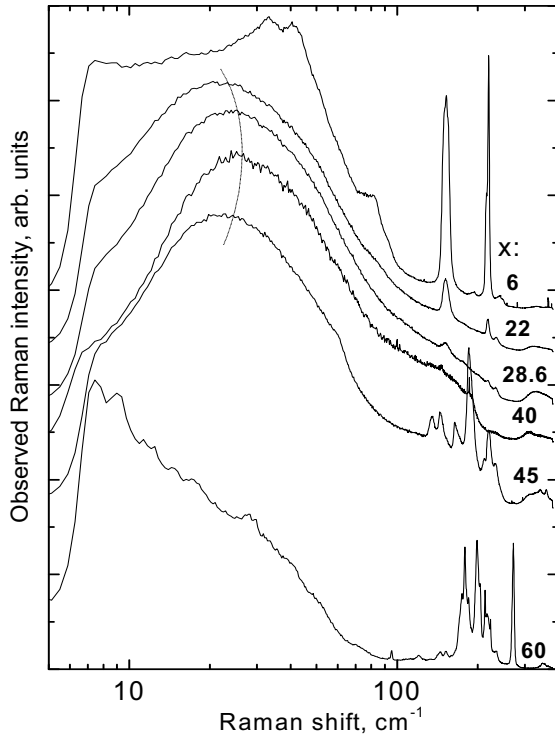


Fig. 2 Depolarized (HV) LF Raman spectra of As_xS_{100-x} glasses.

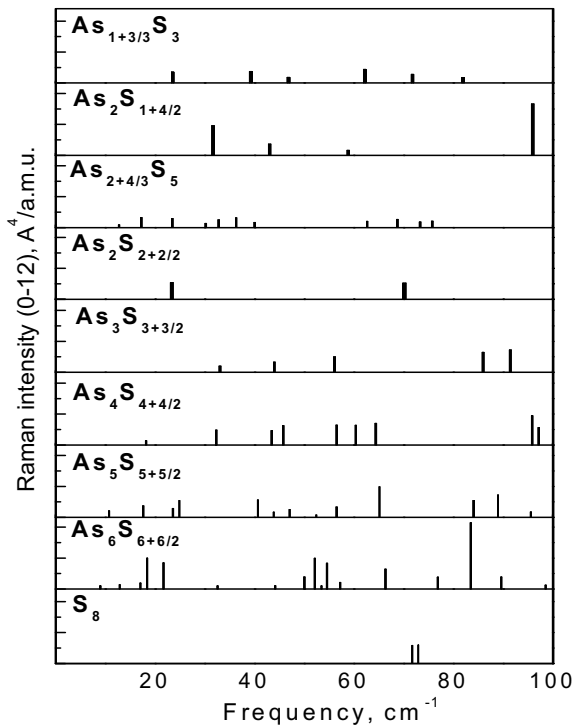


Fig.3 Calculated LF Raman spectra of chain-, ring-like As_nS_m nanoclusters and the S_8 ring.

These bands are very similar to the vibrational modes calculated for S_8 ring (at 72 and 73 cm^{-1}) (see Fig. 3). (The relatively large deviation of the peak positions in the experimental and calculated spectra can be due to the limitations of the calculations and by the influence of the surrounding environment on the S_8 vibrations in the real glass). As we showed earlier [2] the branchy- or chain-like

clusters build of AsS_3 s.u. (but not one pyramid alone) have LF vibrational modes in their calculated spectra that are mostly of torsional type in nature. Also, increasing the length of these clusters (*i.e.* by increasing the cluster size) led to a red shift of the lowest frequency modes. For example, the lowest in frequency vibrational mode at 31 cm^{-1} , calculated for $As_2S_{1+4/2}$ cluster, is shifted to 13 cm^{-1} for $As_{2+4/3}S_5$. Apart from the branchy structures also rings can play an important role in the structure of the glass (it is known that a 12-member ring is the main building block of the As_2S_3 crystal [3]) we extended our cluster approach to ring-like structures of different sizes. The geometries, total energies and stabilities as well as vibrational properties were calculated for these rings. The analysis shows that an 8-membered ring has the highest stability, and thus favorable for amorphous structures. The lowest frequency modes were calculated to 33, 18, 11, and 9 cm^{-1} for 6-, 8-, 10-, and 12-membered rings, respectively. The other modes of the clusters are located in the spectral region of the BP, covering the whole LF spectral range ($<100 cm^{-1}$). The analysis of normal coordinates of these low frequency vibrations indicate that they are torsional and out of plane bending vibrations involving group of atoms and even extend to 3-5 bonds. The atomic motions for some of these vibrations have a “wave-like” character. The low wavenumber vibrations exist in nanoparticles either free or embedded semiconductor (CdS_xSe_{1-x}) and oxide (SnO_2 , TiO_2 , HfO_2). So-called spheroid and torsional modes of LF vibration have free elastic sphere oscillations transposed earlier to free or embedded nanoparticles acoustic modes [1].

IV. CONCLUSION

Our experimental and theoretical results together indicate that small atomic clusters contribute to, at least, the high frequency part of the BP in the Raman spectra of bulk glassy materials. Torsional type of LF clusters vibration exist not only in nanoclusters incorporated in dielectric matrixes but in branchy- or chain-like and 6-, 8-, 10-, and 12-membered rings in bulk glasses in cluster description of their structure.

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