

Boson peak in low-frequency Raman spectra of $\text{As}_x\text{S}_{100-x}$ glasses: nanocluster contribution

Roman Holomb^{*1}, Volodimir Mitsa^{**1}, Patrik Johansson², and Miklos Veres³

¹ Research Institute of Solid State Physics and Chemistry, Uzhhorod National University, Voloshyn 54 str., 88000, Uzhhorod, Ukraine

² Department of Applied Physics, Chalmers University of Technology, 41296 Gothenburg, Sweden

³ Research Institute for Solid State Physics and Optics of the Hungarian Academy of Sciences, PO Box 49, 1525 Budapest, Hungary

Received 1 August 2009, revised 16 October 2009, accepted 19 October 2009

Published online 12 February 2010

PACS 61.43.Fs, 63.22.Kn, 63.50.Lm, 78.30.Ly

* Corresponding author: e-mail holomb@ukr.net, Phone: +38(03122)33020, Fax: +38(03122)33341

** e-mail mitsa@univ.uzhgorod.ua, Phone: +38(03122)33020, Fax: +38(03122)33341

The origin of the Boson peak was investigated using Raman spectroscopy and *ab initio* calculations. Low frequency Raman active vibrational modes of different branchy-, ring- and cage-like As_mS_n nanoclusters were calculated and compared to experimentally determined Raman spectra of $\text{As}_x\text{S}_{100-x}$ glasses with different compo-

sition. A good correlation was found between the spectral features and the calculated Raman modes. The possible structural nature of the Boson peak in arsenic chalcogenides is proposed and discussed.

© 2010 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

1 Introduction Non-crystalline semiconducting materials (especially chalcogenides) are nowadays very important for both potential applications and fundamental investigations [1, 2]. The absence of long-range ordering in the structures is an obstructing factor limiting both the experimental and theoretical approaches to investigate these materials at the nanoscale [3]. However, by using theoretical methods (*ab initio*, molecular dynamics *etc.*) and combining them with experimental results, significant progress has been made in this field during the last decade [1, 4].

One of the most important, intriguing and still mysterious fundamental phenomenon in the physics of non-crystalline solids is the excess contribution to the low-frequency (LF) vibrational states with respect to the predictions of the Debye theory. Inelastic scattering (neutron, Raman) studies reveal a broad peak (usually referred to as the Boson peak (BP)) in the 2–10 meV energy range, the intensity of it being proportional to the density of states ($g(\omega)$) by the rule of $g(\omega)/\omega^2$. On the other hand the Debye theory predicts a constant intensity value for this spectral region [5–7].

Studies of the relaxational and vibrational properties of amorphous solids in the LF ($<100 \text{ cm}^{-1}$) region may con-

tribute to the understanding of anomalous properties at low temperatures, the glass transition and other phenomena observed in amorphous systems. While the relaxation dynamics can be described by the mode coupling theory [8], the vibrational excitations are still unsettled and subject of intense discussions. There are two different prevailing hypotheses [9] in this field. According to the first, the excess vibrational states are due to the localization of the high energy vibrational modes induced by the static disorder in the non-crystalline state. The second is based on the existence of collective propagating modes at high frequencies, whose density of states is reflected by the BP. In the first case the energies in the BP correspond to the energies of high- Q excitations, while the excitations are expected to propagate at energies above the energies of the BP region for the latter.

The BP in the LF Raman spectra of glasses has also been related to the existence of intermediate range ordering (clusters) [10–12]. The idea is that the arrangement of atoms or atomic bonds in such clusters could assist the interpretation of the physics of amorphous systems.

In this work we combined LF Raman scattering measurements on different $\text{As}_x\text{S}_{100-x}$ glasses with *ab initio* DFT

calculations on arsenic sulphide ring-, branchy-like and cage-like nanoclusters, the main building blocks of this glassy network, in order to investigate the compositional dependence of BP and to find correlations between different cluster arrangements and the BP.

2 Experimental and theoretical details

Arsenic sulphide glasses were prepared by melting of elemental arsenic and sulphur in evacuated and sealed quartz ampoules placed in a rocking furnace at 600 °C for 24 h. These glasses were then cooled in air with a cooling rate of 1 K/s. As_xS_{100-x} glasses with compositions of $x=6, 22, 28.6, 40, 45, 60$ were prepared.

LF Raman spectra were measured using a triple grating Dilor-XY800 spectrometer equipped with a CCD detector cooled by liquid nitrogen. The slit width was set to 1 cm^{-1} . The 632.8 nm line of an Ar/Kr-ion laser was used as excitation source. The spectra were measured in macro-Raman configuration using back-scattering geometry. The output power of the excitation source was limited by means of optical filters in order to avoid photo-induced changes in the structure.

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). Optimal geometry, total and formation energies, electronic and vibrational properties were calculated. For better modelling of the chemical environment the dangling bonds of clusters were terminated by H atoms.

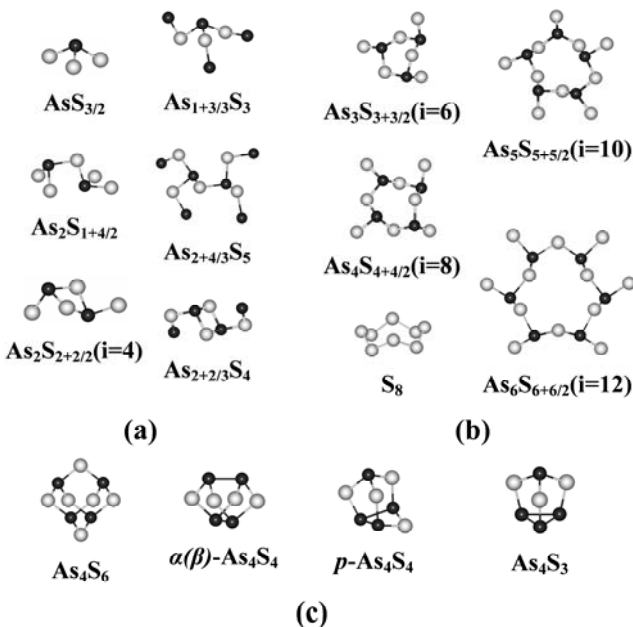


Figure 1 Branchy- (a), ring- (b), and cage-like (c) As_nS_m and S_8 nanoclusters used for calculations.

Ab initio DFT calculations were performed using the quantum-chemical package GAMESS (US) [13]. The DFT method with the pure corrected exchange functional by

Becke [14] and the gradient-corrected correlation functional by Lee *et al.* [15] was applied for geometry optimizations and calculation of the Raman spectra. The Stuttgart RLC ECP [16] basis set modified by the addition of one polarization d-function (nd) identical to that in Pople's 6-31G* [17] basis set was used for the As and S atoms.

Atomic relaxation was taken into account by means of minimization of the total energy of the clusters. The clusters geometries were optimized using the conjugate-gradient algorithm. To eliminate the influence of saturating hydrogen atoms on the vibrations their masses were assigned a very small value (10^{-4} a.u.); thereby the corresponding vibrations are completely suppressed. In addition, the elements of the calculated dipole derivative and polarizability tensors affected by hydrogen atoms were changed to zero prior to spectra computation.

3 Discussion Glassy materials feature the BP in the LF region of their Raman spectra (Fig. 2). The dimensions of structural correlation (cluster sizes) can be calculated

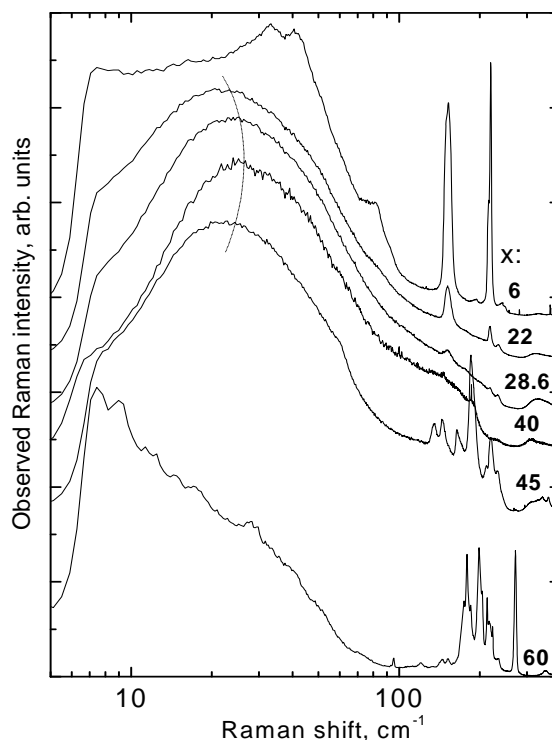


Figure 2 Depolarized (HV) LF Raman spectra of As_xS_{100-x} glasses.

using the position of the maximum of this peak (ω_B) [12,18]. In the mechanical theory of Phillips-Thorpe the intensity of LF vibrations in glasses depends on the average coordination number z [19]. The observed BP positions and coordination numbers for As_xS_{100-x} glasses are summarized in Table 1.

Our earlier studies showed that the 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 [12]. According to the data in Table 1 the highest frequency (26.5 cm⁻¹) of the BP is for the stoichiometric glass (x = 40), thus indicating that this sample contains the largest ordered sequences (clusters).

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

Three types of atomic As_nS_m nanoclusters were used to calculate the LF Raman active modes, namely branchy-, ring-, and cage-like ones. The calculated LF Raman spectra of these nanoclusters are shown in Fig. 3. The calculations led to a surprising result: only the glass-network forming branchy- and ring-like clusters have LF vibrational modes. No LF vibrations were calculated for the cage-like clusters. This is in accordance with the experimental Raman spectra of the polycrystalline sample with a large arsenic excess, where the intensity of the BP significantly decreases (Fig. 2, x = 60). An analysis of the spectral region of valence vibrations (~150–300 cm⁻¹) shows this to be mainly composed of cage-like clusters (As₄S₄, As₄S₃ etc.), for this sample. 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. These bands are very similar to the vibrational modes calculated for S₈ 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 S₈ vibrations in the real glass).

Now let us analyse the other As_nS_m clusters. As we showed earlier [12] the branchy- or chain-like clusters build of AsS₃ s.u. (but not one pyramid alone) have LF vibrational modes in their calculated spectra that are mostly of torsional type in nature. These vibrations are located in the BP region of the Raman spectra. 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 As₂S_{1+4/2} cluster, is shifted to 13 cm⁻¹ for As_{2+4/3}S₅. 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 As₂S₃ crystal) 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 favourable for amorphous structures. The calculated LF Raman active modes of size-dependent *i*-member rings exhibit a trend similar to that observed for branchy structures: the position of the LF modes decreases with increasing cluster sizes. The lowest frequency modes were calculated to 33, 18, 11, and 9 cm⁻¹ for 6-, 8-, 10-, and 12-membered

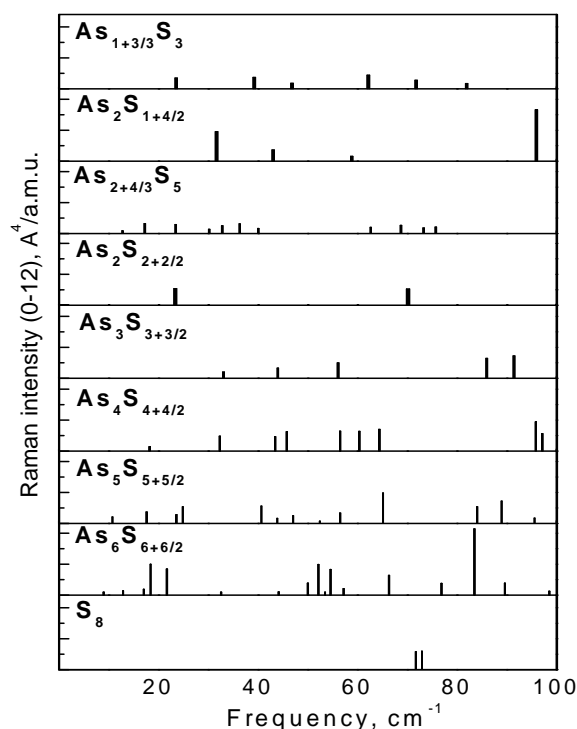


Figure 3 Calculated LF Raman spectra of chain-, ring-like As_nS_m nanoclusters and the S₈ ring.

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 “wavelike” character. The LF vibrational modes were calculated also for a model cluster consisting of two boroxol rings, representing the medium range ordering in the B₂O₃ glass [20]. 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 glassy materials. Moreover, we believe that larger clusters may reproduce the medium range order in the glass and the localized collective LF vibrations can be responsible for the BP.

In conclusion, we have studied the microscopic structural origin of BP in As_xS_{100-x} glasses by using LF Raman and *ab initio* methods. The comparison of composition-dependent BP in the Raman spectra of glasses with the re-

sults of *ab initio* calculations clearly indicate the collective contribution of different nanoclusters of branchy- and ring-like types to the low-frequency spectral region.

Acknowledgements The authors are grateful to Assistant Prof. Aleksandar Matic for his valuable discussions and to Dr. Ezio Zanghellini for his technical assistance (both of Chalmers University of Technology). We thank the Ukrainian Ministry of Education and Sciences for financial support of the DFD project.

References

- [1] M. Popescu, *Non-Crystalline Chalcogenides* (Kluwer Academic Publishers, New York, 2000).
- [2] A.V. Kolobov and J. Tominaga, *J. Mat. Sci.: Mater. Electron.* **14**, 677 (2003).
- [3] A. Feltz, *Amorphous and Glassy Nonorganic Solid State* (Translated from German, Ed. House "Mir", Moscow, 1986).
- [4] V. Mitsa, R. Holomb, M. Veres, and M. Koos, *Raman studies of nanostructured chalcogenide glasses* (Intermix Kiado, Budapest, 2009), p. 104.
- [5] W. A. Phillips, *Amorphous Solids: Low-Temperature Properties* (Springer-Verlag, New York, 1981).
- [6] U. Buchenau, H. M. Zhou, N. Nuker, K. S. Gilroy, and W. A. Phillips, *J. Phys. Rev. B* **34**, 5665 (1986).
- [7] A. P. Sokolov, U. Buchenau, W. Steffen, B. Frick, and A. Wischnewski, *J. Phys. Rev. B* **52**, R9815 (1995).
- [8] W. Götze, *Liquids, Freezing and the Glass Transition* (North-Holland, Amsterdam, 1991), p. 287.
- [9] P. Benassi, A. Fontana, W. Frizzera, M. Montagna, V. Mazzacurati, and G. Signorelli, *Philos. Mag.* **71**, 761 (1995).
- [10] J. C. Phillips, *J. Non-Cryst. Solids* **43**, 37 (1981).
- [11] G. Lucovsky, C. K. Wong, and W. B. Pollard, *J. Non-Cryst. Sol.* **59/60**, 839 (1983).
- [12] R. Holomb and V. Mitsa, *Solid State Commun.* **129**, 655 (2004).
- [13] M. W. Schmidt, K. K. Baldrige, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. J. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. Su, T. L. Windus, M. Dupuis, and J. A. Montgomery, *J. Comput. Chem.* **14**, 1347 (1993).
- [14] A. D. Becke, *Phys. Rev. A* **38**, 3098 (1988).
- [15] C. Lee, W. Yang, and R. G. Parr, *Phys. Rev. B* **37**, 785 (1988).
- [16] EMSL Basis Set Library (<http://www.emsl.pnl.gov/forms/basisform.html>).
- [17] V. A. Rassolov, J. A. Pople, M. A. Ratner, T. L. Windus, *J. Chem. Phys.* **109**, 1223 (1998).
- [18] V. K. Malinovsky, V. N. Novikov, A. P. Sokolov, *J. Non-Cryst. Solids* **90**, 485 (1987).
- [19] M. Thorpe and J. Cai, *J. Non-Cryst. Solids* **114**, 19 (1989).
- [20] T. Uchino and T. Yoko, *J. Chem. Phys.* **105**, 4140 (1996).