

Ab initio calculations and the effect of atomic substitution in the Raman spectra of As(Sb,Bi)₂S₃ films

Olexandr Kondrat¹, Natalija Popovich¹, Roman Holomb^{*1}, Volodimir Mitsa^{**1}, Olexandr Petrachenkov¹, Margit Koós², and Miklos Veres²

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

² 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 9 October 2009, accepted 15 October 2009

Published online 12 February 2010

PACS 61.43.Fs, 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 comparative analysis of the calculated and experimental Raman spectra of non-crystalline As₂S₃, Bi₂S₃ and Sb₂S₃ films (*i.e.* with exchanging As to Sb, Bi) obtained by flash evaporation on glassy and silicon substrates was performed. The spectra were interpreted and analysed using the results of molecular modelling and *ab initio* calculations. The structural models used for

calculations include both basic building blocks and other types of atomic clusters known for As-S, Bi-S, and Sb-S binary systems. The influence of atomic substitution on the nanostructure of flash evaporated As(Sb,Bi)₂S₃ films were investigated, observed photo-induced phenomena and related peculiarities were analysed using results of *ab initio* calculations and discussed in detail.

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

1 Introduction Amorphous chalcogenides is a class of materials with a wide range of potential applications in modern nanotechnology [1]. In addition these materials show a number of interesting peculiarities in their electronic and optical properties which is, first of all, related to their geometrical structure at the nanoscale. Therefore, they are interesting as model objects too, intensively studied for better understanding of ordering and self-organization in amorphous materials, and contribute to the development of generalized theory for non-crystalline state. The information that could be obtained by traditional experimental methods on these materials is limited by absence of long-range ordering in the structure [2]. In recent years remarkable progress was achieved in the study of the structure and properties of amorphous and glassy systems by combining different experimental methods with molecular modelling and *ab initio* calculations [3].

In this work Raman spectroscopy was used together with the *ab initio* DFT calculations to study the nanostructure of As(Sb,Bi)₂S₃ films and to test the applicability of the classical quasi-isotopic approximation to the vibrational spectra during As→Sb→Bi substitution.

During our study we detected also some photo-induced effects and structural rearrangement caused by laser irradiation. The obtained results were analyzed and discussed in detail.

2 Experimental and theoretical details

2.1 Sample preparation and acquisition of the Raman spectra The non-crystalline As(Sb,Bi)₂S₃ films of different thickness (0.5, 1, and 1.5 μm) were obtained by flash evaporation on glassy and silicon substrates.

The Raman spectra of the samples (Fig. 1) were measured using a Renishaw System 1000 Raman spectrometer equipped with a CCD detector. A diode laser operating at 785 nm was used as the excitation source. The spectra were measured in micro-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.

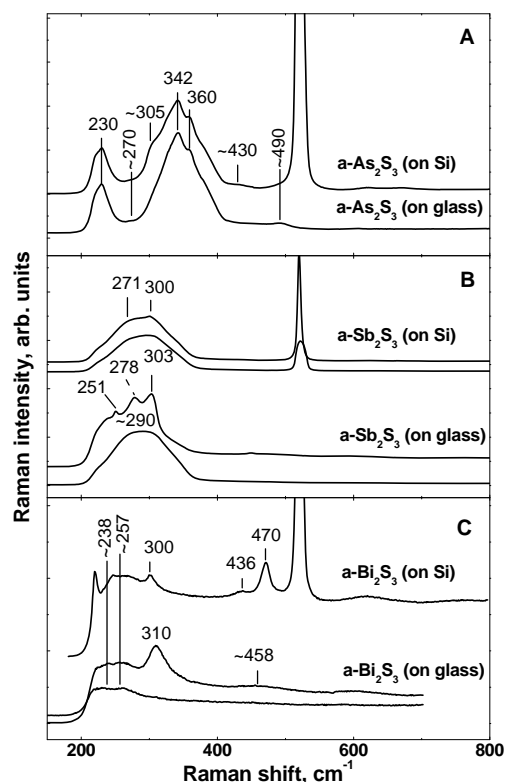


Figure 1 Raman spectra of As₂S₃ (a), Sb₂S₃ (b), and Bi₂S₃ (c) films.

The spectra were interpreted and analyzed using the results of molecular modeling and *ab initio* calculations. The structural models used for calculations include both basic and common building blocks and other types of atomic clusters known for As-S, Bi-S, and Sb-S binary systems, respectively.

2.2 *Ab initio* calculations of vibrational spectra of As(Sb,Bi)_nS_m nanoclusters

Different finite clusters of atoms containing isostructural YS₃ (Y=As,Sb,Bi) pyramidal units were used for calculations. The computational procedure consisted of geometry optimization and *ab initio* calculation of vibrational properties of three different nanoclusters (Fig. 2). The dangling bonds of the clusters were terminated by hydrogen atoms.

Ab initio DFT calculations were performed using the quantum-chemical package GAMESS (US) [4]. Pure corrected exchange functional by Becke [5] and the widely used gradient-corrected correlation functional by Lee, Yang and Parr [6] (BLYP) (i) and hybrid Beck's three-parameters B3 [7] functional, defining the exchange functional as a linear combination of Hartree-Fock local and gradient-corrected exchange terms (B3LYP), were used during geometry optimization and calculation of the Raman spectra. Stuttgart RLC ECP [8] basis set, modified by addition of one polarization d-function (nd) identical to

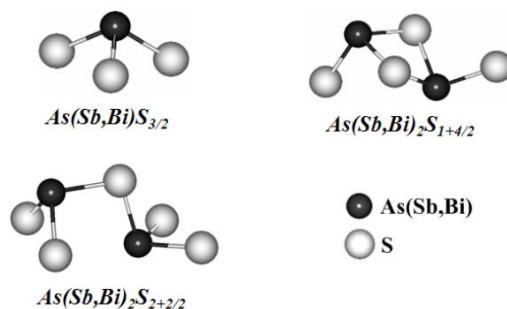


Figure 2 Simplest isostructural models used to determine the role and possibilities of quasi-isotopic substitution approximation in Raman spectra of a-As(Sb,Bi)₂S₃.

that in Pople's 6-31G* [9] basis set, was used for 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 conjugate-gradient algorithm. The vibrational Raman active modes and eigenvectors are computed using standard techniques. To eliminate the influence of saturating hydrogens on the vibrations localized in the defect the masses of these atoms are assigned a very small value (10⁻⁴ a. u.) and the corresponding vibrations are completely suppressed. Also, the elements of the calculated dipole derivative and polarizability tensors affected by hydrogen atoms were changed to zero.

3 Discussion According to the classical quasi-isotopic substitution rule the valence vibrations of X-A and Y-A atomic groups are related to the mass of the X and Y atoms by the following ratio:

$$\frac{\nu_{X-A}}{\nu_{Y-A}} = \sqrt{\frac{m_Y}{m_X}}, \quad (1)$$

where ν_{X-A} and ν_{Y-A} are frequencies of valence X-A and Y-A vibrations; m_X and m_Y are the masses of X and Y atoms, respectively.

The main broad band centered at 342 cm⁻¹ and the shoulder at ~305 cm⁻¹ in the Raman spectra of As₂S₃ films (Fig. 1a) correspond to symmetric and antisymmetric vibrations of AsS₃ pyramids, respectively [10]. The other peaks seen in the spectra at 230, 370, 360, and 490 cm⁻¹ are related to vibrations of molecular-like As-S clusters and S-S bonds [11,12].

The main band in the Raman spectra of Sb₂S₃ films is located at ~290 cm⁻¹ (Fig. 1b). Other Raman bands detected in the spectra at 251, 271, 278, 300, and 303 cm⁻¹ are probably arise from the non-homogeneities and/or poly-crystallinity of the structure of this material at the nanoscale. Using the main bands observed in the Raman spectra of As₂S₃ and Sb₂S₃ films at 342 and at 290 cm⁻¹,

respectively, the deviation of their frequency position from quasi-isotopic substitution approximation rule can be estimated. The deviation was also calculated for the theoretical spectra of the model clusters presented in Fig. 2. The procedure was applied to the Sb→Bi substitution too. The results are summarized in Table 1.

Table 1 Deviation (δ) from quasi-isotopic approximation rule for As→Sb→Bi substitution in As(Sb,Bi)₂S₃ films.

δ (%)	Substitution	
	As→Sb	Sb→Bi
Experimental	11.2	4.7
Theoretical*	20.3	23.0

* Based on the symmetric valence vibrations of pyramids only.

During Sb→Bi substitution, the main broad band in the Raman spectra of Bi₂S₃ films is red-shifted and splits into two peaks centred at ~238 and ~257 cm⁻¹ (Fig. 1c). On the other hand, the calculated frequency for symmetric Bi-S stretching vibrations of BiS₃ pyramids is 307 cm⁻¹. Therefore, in this case the calculated deviation is 4.7 % and 23.0 % for experimental and theoretical results, respectively (Table 1).

While significant deviation from rule (1) for the calculated spectra could be related to the theoretical level used during calculations, both the presence of molecular species of different type in the structure and the differences in local chemical ordering (*i.e.* with a non-isostructural nature of the basic structural units) could play role in the deviations observed for the experimental data. Therefore, the crystal structure of corresponding As₂S₃, Sb₂S₃ and Bi₂S₃ materials was analyzed in detail [13–15].

Figures 3a and 3b show the structure of Sb₂S₃ and Bi₂S₃ crystals, respectively. It can clearly be seen that the local structure of Sb₂S₃ consists of not only SbS₃ pyramids but SbS₅ structural units too. One-, two-, and threefold coordinated sulphur atoms can be observed in the local structure of Bi₂S₃. Beside BiS₃ pyramids SBi₃ building blocks can also be detected.

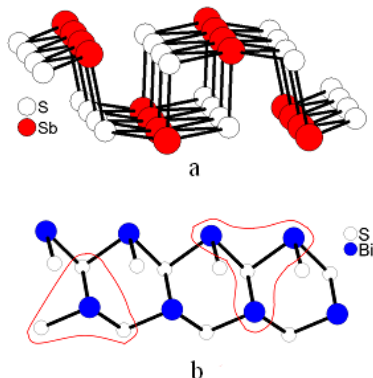


Figure 3 Geometrical structure of stibnite, Sb₂S₃ (a) and bismuthinite, Bi₂S₃ (b) layers.

To understand the influence of such a “wrong” coordination on the Raman spectra of these materials, *ab initio* calculations were performed on a quasi-ring model cluster (Fig. 4). The comparison of the experimental Raman spectra of Bi₂S₃ films shows a good agreement with the results of the calculation. According to the calculated spectra and normal mode analysis the band at 310 cm⁻¹ is related to valence vibrations of Bi=S units with under-coordinated S atoms.

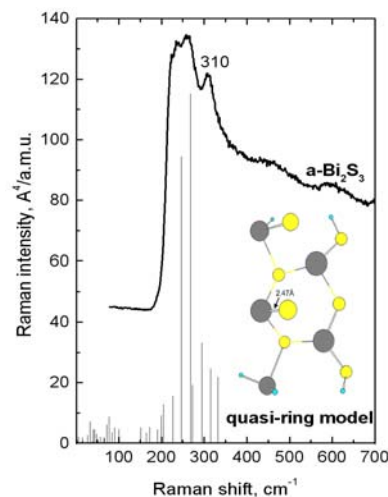


Figure 4 Comparisons of the experimental Raman spectra of Bi₂S₃ film and calculated spectra for quasi-ring model optimized at DFT/BLYP/LANL2DZ ECP level of theory.

Light induced structural modifications were also probed all of the studied films by micro-Raman spectroscopy. It was found that the photo-induced structural transformations in As₂S₃ films are very similar to those observed and described by us earlier for glassy arsenic trisulphide [12,16]. No significant laser-induced effects were observed in the microstructure of Sb₂S₃ films.

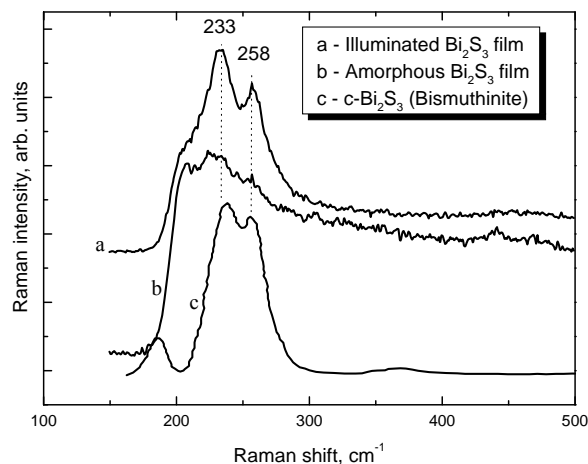


Figure 5 Photo-induced crystallization of Bi₂S₃ films. The sample was illuminated by laser irradiation.

The illumination of Bi₂S₃ films with a laser having photon energy of 2.54 eV and intensity of $\sim 10^3$ W/cm² lead to photo-induced transformations depicted in Fig. 5. The comparison of the Raman spectra of illuminated Bi₂S₃ films and crystalline Bi₂S₃ indicates that photo-induced crystallization takes place during the light treatment of the sample.

4 Conclusions In summary, in this paper the structure of As(Sb,Bi)₂S₃ films was investigated at the nanoscale by micro-Raman spectroscopy and *ab initio* DFT calculations in order to establish the applicability of quasi-isotopic substitution rule on the vibrational spectra of this family of amorphous systems. It was shown that the deviation from the rule is connected with the absence of iso-structurality in local chemical ordering of these materials. The related peculiarities observed in the Raman spectra of these materials were interpreted using the results of cluster modelling and *ab initio* calculations. Light induced changes in these amorphous films were also investigated.

Acknowledgements The authors are grateful to Assistant Prof. Patrik Johansson (Chalmers University of Technology) for many helpful discussions. The financial support from DB 702 and UA-2/2006 project is also acknowledged.

References

- [1] A.V. Kolobov, J. Tominaga, *J. Mater. Sci.: Mater. Electron.* **14**, 677 (2003).
- [2] A. Feltz, *Amorphous and Glassy Nonorganic Solid State* (Translated from German, Ed. House "Mir", Moscow, 1986).
- [3] V. Mitsa, R. Holomb, M. Veres, M. Koos, *Raman Studies of Nanostructured Chalcogenide Glasses (Intermix Kiado, Budapest, Hungary, 2009)*, p. 104 (in: Hungarian).
- [4] 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, J. A. Montgomery, *J. Comput. Chem.* **14**, 1347 (1993).
- [5] A. D. Becke, *Phys. Rev. A* **38**, 3098 (1988).
- [6] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **37**, 785 (1988).
- [7] A. D. Becke, *J. Chem. Phys.* **98**, 5648 (1993).
- [8] EMSL Basis Set Library (<http://www.emsl.pnl.gov/forms/basisform.html>).
- [9] V. A. Rassolov, J. A. Pople, M. A. Ratner, T. L. Windus, *J. Chem. Phys.* **109**, 1223 (1998).
- [10] G. Lucovsky and R. Martin *J. Non-Cryst. Solids.* **8–10**, 185 (1972).
- [11] R. M. Holomb, V. M. Mitsa, *J. Opt. Adv. Mater.* **6**, 1177 (2004).
- [12] R. Holomb, V. Mitsa, P. Johansson, N. Mateleshko, A. Matic, M. Veresh, *Chalc. Lett.* **2**, 63 (2005).
- [13] N. Morimoto, *Mineralog. J.* **1**, 160 (1954).
- [14] A. Kyono, M. Kimata, M. Matsuhisa, Y. Miyashita, K. Okamoto, *Phys. Chem. Miner.* **29**, 254 (2002).
- [15] A. Kyono, M. Kimata, *Am. Mineral.* **89**, 932 (2004).
- [16] R. Holomb, N. Mateleshko, V. Mitsa, P. Johansson, A. Matic, M. Veres, *J. Non-Cryst. Solids* **352**, 1607 (2006).