

High-pressure Raman investigation of the semiconductor antimony oxide

Aihui Geng^{1,2}, Lihua Cao^{1,2}, Chunming Wan^{*1}, and Yanmei Ma^{**3}

¹ State Key Lab on High Power Semiconductor Laser, Changchun University of Science and Technology, 130022 Changchun, P.R. China

² Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, 130012 Changchun, P.R. China

³ Department of Agronomy, Jilin University, 130062 Changchun, P.R. China

Received 29 July 2010, revised 18 September 2010, accepted 19 September 2010

Published online 11 April 2011

Keywords high-pressure Raman, diamond anvil cell, antimony trioxide

* Corresponding author: e-mail wcm@cust.edu.cn, Phone: +00 86 431 85582007, Fax: +00 86 431 85582007

** e-mail ymma@jlu.edu.cn, Phone: +00 86 431 87836474, Fax: +00 86 431 87836474

The *in situ* high-pressure behavior of the semiconductor antimony trioxide (Sb₂O₃) has been investigated by Raman spectroscopy techniques in a diamond anvil cell up to 20 GPa at room temperature. New peaks in the external lattice mode range emerged at a pressure above 8.6–15 GPa, suggesting

that the structural phase transition occurred. The pressure dependence of Raman frequencies was obtained. The band at 139 cm⁻¹ (assigned to group mode) has a pressure dependence of -0.475 cm⁻¹/GPa and reveals significant softening at high pressure.

© 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

1 Introduction Antimony trioxide (Sb₂O₃) is a transparent material with an indirect band gap of 3.3 eV and has been widely used in fields of catalysis, fire retardants, glasses, sensors, as anode material for the Li-ion batteries, and retardants for rubber, ceramics, enamels, fabrics, and fiber products [1–7]. Moreover, the Sb₂O₃ thin film behaves as an n-type semiconductor [8], which invites its photovoltaic applications. Sb₂O₃ exists mainly in two crystalline forms, namely the cubic senarmontite form and the orthorhombic valentinite [9]. Senarmontite (cubic Sb₂O₃) is stable phase at low temperature $T < 570$ K and has a structure based on Sb₄O₆ molecules, in which SbO₃(E) pyramids are linked at their corners to form a cage-like structure (E being lone pair of electrons); Valentinite (orthorhombic Sb₂O₃) is high temperature phase stable above 570 K and also consists of SbO₃(E) pyramids and has a double chain structure consisting of four membered rings of pyramids [9,10].

Recent research on Sb₂O₃ has attracted the synthesis and preparation of nanoparticles [11–16] such as nanospheres, nano-wires, nanobelts and nano-rods [17–21], because of applications in the manufacture of advanced nanodevices. However, very few reports are available [10, 22–25] regarding the Raman studies of Sb₂O₃ either in the nano-material form or in the bulk form. Mestl et al. [9]

have investigated the spectroscopic behavior of Sb₂O₃/Sb₂O₄ in oxidizing and reducing atmospheres. Gilliam et al. [25] have carried out the first ab initio theoretical study of tetraantimony hexoxide (Sb₄O₆). They calculated the normal mode frequencies, intensities, and the corresponding vibrational assignments of Sb₄O₆ in T_d symmetry. We found no the reports of high-pressure behavior on Sb₂O₃. In fact, the pressure plays an important role in the study of semiconductors. Even modest pressures of 1 to 2 GPa can induce significant change in the crystal and electronic structures of semiconductors. This letter presents the *in-situ* Raman spectroscopy measurements of Sb₂O₃ up to pressure of 20 GPa. The results show that new peaks in the external lattice mode range emerged at high pressure. We observed the pressure shift of Raman modes during compression.

2 Experiment Commercially available Sb₂O₃ powder (99 %) was used. To determine the crystal structure of Sb₂O₃ used, an X-ray powder diffraction pattern was recorded. The measurement reveals that Sb₂O₃ adopts orthorhombic structure (Fig. 1). The observed Bragg peaks agree well with the reference data of Sb₂O₃ (PCPDF card number 11-0689). For high pressure experiments, the sample was finely ground and loaded into a diamond-anvil cell

© 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

with anvil faces diameter of 500 μm together with a small chip of ruby. A T301 stainless steel gasket was preindented to a thickness of 80 μm and a hole of 200 μm was drilled in the center of the preindented area. The pressure-transmitting medium was mixture of ethanol-methanol-water (16:3:1). The pressure was calibrated by the well-known ruby fluorescence method [26]. The Raman spectra were recorded at room temperature by a Renishaw-1000 Raman using the 514.5 nm line of Ar^+ laser as the excitation source. The scattered light was collected in backscattering geometry.

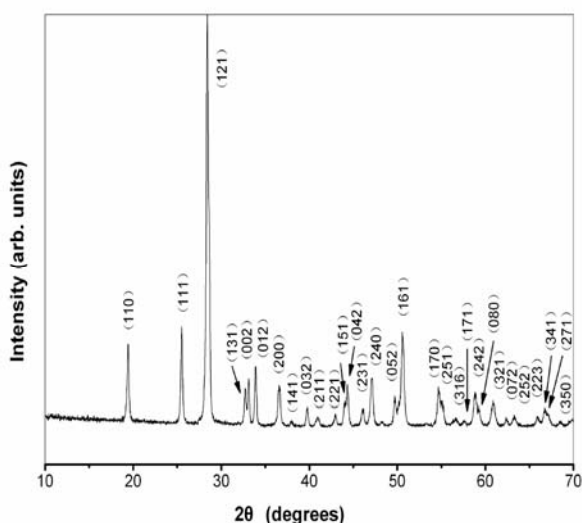


Figure 1 X-ray diffraction pattern of Sb_2O_3 at ambient conditions.

3 Result and discussion Sb_2O_3 , as important V-VI group semiconductors materials, have attracted a great deal of attention with regard to their thermoelectric effects and structural properties. Raman spectroscopy has been known to be one of the most convenient and powerful tools to study structural characters of materials through the solid-state effects on dynamical properties. It provides valuable information on local and cooperative changes during pressure-related transformations between phases. Orthorhombic form Sb_2O_3 can be considered to be consisting of four SbO_3 (E) pyramids (E being lone pair of electrons) arranged into the Sb_4O_6 molecular ring structure with a T_d symmetry [10,25]. Each oxygen is bridged between two SbO_3 pyramids. Gilliam et al. [25] gave decomposition of the reducible representation of the vibrational degrees of freedom with the T_d point group.

$\Gamma_{\text{vib}} = 2A_1 + 2E + 2T_1 + 4T_2$ of which A_1 , E and T_2 are Raman active modes. Figure 2 shows some representative Raman spectra of Sb_2O_3 in the frequency range of 100–800 cm^{-1} at different pressures. At ambient conditions (on bottom in Fig. 2), the position of Raman peaks observed are in good agreement with published other work [20–23], which is characteristic of the orthorhombic valentinite form of

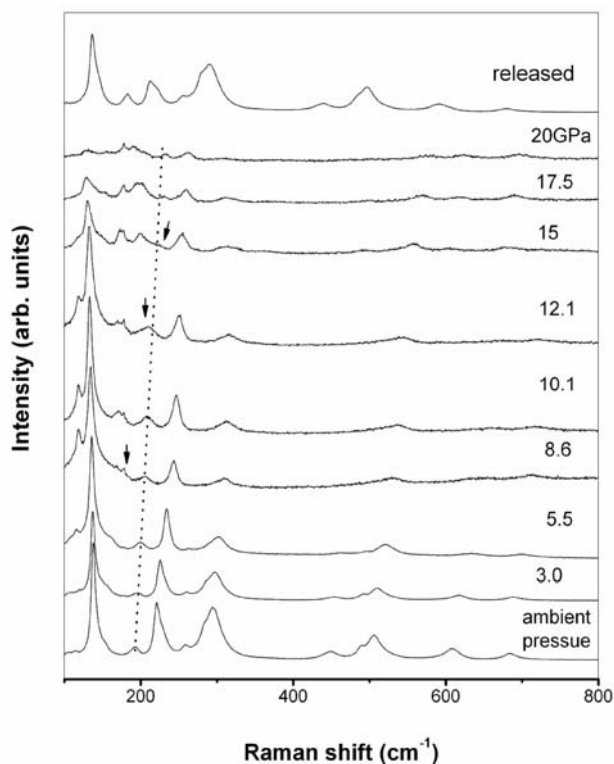


Figure 2 Selected Raman spectra of Sb_2O_3 as function of pressure at room temperature. The arrows indicate new bands which appear at a pressure about 8.6 GPa, 12.2 GPa and 15 GPa, respectively. The dash line indicates that the band at 192 cm^{-1} at ambient pressure gradually disappears with increasing pressure. The top panel is a Raman spectrum at ambient pressure after decompressing from 20 GPa.

Sb_2O_3 . All signals below 400 cm^{-1} belong to the external lattice mode, which is controlled by the crystal space group and unit cell coupling. Those above 400 cm^{-1} , in the internal mode region (400–800 cm^{-1}), is mainly controlled by the spectral features of polymeric Sb-O chains [22]. The internal modes are further classified into symmetric, ν_s , and asymmetric, ν_{as} , stretching modes at 684 and 608 cm^{-1} beside the symmetric, δ_s , and asymmetric, δ_{as} , bending modes located 506 and 449 cm^{-1} [10], respectively.

During the compression study, the Raman spectrum contained only features assigned to orthorhombic valentinite form of Sb_2O_3 up to pressure of 0 ~ 8 GPa (Fig. 2). At 8.6 GPa, a new band appears at 178 cm^{-1} in the low frequency range and becomes clearer at higher pressure (marked with arrows in Fig. 2). The shoulder peak 169 cm^{-1} becomes also clearer. Moreover, the shift of band at 169 cm^{-1} is faster than that of 178 cm^{-1} with the increase pressure. At about 17.5 GPa, the two new bands merge into a band. In addition, another two peak emerge at 200, and 228 cm^{-1} in the low frequency range when increasing pressure to 12.1 and 15 GPa (marked with arrows in Fig. 2), respectively. These bands show a pressure-induced increase in intensity and shift, and simultaneously the bands as-

signed to the orthorhombic Sb_2O_3 weaken and disappear gradually. Such as the strongest Raman band of the orthorhombic form Sb_2O_3 near 139 cm^{-1} is only just visible in the spectrum at 20 GPa. The dash line in the Fig. 2 also indicates that the band at 192 cm^{-1} gradually disappears with increasing pressure. So we suggest that the structural phase transition occurs at high pressure under room temperature and is very sluggish. The top pattern in Fig. 2 presents the Raman spectrum when the pressure is released to ambient. It has the same pattern as that of the starting material except for broader features, indicating the reversibility for the phase transition.

The shifts of Raman frequencies as a function of observed pressure from 0 to 20 GPa are depicted in Fig. 3. We can see that most of the modes exhibit positive changes in frequency with pressure, as expected, but the band at 139 cm^{-1} (assigned to group mode) shows a frequency decrease with increasing pressure. It has a pressure dependence of $-0.475\text{ cm}^{-1}/\text{GPa}$ and reveals significant softening at high pressure. In addition, the average pressure derivative of the high-frequency modes ($400\text{--}800\text{ cm}^{-1}$) is larger than that of the low-frequency modes (smaller than 400 cm^{-1}) ($0\text{--}2\text{ cm cm}^{-1}/\text{GPa}$). The pressure dependences the observed bands and assignments are presented in Table 1. Some observed peaks gradually become broadened with increasing pressure, such as the new peak at 200 cm^{-1} at 12.1 GPa. The broadened bands result from the SbO_3 tetrahedra distortion.

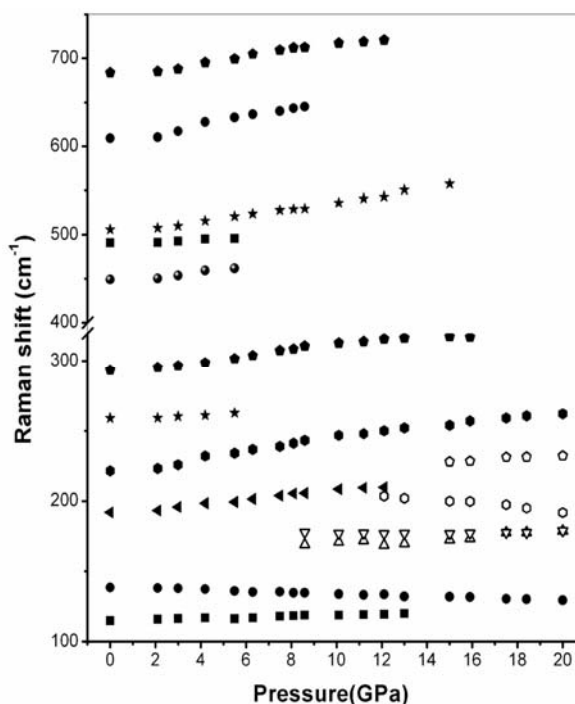


Figure 3 Pressure dependence of Raman modes of Sb_2O_3 during compression from 0 to 20 GPa. Open symbols represent new Raman bands which appear at 8.6 GPa, 12.1 GPa and 15 GPa, respectively.

Table 1 Ambient Raman frequency, their pressure dependences and assignments for orthorhombic valentinite form of Sb_2O_3 .

Ref. [10] $\nu\text{ (cm}^{-1}\text{)}$	Ref. [22] $\nu\text{ (cm}^{-1}\text{)}$	This study $\nu\text{ (cm}^{-1}\text{)}$	$d\nu/dP$ ($\text{cm}^{-1}/\text{GPa}$)	Assignments [10]
–	103	104	–	Group
–	–	115	0.321	Group
–	140	139	-0.475	Group
–	194	192	1.639	Group
219	223	223	2.155	Group
256	269	259	0.672	Group
297	294	293	1.770	Group
375	–	–	–	Group
451	449	449	2.499	δ_{as}
–	–	491	0.977	
502	502	506	3.579	δ_{s}
597	602	608	4.660	ν_{as}
683	690	684	3.548	ν_{s}
713	–	–	–	ν_{s}

ν_{s} , symmetric stretching mode, ν_{as} , asymmetric stretching mode,
 δ_{s} , symmetric bending mode, δ_{as} , asymmetric bending mode

4 Conclusion In summary, *in situ* high-pressure behavior of transparent semiconducting Sb_2O_3 was investigated using Raman spectrum up to 20 GPa in a diamond anvil cell (DAC) at room temperature. New Raman peaks are observed in the external lattice mode range at pressure of about 8.6, 12.1, and 15 GPa, respectively. We suggest that

Sb_2O_3 undergoes the structural phase transitions under high pressures. The structural transition is reversibility. We obtained the pressure dependence of Raman frequencies and found low frequency mode at 139 cm^{-1} shows significant softening at high pressure. The broadened bands result from the SbO_3 tetrahedra distortion.

Acknowledgements The authors are grateful to Qiliang Cui and Chunli Ma for help during the Raman experiments. This work was supported by the basic research funding (No. 421031216604) in Jilin University.

References

- [1] F. Li, W. Jianhuai, L. Jiongtian, W. Bingguo, and S. Shuo-jiang, *J. Compos. Mater.* **41**, 1487 (2007).
- [2] K. Ozawa, Y. Sakka, and M. Amano, *J. Mater. Res.* **13**, 830 (1998).
- [3] D.J. Dzimitrowicz, J.B. Goodenough, and P.J. Wiseman, *Mater. Res. Bull.* **17**, 971 (1982).
- [4] H. Bryngelsson, J. Eskhult, L. Nyholm, M. Herranen, O. Alm, and K. Edstrom, *Chem. Mater.* **19**, 1170 (2007).
- [5] J. Spengler, F. Anderle, E. Bosch, R. Grasselli, et al., *Phys. Chem. B* **105**, 10772 (2001).
- [6] B. Duh, *Polymer* **43**, 3147 (2002).
- [7] H.H. Liu and Y.J. Iwasawa, *Phys. Chem. B* **106**, 2319 (2002).
- [8] M. Metikos-Hucovic and B. Lovrecek, *Electrochim. Acta* **23**, 1371 (1978).
- [9] G. Mestl, P. Ruiz, B. Delmon, and H. Knozinger, *J. Phys. Chem.* **98**, 11276 (1994).
- [10] M. Nalin, Y. Messaddeq, S. J. L. Ribeiro et al., *J. Mater. Chem.* **14**, 3398 (2004).
- [11] Y. Hu, H. Zhang, and H. Yang, *J. Alloys Compd.* **428**, 327 (2007).
- [12] P. Christian and P. O'Brien, *J. Mater. Chem.* **15**, 4949 (2005).
- [13] D.W. Zeng, C.S. Xie, B.L. Zhu, and W.L. Song, *Mater. Lett.* **58**, 312 (2004).
- [14] G.J. Zhu, X.M. Feng, X.J. Yang, X. Wang, and L.D. Lu, *Chin. J. Inorg. Chem.* **21**, 441 (2005).
- [15] C.H. Xu, S.Q. Shi, C. Surya, and C.H. Woo, *J. Mater. Sci.* **42**, 9855 (2007).
- [16] L. Feng, J. Liu, L. Liao, and J. Wu, *J. Chem. Ind. Eng.* **56**, 2245(2005).
- [17] Z. Zhang, B. Li, Y. Zhao, X. Xu, C. Zhang, and Z. Wu, *Chem. Lett.* **35**, 1026 (2006).
- [18] D. Sendor, T. Weirich, and U. Simon, *Chem. Commun.* 5790 (2005).
- [19] X. Chen, X. Wang, C. An, J. Liu, and Y. Qian, *Mater. Res. Bull.* **40**, 469 (2005).
- [20] B.S. Naidu, M. Pandey, V. Sudarsan, R.K. Vatsa, and R. Tewari, *Chem. Phys. Lett.* **474**, 180 (2009).
- [21] Z. Deng, D. Chen, F. Tang, X. Meng, J. Ren, and L. Zhang, *J. Phys. Chem. B* **110**, 18225 (2006).
- [22] C.A. Cody, L. Dicarolo, and R.K. Darlington, *Inorg. Chem.* **18**, 1572 (1979).
- [23] I. R. Beattie, K. M. S. Livingston, G. A. Ozin, and D. J. Reynolds, *J. Chem. Soc. A* 449 (1970).
- [24] P.J. Miller and C.A. Cody, *Spectrochim. Acta* **38A**, 555 (1982).
- [25] S.J. Gilliam, J.O. Jensen, A. Banerjee, D. Zeroka, S.J. Kirkby, and C.N. Merrow, *Spectrochim. Acta A* **60**, 425 (2004).
- [26] H.K. Mao and P.M. Bell, *Year Book Carnegie Inst. Wash.* **77**, 904 (1978).