

Relative Oxidation States of Antimony on Ternary Chalcogenides $\text{Ge}_{n-2}\text{Sb}_4\text{Se}_{n+2}$ ($n = 4, 5$)

Guan-Ruei Chen (陳冠睿)¹, Ho-Chen Hsieh (謝和謙)², Chia-Wei Yang (楊家維)¹, and Chi-Shen Lee (李積琛)^{1,3*}

¹Department of Applied Chemistry, National Chiao Tung University, Hsinchu, Taiwan

²Program for Science and Technology of Accelerator Light Source, National Chiao Tung University, Hsinchu, Taiwan

³Center for Emergent Functional Matter Science, National Chiao Tung University, Hsinchu, Taiwan
chishen@mail.nctu.edu.tw

Abstract

Ternary chalcogenides, $\text{Ge}_{n-2}\text{Sb}_4\text{Se}_{n+2}$ ($n = 4, 5$), were synthesized under a solid state reaction at 475 °C. These compounds are the first crystalline selenides in ternary Ge-Sb-Se system that feature a layered SnSe-type structure containing a zig-zag $\infty^1[\text{Sb}_2\text{Se}_2]^{2-}$ 1D chain with unusual Sb^+-Sb^+ contact. The as-synthesized compounds exhibit interesting thermoelectric properties correlated to the $\infty^1[\text{Sb}_2\text{Se}_2]^{2-}$ chain and disordered sites with varies Ge/Sb compositions. To understand the oxidation state of antimony, we combined X-ray diffraction, X-ray photoelectron spectroscopy, X-ray absorption spectroscopy and DFT calculation to study their structures and relative oxidation states of antimony. The PXRD and XANES experiments were performed with the synchrotron radiation source in NSRRC. The results of XPS and XANES suggest the relative oxidation states of antimony atom in $\text{Ge}_{n-2}\text{Sb}_4\text{Se}_{n+2}$ ($n = 4, 5$) are lower than that of Sb atom in Sb_2Se_3 and higher than antimony element. Furthermore, DFT calculations revealed different partial density of states between the Sb sites in Sb-Sb contact and isolated Sb atoms.

Keywords - Crystal structure, Chalcogenides, Thermoelectrics, Antimony, Oxidation state

Introduction

2D Semiconductors, such as black phosphorous or binary selenide SnSe, have attracted attention for their unique structural features and chemical compositions that lead to special physical properties and potential applications including supercapacitor [1] and thermoelectric devices [2]. Especially, SnSe in the form of single-crystal show an optimized thermoelectric figure of merit (ZT) 2.6 at 650 °C, which contributed to its ultralow thermal conductivity and high electrical conductivity [2]. To enhance thermoelectric properties, the effects of complex structures and anisotropic bonding characteristics on their physical properties are interesting to solid state chemists, which may play important roles in thermal and electrical conductivity. In this research, we identified two novel ternary selenides, GeSb_2Se_3 and $\text{Ge}_3\text{Sb}_4\text{Se}_7$ [3], which may provide a new structure-property correlation for thermoelectric applications.

Experiments

$\text{Ge}_{n-2}\text{Sb}_4\text{Se}_{n+2}$ ($n = 4, 5$) were synthesized by a solid state sintering method. All operations were performed in a dry N_2 filled glove box to prevent reagents from deteriorating (for germanium mainly). In a typical experiment, powder of germanium, antimony and selenium as reactants were mixed uniformly with a mortar and pestle, and then, the stoichiometric mixture was loaded in a quartz tube as the reaction container, which was sealed under a vacuum ($\sim 10^{-3}$ mbar) with an oxyhydrogen flame. The sealed ampoules were placed in the furnace, heated from room temperature to 475 °C in 1 day, held at 475 °C for 3 days and this was followed by quenching in water at a normal temperature. Products of silvery ingot formed, showing board-shaped crystals on the surface of the ingot. The experiments were also repeated at 550 °C and above, but

there were no title compounds and Sb_2Se_3 was the major product instead.

Crystal structures of both compounds were determined with suitable single crystals. Phase identification and Rietveld refinement were carried out with synchrotron PXRD (beamline TPS-09A). In order to understand the oxidation states of antimony, XPS on 3d region and XANES on K-edge (beamline TPS-44A) and L_3 -edge (beamline TLS-BL16A1) were performed. The edge positions for XANES were determined by the first derivative maxima method. DFT calculations was based on the Stuttgart TB-LMTO-ASA program for DOS and COHP, and the WIEN2k program package for the band structures.

Thermoelectric properties including Seebeck coefficient (S), electrical conductivity (σ), thermal diffusivity (α) and specific heat capacity (c_p) were measured. The efficiency (so-called figure of merit or ZT value) were determined by the equation, $ZT = \sigma S^2 T / \kappa$, where thermal conductivity (κ) is derived from the relation, $\kappa = \alpha \rho c_p$, and ρ is the bulk density.

Results

The structures of $\text{Ge}_{n-2}\text{Sb}_4\text{Se}_{n+2}$ ($n = 4, 5$) were solved with single crystals and feature unique 2D layers composed of $\infty^1[\text{Sb}_2\text{Se}_2]^{2-}$ chains and $\infty^1[\text{Ge}_{n-2}\text{Sb}_2\text{Se}_n]^{2+}$ ribbons with different lengths, as shown in Fig. 1. Unusual Sb^+-Sb^+ contact was observed in $\infty^1[\text{Sb}_2\text{Se}_2]^{2-}$ units and satisfied charge-balanced models. In addition, Rietveld refinements showed no sign of impurity phase.

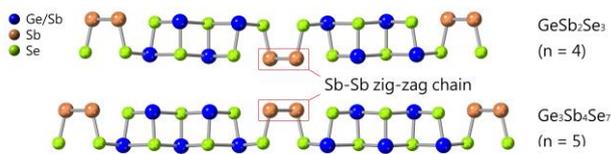


Fig. 1. Chemical structures of GeSb₂Se₃ (upper) and Ge₃Sb₄Se₇ (lower) made up of units with different lengths.

XPS measurements revealed the binding energies (528.7 and 538.1 eV) on Sb 3d region are located between the elements Sb (Sb⁰) and Sb₂Se₃ (Sb³⁺). On the other hand, the XANES of Sb L₃-edge on the metallic Sb, Sb₂Se₃, GeSb₂Se₃ and Ge₃Sb₄Se₇ exhibited a slight shift from low energy to high energy [4], shown in Fig. 2. Both results of XPS and XANES indicated the similar trends on the relative oxidation states of antimony atoms in the two title compounds. Besides, according to DFT calculations, the difference of partial DOS between the Sb sites in Sb-Sb contact and isolated Sb is consistent with the models containing different oxidation states, and the results of COHP could also confirm the possibility of Sb-Sb contact, as shown in Fig. 3.

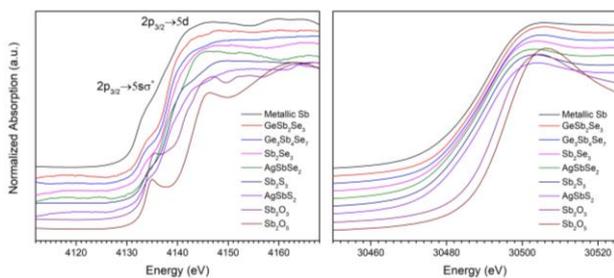


Fig. 2. XANES of GeSb₂Se₃, Ge₃Sb₄Se₇, Sb₂Se₃, metallic Sb and other related compounds on Sb L₃-edge (left) and K-edge (right).

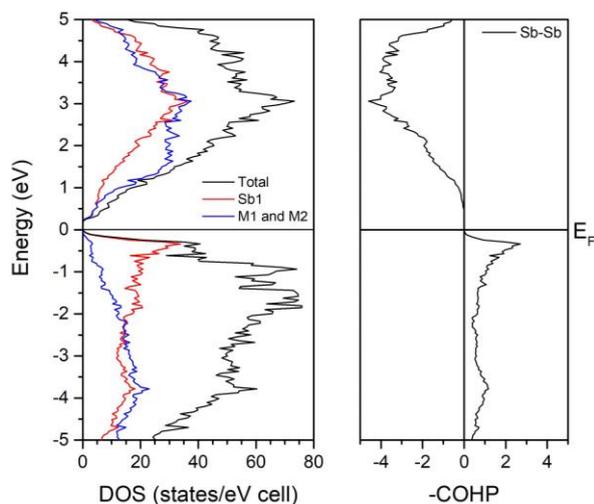


Fig. 3. Calculated DOS (left) and COHP (right, of Sb-Sb contact) curves for GeSb₂Se₃. The partial DOS of two Sb sites are in red and blue colors, respectively.

Both title compounds exhibit n-type semiconducting properties. The maximum ZT values for GeSb₂Se₃ and Ge₃Sb₄Se₇ were 0.036 and 0.007, respectively, at 425 K

and these are significantly higher than the values for GeSe ($\sim 10^{-5}$ at 400K) and Sb₂Se₃ ($\sim 10^{-8}$ at 300K). This appearance could be correlated to the higher electrical conductivity resulting from the $\infty^1[\text{Sb}_2\text{Se}_2]^{2-}$ chain and lower thermal conductivity caused by disordered sites with different Ge/Sb compositions, and it also shows the potential as thermoelectric materials.

Discussion

With the measurements of XPS on 3d region, XANES on Sb L₃-edge, as well as DFT calculations, the relative oxidation states of antimony in selenides were investigated. Both XPS and XANES measurements indicated the similar trends from low to high energies. XANES on Sb K-edge were performed (Fig. 2.) but showed ambiguous trend between the metallic antimony and antimony selenides, and the small energy differences made it difficult to distinguish the oxidation states. Similar results were also reported on XANES study for antimony sulphides [5].

Acknowledgments

This work is supported by the Ministry of Science and Technology, Taiwan (Grant No. MOST 107-2113-M-009-006) and the Center for Emergent Functional Matter Science of National Chiao Tung University from The Featured Areas Research Center Program within the framework of the Higher Education Sprout Project by the Ministry of Education (MOE) in Taiwan. We thank Dr. Ting-Shan Chan and Dr. Jeng-Lung Chen for XAS measurements (beamline TLS-BL16A1 and TPS-44A, NSRRC).

References

- [1] C. Zhang, H. Yin, M. Han, Z. Dai, H. Pang, Y. Zheng, Y.-Q. Lan, J. Bao and J. Zhu, "Two-Dimensional Tin Selenide Nanostructures for Flexible All-Solid-State Supercapacitors," *ACS Nano*, vol. 8, no. 4, pp. 3761-3770, 2014.
- [2] L.-D. Zhao, S.-H. Lo, Y. Zhang, H. Sun, G. Tan, C. Uher, C. Wolverton, V. P. Dravid and M. G. Kanatzidis, "Ultralow thermal conductivity and high thermoelectric figure of merit in SnSe crystals," *Nature*, vol. 508, pp. 373-377, 2014.
- [3] G.-R. Chen, C.-H. Li, C.-Y. Yu, M.-F. W. and C.-S. Lee, "Ternary Chalcogenides GeSb₂Se₃ and Ge₃Sb₄Se₇ Containing a $\infty^1[\text{Sb}_2\text{Se}_2]^{2-}$ 1D Chain and a 2D Structure Related to SnSe," *Inorg. Chem.*, vol. 59, no. 16, pp. 11207-11212, 2020.
- [4] J. M. Durand, P. E. Lippens, J. Olivier-Fourcade, J. C. Jumas and M. Womes, "Sb L_{III}-edge XAS study of the ternary system Sb₂S₃-As₂S₃-Tl₂S," *J. Non-Cryst. Solids*, vol. 194, no. 1, pp. 109-121, 1996.
- [5] S. E. Fawcett, R. A. Gordon and H. E. Jamieson, "Optimizing experimental design, overcoming challenges, and gaining valuable information from the Sb K-edge XANES region," *Am. Mineral.*, vol. 94, no.10, pp. 1377-1387, 2009.