

SIMPLE WET CHEMICAL SYNTHESIS OF SURFACTANT-FREE SILVER ANTIMONY SULPHIDE (AgSbS₂) FLOWER-LIKE NANOSTRUCTURES

E. SAKSORNCHAI^a, J. KAVINCHAN^{a*}, S. THONGTEM^{b,c},
T. THONGTEM^{c,d,*}

^a*School of Science, University of Phayao, Phayao 56000, Thailand*

^b*Department of Physics and Materials Science, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand*

^c*Materials Science Research Center, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand*

^d*Department of Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand*

Silver antimony sulphide (AgSbS₂) flower-like nanostructures were successfully synthesized by a simple wet chemical method from silver nitrate (AgNO₃), antimony chloride (SbCl₃) and thioacetamide (C₂H₅NS) in ethylene glycol (EG) without using any surfactant. In this research, the first simple wet chemical method was developed for synthesizing AgSbS₂ nanostructures that very simple, rapid, surfactant-free, low-cost method and large-scale-production. X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) illustrate that the as-prepared products were cubic AgSbS₂ flower-like nanostructured clusters. The energy gap (E_g) was determined by UV-visible absorption to be 1.80 eV, including 688 nm emission wavelength by photoluminescence (PL) spectroscopy.

(Received October 1, 2017; Accepted November 10, 2017)

Keywords: Silver Antimony Sulphide, Simple Wet Chemical Synthesis, X-ray diffraction

1. Introduction

The semiconductor metal chalcogenide materials have attracted considerable attention due to their unique electronic and optical properties and potential application in photovoltaic or photoelectrochemical devices, such as thin film solar cells [1-5]. Presently, the ternary chalcogenide compounds such as AgSbS₂, Ag₃SbS₃, AgInS₂ and AgGaS₂ are the excellent candidates used for solar energy conversion, optical memories and thermoelectric technologies due to their optimum energy gap [1-8]. The ternary Ag-Sb-S semiconductor system has two phases: AgSbS₂ and Ag₃SbS₃ [3]. Nevertheless, an appropriate electrical property of AgSbS₂, is a good candidate for the thin film absorption material [1,4,6-7] and it has a high absorption coefficient, making it a potential solar absorber [2-3,5].

A variety of procedures were used for synthesize this material: amorphous AgSbS₂ films [7] and AgSbS₂ thin films [9] prepared by pulsed laser deposition (PLD), AgSbS₂ silk-like nanoflowers [2] and AgSbS₂ nanospheres [10] synthesized via solvothermal method, AgSbS₂ nanostructures synthesized by cyclic microwave radiation [11] and AgSbS₂ nanocrystals prepared by the colloidal method [12]. However, the pure phase and stoichiometric of AgSbS₂ is frequently very difficult to prepare. The impurity phase, including Ag₃SbS₃ and Sb₂S₃ exists among AgSbS₂ product due to the large differences in the solubility product constants (K_{sp}) between intermediate products Ag₂S (1.6 x 10⁻⁴⁹) and Sb₂S₃ (2.9 x 10⁻⁵⁹) [10].

Herein, the first simple wet chemical method was developed for successfully synthesizing AgSbS₂ nanostructures. Since, this process is very convenient, rapid, simple, inexpensive,

* Corresponding authors: jutaratkp@gmail.com

surfactant-free and large-scale-production [13-14]. Specially, no specific equipments were required and can be developed for synthesizing other ternary metal chalcogenides.

2. Experimental

In the typically synthesis, all of chemical reagents were analytical grades (AR grade). The starting materials, including 2 mmol of silver nitrate (AgNO_3 , 99.0% Sigma-Aldrich), 2 mmol of antimony chloride (SbCl_3 , 99.0% Sigma-Aldrich) and 4 mmol of thioacetamide ($\text{C}_2\text{H}_5\text{NS}$, 99.0% Sigma-Aldrich) were dissolved in 30 ml of ethylene glycol (EG, 99.5% QR&C) with 15 min vigorous stirring. After that the mixed solution was heated at 160°C for 10, 20 and 30 min, respectively. Finally, the gray metallic precipitates were synthesized, separated by filtration, washed with absolute ethanol and dried at 70°C for 24 h.

The products were characterized by an X-ray diffractometer (XRD, SIEMENS D500) operating at 20 kV, 15 mA, and using Cu-K_α line from a copper target; a scanning electron microscope (SEM, JEOL JSM-6335F); a transmission electron microscope (TEM, JEOL JEM-2010); a selected area electron diffractometer (SAED) operating at 200 kV; a fluorescence spectrometer (FP-8500 Jasco) using 300 nm excitation at room temperature and a UV-visible spectrometer (Lambda 25 PerkinElmer) using a UV lamp with the resolution of 1 nm.

3. Results and discussion

Crystalline phases of the as-prepared products were analyzed by an X-ray diffractometer. Fig. 1 illustrates the XRD spectra of AgSbS_2 precipitates, synthesized by wet chemical method at 160°C for 10-30 min, were compared to the JCPDS database no. 17-0456 of AgSbS_2 [15]. They were specified to correspond with $\text{Fm}\bar{3}\text{m}$ space group symmetry [15]. All of the diffraction peaks at 27.31° , 31.64° , 45.35° , 53.75° , 56.34° , 66.07° , 72.89° and 75.13° were respectively indexed to the (111), (200), (220), (311), (222), (400), (331) and (420) plane of pure cubic AgSbS_2 phase. By increasing the lengths of time from 10 to 30 min, the XRD peaks became gradually stronger and narrower – showing that the increase in crystallinity. This result is consistent with the EDX spectrum (Fig. 3c) of the product synthesized at 160°C for 30 min which indicates that the atomic ratio of Ag, Sb and S is close to 1:1:2. By increasing the reaction time from 30 min to 40 min and 60 min, the gray metallic precipitates were turned into the orange colloidal complexes due to the large differences in K_{sp} between intermediate products such as the intermediate of Sb_2S_3 (orange colloidal complexes) [10,16].

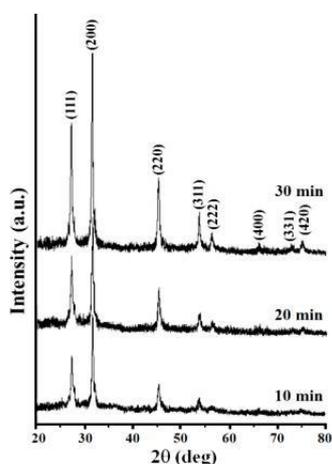
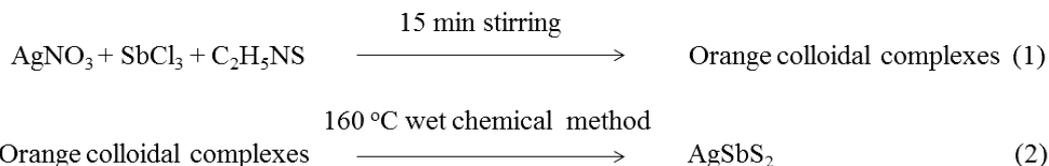


Fig. 1 XRD spectra of AgSbS_2 Synthesized in the solution via simple wet chemical method at 160°C for 10, 20 and 30 min, respectively

In this study, AgNO_3 , SbCl_3 and $\text{C}_2\text{H}_5\text{NS}$ were mixed in EG by 15 min stirring, and orange colloidal complexes were formed (eq.1). Then, the orange colloidal complexes which were the intermediate products, were transformed into AgSbS_2 gray metallic precipitates (eq.2) [11,16]. These products were washed with absolute ethanol and thus contain no impurities.



The morphology investigation was carried out by a field emission scanning microscope, transmission electron microscope, and selected area electron diffractometer. SEM images (Fig. 2a-c) show AgSbS_2 products synthesized at different length of time. The as-obtained AgSbS_2 products were composed of a number of nanostructures clustered together in a group. The irregular shapes were produced at 10 min (Fig. 2a). When increasing the reaction time, AgSbS_2 molecules nucleated, followed by clustering of nuclei to form AgSbS_2 flower-like clusters (Fig. 2b-c) – caused by the length of time was prolonged. The atoms had more chance to arrange themselves in the crystal lattice to form nanocrystalline flowers [16].

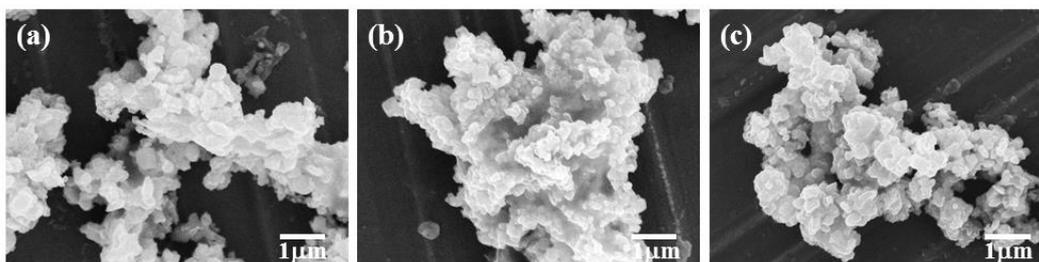


Fig. 2 SEM images of AgSbS_2 precipitates synthesized by simple wet chemical method at 160°C for (a) 10 min (b) 20 min and (c) 30 min.

Fig. 3a-b show TEM and SAED pattern of AgSbS_2 product synthesized at 160°C for 30 min. This result reveals a number of flower-like nanostructures with individual size of 80-100 nm to form AgSbS_2 flower-like clusters. The SAED pattern (Fig. 3b) was composed of the bright spots of diffuse concentric rings, specified as polynanocrystalline AgSbS_2 that attributed to (111), (200), (220) and (311) diffraction planes. This data confirm that the AgSbS_2 nanostructures are well crystalline – in accordance with the XRD result [15]. Fig. 3c shows the EDX spectrum of sample synthesized at 160°C for 30 min. The quantification of the EDX spectrum presents the existence of Ag, Sb and S elements. The atomic ratio of Ag, Sb and S is close to 1:1:2, which respects to the stoichiometry of AgSbS_2 . The other signals came from the supporting aluminium holder, the coated gold, and the environmental [17]. No impurities were founded in EDX spectrum.

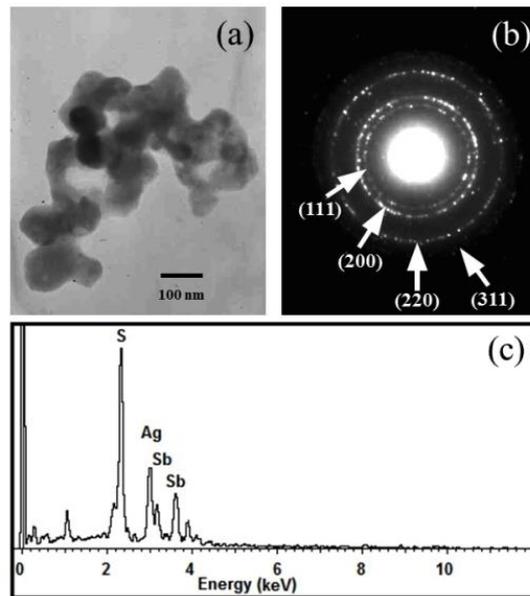


Fig. 3 (a) TEM image, (b) SAED pattern, and (c) EDX spectrum of AgSbS_2 synthesized by simple wet chemical method at 160°C for 30 min

The optical properties were observed by a UV-visible spectrometer and a fluorescence spectrometer. Photoluminescence (PL) of AgSbS_2 nanostructured flowers synthesized at 160°C for 30 min was excited by 300 nm wavelength at room temperature. The PL emission (Fig. 4a) was detected at 688 nm (1.80 eV) – in accordance with the optical transmission of AgSbS_2 determined by Tipcompor et al [16]. Moreover, the direct energy gap (E_g) of this sample was defined to be 1.80 eV. As can be seen in Fig. 4b, the direct energy gap was determined according to the Tauc equation [17-18] which can be presented as:

$$(\alpha h\nu)^{1/n} = A(h\nu - E_g),$$

where α is the adsorption coefficient of the material, h is the Planck's constant, ν is the photon frequency, A is a proportionality constant, and E_g is the optical band gap energy. The parameter n is a pure number associated with the different types of electronic transitions: $n=1/2$, 2, $3/2$, or 3 for the direct-allowed, indirect-allowed, direct-forbidden and indirect-forbidden transition, respectively [17,19]. For AgSbS_2 , the direct-allowed transition is applied. Its band gap, determined by extrapolation of the curve to $\alpha=0$, corresponds to the 1.80 eV, very close to 1.89 eV of AgSbS_2 nanostructured flowers determined by Tipcompor et al. [16], 1.88 eV energy gap of AgSbS_2 nanoparticles determined by Yang et al. [5], 1.75 eV energy gap of AgSbS_2 nanostructures reported by Kavinchan et al. [11] and 1.70 eV of AgSbS_2 nanoparticles reported by Ho et al. [3]. Hence, this material is one of promising materials used for nanodevices and solar energy converters [3,5]. Generally, different morphologies, sizes and crystalline degrees can play a role in the properties of products, such as photoluminescence (PL) and energy gap [14,20].

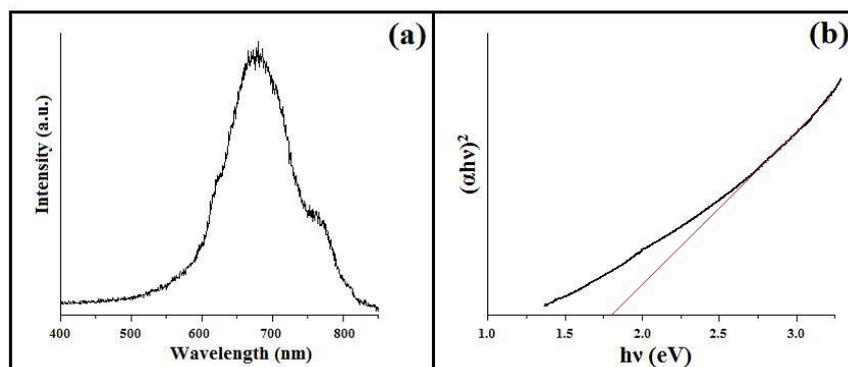


Fig. 4. (a) Photoluminescence and (b) the $(\alpha hv)^2$ and hv plot of $AgSbS_2$ flower-like clusters synthesized at $160^\circ C$ for 30 min

4. Conclusions

Pure and well-crystalline $AgSbS_2$ flower-like nanostructures were successfully synthesized via using a very simple wet-chemical method at $160^\circ C$ for 30 min. This approach can be applied to other ternary chalcogenides due to its rapid, simple, surfactant-free and low-cost method. The characterization of the product shows the pure cubic phase of $AgSbS_2$ flower-like nanostructures. Its band gap energy, determined by Tauc plot, is 1.80 eV that can be used for optical nanodevices and solar energy converters.

Acknowledgements

This work was supported by the revenue budget in 2017 (SC08/2560), School of Science, University of Phayao and the authors wish to thank Center of Excellence in Materials Science and Technology, Chiang Mai University, for financial support under the administration of Materials Science Research Center, Faculty of Science, Chiang Mai University.

References

- [1] T. Daniel, J. Henry, K. Mohanraj, G. Sivakumar, *Materials Chemistry and Physics* **181**, 415 (2016).
- [2] M. Han, J. Jia, W. Wang, *Materials Letters* **179**, 130 (2016).
- [3] Y. R. Ho, M. W. Lee, *Electrochemical Communications* **26**, 48 (2013).
- [4] J. Gutwirth, T. Wágner, E. Kotulánová, P. Bezdička, V. Peřina, M. Hrdlička, M. Vlček, Č. Drařar, M. Frumar, *Journal of Physics and Chemistry of Solids* **68**, 835 (2007).
- [5] W. C. Yang, M. W. Lee, *Journal of The Electrochemical Society* **161**(3), H92 (2014).
- [6] J. G. Garza, S. Shaji, A. C. Rodiquez, T. K. Das Roy, B. Krishnan, *Applied Surface Science* **257**, 10834 (2011).
- [7] T. Wagner, J. Gutwirth, P. Nemeć, M. Frumar, T. Wagner, M. Vlcek, V. Perina, A. Mackova, V. Hnatovitz, *Applied Physics A: Materials Science & Processing* **79**, 1561 (2004).
- [8] S. Berri, D. Maouche, N. Bouarissa, Y. Medkour, *Materials Science in Semiconductor Processing* **16**, 1439 (2013).
- [9] J. Gutwirth, T. Wágner, P. Němec, S. O. Kasap, M. Frumar, *Journal of Non-Crystalline solids* **354**, 497 (2008).
- [10] L. Yu, M. Han, Y. Wan, J. Jia, G. Yi, *Materials Letters* **161**, 447 (2015).
- [11] J. Kavinchan, S. Thongtem, E. Saksornchai, T. Thongtem, *Chalcogenide Letters* **12**(6), 325 (2015).

- [12] B. Zhou, M. Li, Y. Wu, C. Yang, W. H. Zhang, C. Li, *Chemistry- A European Journal* **21**, 11143 (2015).
- [13] A. A. Ashkarran, *Materials Science in Semiconductor Processing* **17**, 1 (2014).
- [14] J. Kavinchan, T. Thongtem, S. Thongtem, E. Saksornchai, *Journal of Nanomaterials* **2013**, ID719679 (2013).
- [15] Powder Diffract. File, JCPDS-ICDD, 12 Campus Boulevard, Newtown Square, PA 19073-3273, USA, 2001.
- [16] N. Tipcompor, S. Thongtem, T. Thongtem, *Journal of Nanomaterials* **2013**, ID970489 (2013).
- [17] N. Chumha, T. Thongtem, S. Thongtem, D. Tantraviwat, S. Kittiwachana, S. Kaowphong, *Ceramic International* **42**, 15643 (2016).
- [18] T. Omata, K. Nose, S. Matsuo, *Journal of Applied Physics* **105**, 073106-1 (2009).
- [19] L. Liu, Y. Jiao, Q. Guo, W. Zhao, W. Dai, J. Xiang, C. Gao, W. Yu, X. Li, *Chalcogenide Letters* **14**(9), 373 (2017).
- [20] H. I. Ikeri, A. I. Onyia, P. U. Asogwa, *Chalcogenide Letters* **14**(2), 49 (2017).