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ONE-STEP MICROWAVE ASSISTED SYNTHESIS OF COPPER ANTIMONY SULPHIDE (Cu_3SbS_4) NANOSTRUCTURES: OPTICAL PROPERTY AND FORMATION MECHANISM STUDY

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Famatinite (Cu_3SbS_4) nanostructures were successfully synthesized by one-step microwave radiation method in ethylene glycol. X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) reveal that the as-synthesized products were pure tetragonal Cu_3SbS_4 nanostructures. The direct band was determined by UV-visible absorption to be 1.30 eV that is one of the promising materials using as a potential solar absorber. Additionally, a possible formation mechanism was proposed in this study.

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1. Introduction

Presently, the researchers pay more attention to the metal chalcogenide nanomaterials due to their unique optical and electronic properties. They have potential applications in photovoltaic and thermoelectric technologies [1-5]. Typically, the ternary chalcogenide compounds were synthesized by thermal evaporation in vacuum [1], microwave irradiation [2, 4, 6], chemical bath deposition technique [3], simple wet chemical synthesis [7] and solvothermal method [8]. The ternary copper sulfides based on Cu-Sb-S type materials are considered significantly as alternative absorbers due to their promising properties and low cost, as well as be composed of non-toxic elements [4, 9-11]. These ternary chalcogenide compounds including famatinite (Cu_3SbS_4), chalcostibite ($CuSbS_2$), skinnerite (Cu_3SbS_3) and tetrahedrite ($Cu_{12}Sb_4S_{13}$) are semiconductor which have the energy band gaps in the range of 0.5-2.0 eV [4,11-13]. Cu_3SbS_4 is a p-type semiconductor with a direct band gap, which varies between 1.0-1.8 eV depending on the crystal structure [2, 4, 14]. Among the metal chalcogenides, Cu_3SbS_4 semiconductor is one of the promising materials that has been found its optimum band gap and high adsorption coefficient for using as a potential solar absorber [15].

However, the pure phase of Cu_3SbS_4 is very difficult to synthesis. The impurity phases include Sb_2S_3, Cu_7S_4, CuS and $CuSbS_2$ exist among products due to the large differences in the solubility product constants (K_{sp}) between intermediate products [16]. There are a few researches were reported on the synthesis of Cu_3SbS_4: chemical bath deposition technique [3], hydrothermal route [15, 17], solvothermal route [18], hot-injection method [19], and microwave irradiation [2, 4]. In this research, Cu_3SbS_4 was synthesized by one-step microwave radiation method in ethylene glycol. Since, this procedure is very rapid, simple, low-cost, and effective. Moreover, the as-

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synthesized products in this study were produced without using any additives or surfactants – resulting this procedure was used with low temperature and non-toxic chemical requirements [6, 20-21].

2. Experimental

All chemical reagents were analytical grades (AR grade). Cu_3SbS_4 was synthesized by one-step microwave radiation method. The starting materials, including 2 mmol of copper nitrate monohydrate ($Cu(NO_3)_2 \cdot H_2O$), 2 mmol of antimony acetate $(CH_3CO_2)_3Sb$, and 4 mmol of sodium thiosulphate pentahydrate ($Na_2S_2O_3 \cdot 5H_2O$) were dissolved in 30 ml of ethylene glycol (EG) and followed by 15 min vigorous stirring. Then, the mixed solutions were irradiated by 300 W, 450 W and 600 W of cyclic microwave radiation 10-30 min. Finally, the precipitates were prepared, washed with absolute ethanol and dried at 70 ^{O}C for 24 h for further analyses.

The as-obtained products were characterized by using an X-ray diffractometer (XRD, Rigaku MiniFlex600) operating at 40 kV, 15 mA and using Cu-K_α line (λ= 0.15406 nm) in 2θ = 20-60 degree. The morphology and particle size were determined by a scanning electron microscope (SEM, JEOL JSM-6335F), a transmission electron microscope (TEM, JEOL JEM-2010) and a selected area electron diffractometer (SAED) operating at 200 kV. Moreover, the optical property was investigated by a UV-visible spectrometer (Lambda 25 PerkinElmer) using a UV lamp with the resolution of 1 nm.

3. Results and discussion

An X-ray diffractometer was used for characterization of the products. Fig. 1 shows the XRD spectra of the as-synthesized products that prepared by one-step microwave radiation method at 300 W for 10, 20 and 30 min, respectively. The XRD patterns were compared with the JCPDS database no. 71-0555 of Cu_3SbS_4, no. 02-0557 of $CuSbS_2$, no. 01-0538 of Sb_2S_3, no. 79-2321 of CuS and no. 33-0489 of Cu_7S_4 [22]. The starting materials include $Cu(NO_3)_2 \cdot H_2O$, $(CH_3CO_2)_3Sb$ and $Na_2S_2O_3 \cdot 5H_2O$ were mixed in ethylene glycol. In this research, a possible formation mechanism of Cu_3SbS_4 was controlled by the hydrolysis of sodium thiosulphate pentahydrate as a sulfur source and S^{2-} ions release from sodium thiosulphate pentahydrate through hydrolysis [4, 23]. Then, CuS, Cu_7S_4 and Sb_2S_3 phases were occurred at first 10 min of reaction time, but no Cu_3SbS_4 phase was occurred at this stage. After that, metal sulfide phases including Cu_3SbS_4, $CuSbS_2$, Sb_2S_3, CuS and Cu_7S_4 were formed at this stage. Finally, the pure phase of Cu_3SbS_4 was produced at 30 min. The impurities such as Sb_2S_3 and Cu_7S_4 were also found in the mixed precipitates of the as-synthesized products due to the large different in the solubility product constants (K_{sp}) between the intermediate of Sb_2S_3 (2.9×10^{-59}) and Cu_7S_4 (1.0×10^{-31}) [4, 16]. At 300 W for 30 min in ethylene glycol, the XRD result reveals the pure phase of Cu_3SbS_4 with I-42m space group. All of the diffraction peaks at 23.34^o, 28.71^o, 29.92^o, 33.25^o, 37.32^o, 38.27^o, 41.06^o, 45.33^o, 47.77^o, 50.83^o, 50.91^o, 53.79^o, 56.65^o, 57.39^o and 59.44^o were specified to the (110), (112), (103), (200), (202), (211), (114), (213), (220), (222), (006), (310), (312), (303) and (224) plane of pure tetragonal Cu_3SbS_4 phase. These precipitates contain no impurities. By increasing the lengths of time from 10 to 30 min, the crystalline phase turn into the pure phase of Cu_3SbS_4 – resulting the dark orange colloidal complexes were turned into the black precipitates [16].

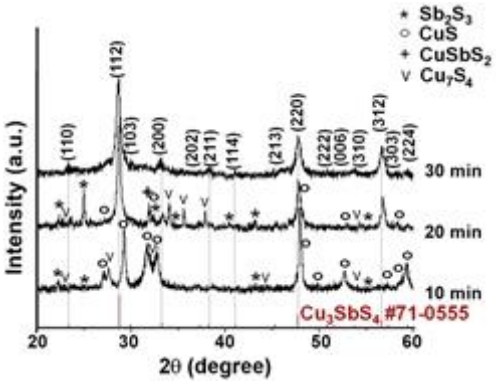


Fig. 1. XRD spectra of the as-synthesized products at 300 W for 10 min, 20 min, and 30 min, respectively.

Fig. 2 illustrates the XRD spectra of the as-synthesized products that prepared by one-step microwave radiation method at 300 W, 450 W and 600 W for 30 min, respectively. The impurities including Sb_2S_3 and $CuSbS_2$ phases that were formed with the increasing of microwave power at 450 W. When the microwave power was increased to 600 W, the impurity phase of Sb_2S_3 was produced at this stage due to this condition was the optimum condition to form Sb_2S_3 [4, 24]. Consequently, it should be noted that the pure phase of Cu_3SbS_4 nanostructures were successfully synthesized by one-step microwave radiation method at 300 W for 30 min.

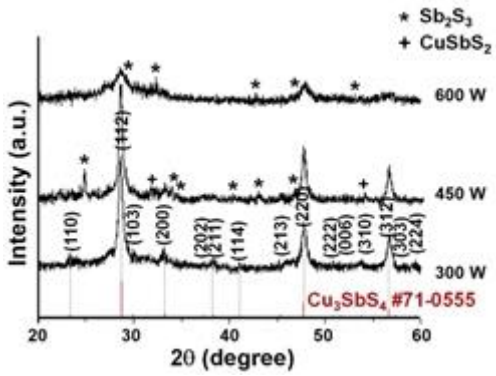


Fig. 2. XRD spectra of the as-synthesized products at 300 W, 450 W, and 600 W for 30 min, respectively.

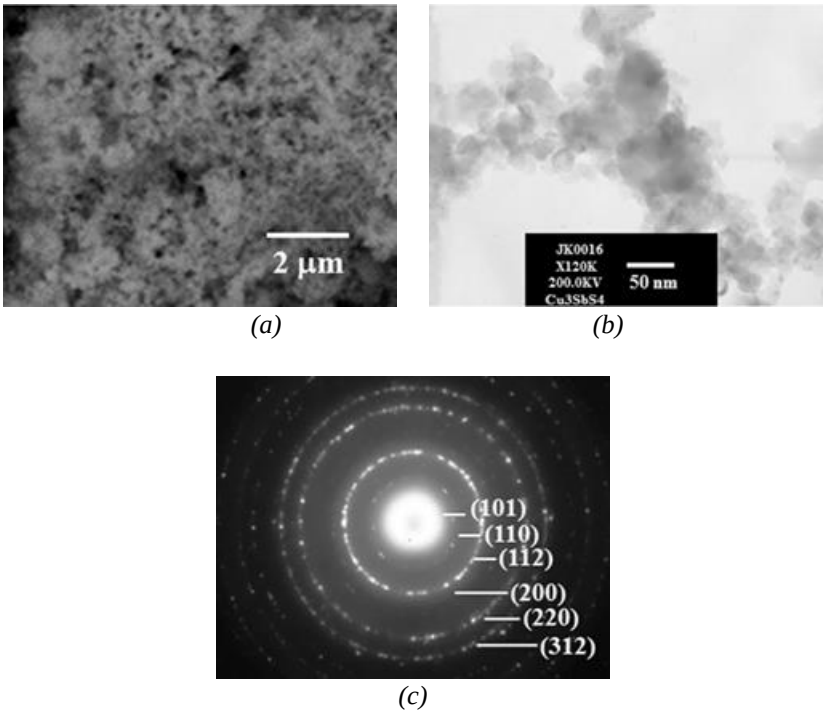
The possible mechanism was proposed from these XRD results [4]. Firstly, the metal ions in mixed solutions react with sulfur ion to form sulfides. At pH 5 as an acidic medium, thiosulfate ions released slowly of sulfide ions to combine with the metal ions [24-25]. Then, Cu_7S_4 was formed due to the sulfur rich ions in mixed solution at this stage. Moreover, Sb_2S_3 was also firstly produced in this first stage. With the increasing of reaction time at 20 min, the $CuSbS_2$ phase was found in the as-synthesized product. As time passed (30 min.), Sb_2S_3 disappeared gradually and Cu_7S_4 was transformed into CuS. Finally, Cu_3SbS_4 nanostructures were produced from $CuSbS_2$ and CuS which the possible mechanism was described as follows [4, 24]:

$$xM^{n+} + yS^{2-} \longrightarrow zM_2S_n \quad (1)$$

$$Cu_7S_4 + 3S \longrightarrow 7CuS \quad (2)$$

$$CuSbS_2 + 2CuS \longrightarrow Cu_3SbS_4 \quad (3)$$

To reveal the shape and size of the as-obtained products, a field emission scanning microscope, transmission electron microscope, and selected area electron diffractometer were used for investigation. SEM image, TEM image and SEAD pattern of Cu_3SbS_4 synthesized at 300 W for 30 min represent in Fig. 3. The as-obtained Cu_3SbS_4 precipitates were composed of particles clustered together in a group. This image reveals a number of nanoparticles with individual size of 10-30 nm to form Cu_3SbS_4 clusters. The SAED pattern illustrates a bright spot of diffuse concentric rings which specified as polynanocrystalline Cu_3SbS_4 that attributed to (101), (110), (112), (200), (220) and (312) diffraction planes – in good accordance with the XRD pattern [22].



(a) *(b)*

(c)

Fig. 3. (a) SEM image (b) TEM image and (c) SAED pattern of Cu_3SbS_4 synthesized by one-step microwave radiation method at 300 W for 30 min.

The element composition of the product can be investigated by EDX spectrum. As can be seen in Fig. 4, EDX analysis reveals the atomic ratio of Cu, Sb and S from the as-synthesized product is close to 3:1:4 which corresponding to the stoichiometry of Cu_3SbS_4. No impurities were detected in this spectrum, confirming that the as-synthesized product was pure phase of Cu_3SbS_4 [2].

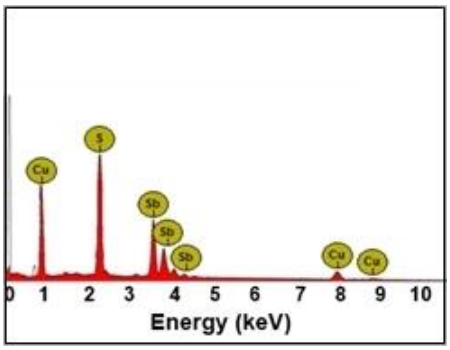


Fig. 4. EDX spectrum of Cu_3SbS_4 synthesized by one-step microwave radiation method at 300 W for 30 min.

Additionally, the optical property was observed by a UV-visible spectrometer, the direct-allowed transition is applied. Fig. 5 shows the Tauc plot of $(\alpha h\upsilon)^2$ and $h\upsilon$ [10, 26] which can be presented the equation as: $(\alpha h\upsilon)^{1/n} = A(h\upsilon - E_g)$, where α is the adsorption coefficient of the material, h is the Planck's constant, υ is the photon frequency, A is a proportionality constant, and E_g is the optical band gap energy. The direct Eg, determined by extrapolating the linear portion curve to zero absorption [26-27]. In this research, the direct energy gap (Eg) of Cu_3SbS_4 was found at 1.30 eV, close to the other reports which found at 1.10 eV of flower-like Cu_3SbS_4 particles reported by Chen *et al.* [4] and 1.10 eV of Cu_3SbS_4 nanocrystal reported by Embden *et al.* [14]. Typically, a variety of sizes and morphologies of crystalline phase can play a key role of energy gap. This band gap energy suggests that this material has potential application for solar energy absorbers [2, 4].

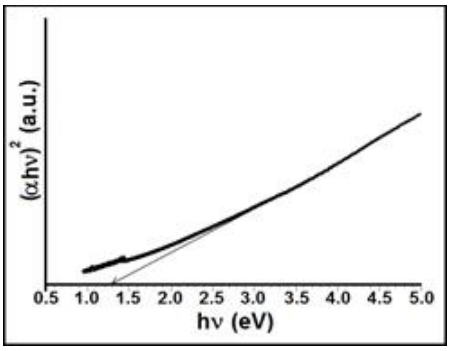


Fig. 5. the $(\alpha h\upsilon)^2$ and $h\upsilon$ plot of Cu_3SbS_4 nanostructures synthesized by one-step microwave radiation method at 300 W for 30 min.

4. Conclusions

In this research, pure phase of tetragonal Cu_3SbS_4 nanostructures were successfully synthesized by one-step microwave radiation method in ethylene glycol at 300 W for 30 min. This method can be applied to other metal chalcogenides because its fast, very simple, surfactant-free and low-cost method. A possible formation mechanism was proposed relating with the experimental results. Its band gap energy was also determined by Tauc plot, is 1.30 eV that can be used for a potential solar absorber.

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