VNU Journal of Science: Mathematics – Physics, Vol. 40, No. 3 (2024) 70-76

VNU Journal of Science: Mathematics - Physics

Journal homepage: https://js.vnu.edu.vn/MaP

Original Article

Single Step Synthesis of Cu_2ZnSnS_4 by Microwave Combustion Method

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Received 9 May 2024
Revised 5 June 2024; Accepted 29 July 2024

Abstract: We report a novel single step process to synthesize Cu_2ZnSnS_4 nanopowder. Our novel approach is based on combustion method assisted with microwave irradiation. The obtained results showed that the precursors can be quickly decomposed in the microwave field to form Cu_2ZnSnS_4 nanopowder. The effects of fuel and microwave power on structures and properties of the nanopowder were investigated thoroughly by Raman spectroscopy. This synthesis process is promising for large scale fabrication of light absorbing materials for photovoltaic devices because it is facile, low cost, non-vacuum, single step and time saving.

*Keywords: M*icrowave irradiation; combustion; Cu_2ZnSnS_4; light absorber; Raman.

1. Introduction

Cu_2ZnSnS_4 (CZTS) has been intensively studied for about two last decades as a potential candidate for replacing $Cu(In,Ga)S_2$ (CIGS) solar cells. Until now, the recorded efficiency of CZTS solar cell is still lower than that of CIGS solar cell [1-3]. However, CZTS is composed of only abundant earth elements, so it is expected that the price of CZTS solar would be much lower than CIGS solar cell [4]. Hence, it is still worth to exchange some percentage of efficiency for a better price.

Up to now, various methods have been developed for manufacturing CZTS material such as: sputtering [5], thermal evaporation [6], sol-gel [7], direct solution method [8], hot injection [9], hydrothermal method [10, 11], etc. In general, these techniques are categorized into physical methods (vacuum) and chemical methods (non-vacuum). In fact, further heat treatment in sulfur rich ambient like S, H_2S, etc. is normally required to obtain a high quality CZTS with good performance [12-15]. This

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https//doi.org/ 10.25073/2588-1124/vnumap.4932

annealing step results in some disadvantages such as long time and harm to environment. Furthermore, synthesis of CZTS is a challenging task because CZTS exists only in an extremely small area in the ternary phase diagram of Cu_2S, ZnS and SnS [16]. It has been shown that secondary phases such as binary and ternary compounds (Cu_2S; ZnS; Cu_2SnS_3, Cu_3SnS_4, etc.) are much easier to form than CZTS. Hence, fabrication of pure and single phase CZTS is an important but challenging task. Hence to obtain pure phase of CZTS, it requires a careful control of synthesizing parameters as well as long time for conversion from precursor into CZTS. For those reasons, seeking for single step synthesis of CZTS is important and attracted interest of many researchers.

Combustion was proposed as a promising method for synthesizing of complex metal oxides compound such as different perovskites with main advantages of short reaction time, low temperature, and homogenous product in form of nanocrystals [17-21]. Recently microwave was combined into combustion to accelerate and enhance reaction. Microwave is extremely important in this method because it generates hot spots inside the precursor mixture to efficiently ignite the combustion reaction, which is some time not able to attain with normal combustion especially for some chemical inert metal precursor [17, 19, 22].

There were only a few reports on synthesis of CZTS by combustion [3, 20, 23], however further heat treatment in sulfur environment is still required. In these works, the combustion was used to convert precursors into complex metal oxides before sulfurization is applied to get single phase CZTS, so these processes are not single step process. Annealing process is still conducted in sulfur rich ambient, which might result in some negative effects to the environment.

Here, we proposed a single-step microwave combustion process without any sulfurization for fabrication of CZTS nanopower in an extremely short time. The product was characterized with different techniques such as X-ray diffraction, Raman spectroscopy, scanning electron microscopy, energy dispersive spectroscopy.

2. Experiment

CZTS was fabricated by combustion method assisted with microwave irradiation. The method is simple and fast without further annealing process. In the first step, we prepare precursors for combustion reaction by mixing 50 ml solutions of 0.2 M $Cu(NO_3)_2$, 0.1 M $Zn(NO_3)_2$, 0.1 M $SnCl_2$. The mixture of three salts was then stirred by a magnetic stirrer under heating at 70 ^oC. While stirring, thiourea (CH_4N_2S) was added drop wise into the mixture until the amount of thiourea is equal to the total molar of metal. All the chemicals were of analytical grade and were used without further purification.

Thiourea was served as both complex agent and sulfur source. After adding of thirourea, the mixture gradually turned into a milky solution.

Then, citric acid, which serves as a buffer to increase the solubility of the mixture as well as fuel for combustion reaction in the next stage, is added under vigorous stirring in 30 min. The mixture was stirred gently for two hours to ensure sufficient complexation between metal ions, citrate and thiourea, which is critical to obtain a homogenous product. At the end of this stage, we obtained a uniform complex gel. The obtained complex gel was then transferred into a microwave oven. The microwave power was set at 450; 700 and 900 W while the molar ratio F of citric acid/metal ion is fixed at 1:1.

After a few seconds, the combustion reaction occurred and released a massive amount of gas and heat supporting for the formation of kesterite phase of CZTS. The effect of fuel amount was observed by preparing three samples with F = 1:1; 2:1; and 3:1. The reaction ends in about 90 s. The product was then washed thoroughly with distilled water.

The structures of the samples were checked by using X-ray difftaction (XRD) on a diffractometer D5005, Bruker. Raman spectra were collected on HR 800, Horiba Jobin Yvon, with excitation line 632.8 nm of He Ne laser.

3. Results and Discussion

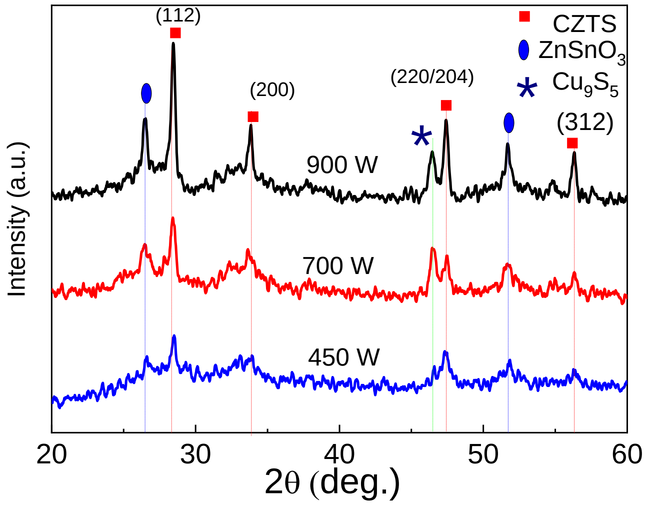

Figure 1. XRD patterns of CZTS with different microwave power.

We investigaqted the influence of concentration of citric acid and microwave power on the growth of CZTS crystal phase. It is well-known that the amount of fuel is extremely important to the formation of nanoproducts in combustion method because it provides heat for reaction. In our case, microwave irradiation plays the role of triggering combustion reaction. Temperature at hot spots generated by microwave field can be as high as several hundred of Kelvin. Such high temperature is necessary condition for ignition of the combustion at some points and the start the chain reaction for the formation of Cu_2ZnSnS_4 crystal phase.

XRD patterns of CZTS prepared at different reaction power 900 W, 700 W, 450 W are shown in Fig. 1. XRD patterns of all samples (F=1) show peaks corresponding to reflection from (112), (200), (220)/(204), (312) planes, which are characteristic peaks of kesterite structure of CZTS. It is noted that the diffraction peaks of sample prepared with microwave power of 900 W are sharper and stronger than those of the other samples. The results suggested that CZTS prepared at higher power had better crystalline quality. Further investigation shows that using larger power would not offer better product. This can be understood that microwave irradiation only played the role of generating hot spots to ignite combustion reaction. XRD patterns also indicate the formation of other Cu-Zn-Sn compounds as secondary phase such as $ZnSnO_3$ and Cu_9S_5.

In microwave combustion method, while microwave provides hot spots for starting combustion process, fuel provides energy in term of heat for the formation of the products. Due to the phase instability, secondary phases are easily formed during growth and post growth of CZTS. However, the stoichiometry of the final product can be obtained by fine tuning the precursor's composition. XRD measurements cannot clearly resolve some other secondary phases such as ZnS, Cu_xSnS_{x+1}, Sn_xS_y,

$Cu_{2-x}S$ from main phase CZTS, so Raman spectroscopy was used to analyze phase composition of the samples. Fig. 2 shows Raman spectra of samples prepared with different ratios of metal to citric acid. As can be seen from the Raman spectra, all samples showed characteristic A_1 peak of CZTS at 331 cm^{-1}.

The sample prepared with ratio F=1:1 shows the existence of secondary phases such as SnS, $Cu_{2-x}S$. In agreement with XRD data as shown above, it can be seen that increasing amount of fuel results in forming CZTS of better crystallinity. However, we still observed Raman peaks of some secondary phases such as SnS and Cu_xS at low intensity. These narrow bandgap secondary phases even at low concentration can degrade the quality of solar cell based on CZTS because they increase short circuit current and lower efficiency of solar cell.

When fuel ratio F increases upto 2, the A1 peaks of CZTS becomes dominant in the spectrum. However, this peak is still quite broad, which might be the convolution of several peaks including some from Cu_2SnS_4 (CTS) phase at 337 cm^{-1}; 352 cm^{-1}. A clear trace of SnS was also implied by the Raman peak at 213 cm^{-1}.

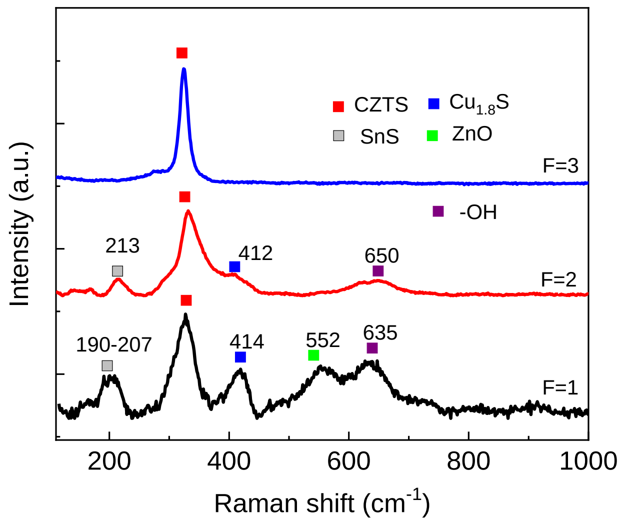

Figure 2. Raman spectra of CZTS prepared with different ratio between metal ions and citric acid.

In comparison with the samples prepared with less fuel, the sample with ratio F = 3 is single phase, demonstrated by clear Raman peaks of CZTS. The sharp Raman A1 peak is dominated in the spectrum of sample. It should be noted that continuing to increase F ratio will not result in better quality of the product. During combustion reaction, a huge amount of gas (NO_2, CO_2.) was formed. Gas would dissipate heat to environment. Therefore, when fuel was used at larger amount, less heat is available for the formation of kesterite phase and the product might not be crystallized. The reaction pathway of the self combustion process can be understood as follow. In the first step, Cu^{2+}, Zn^{2+}, Sn^{2+} coordinate with thiuorea (Tu) molecules to form Cu-Tu, Zn-Tu, Sn-Tu complexes in the solvent. The Cu-Tu complexes firstly decomposed to $Cu_{2-x}S$ nucleus under excitation of microwave irradiation at hot spots of the electromagnetic field. In second stage the Zn-Tu and Sn-Tu complexes decompose to ZnS and SnS then $Cu_{2-x}S$ reacts with them to form CZTS.

EDS spectrum of CZTS prepared at 900 W and ratio F=3 is shown in Fig. 3. Only peaks of Cu, Zn, Sn and S appear in the spectrum. The absence of other peaks confirms the purity of the sample. EDS analysis shows elemental ratios closed to stoichiometry: [Cu]/[Sn]=0.93 and [Zn]/[Sn]=1.05.

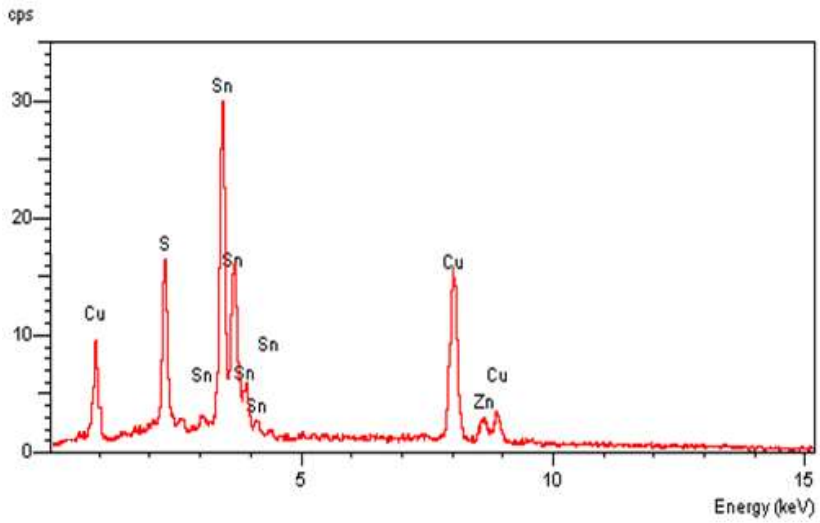

Figure 3. EDS spectrum of CZTS at 900 W and ratio F=3.

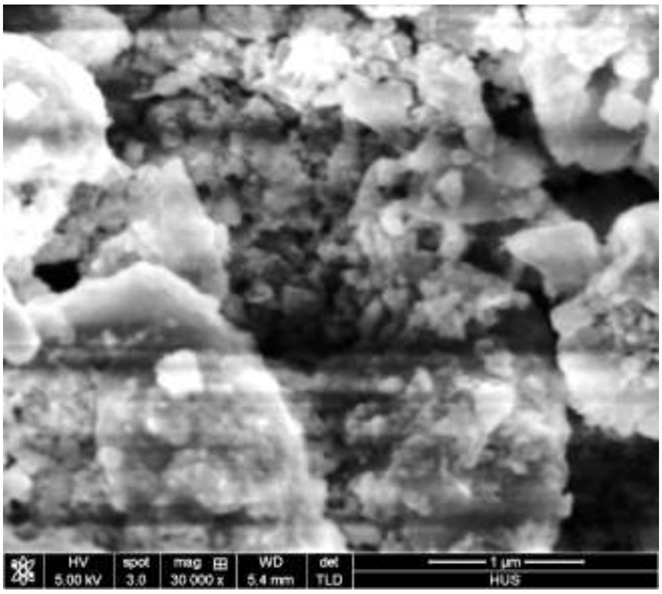

Figure 4. SEM image of CZTS preapared at 900 W and F=1:3.

Morphology of the as-produced nanoproducts was investigated by scanning electron microscopy (SEM), as shown in Fig. 4. The SEM image showed a large grain size of CZTS, which is beneficial for fabrication of high efficiency solar cells.

4. Conclusion

CZTS powder has been synthesized through a single step, simple, low-cost combustion method assisted with microwave irradiation. The obtained results showed that the microwave power and the ratio of acid citric/metal play important roles on the formation of single phase CZTS product. One can suggest that the combustion method assisted with microwave irradiation is a very promising method to prepare CZTS materials in term of low cost, time saving and ease for scale the production.

Acknowledgments

This research is funded by the Vietnam Ministry of Education and Training under grant number B2023-MDA-01.

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