MICROWAVE-ASSISTED SOLVOTHERMAL SYNTHESIS AND CHARACTERIZATION OF NANOSTRUCTURED Cu_2SNS_3 ARCHITECTURES

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Abstract

The ternary Cu-Sn-S system, as an important I-IV-VI group semiconductor with small or mid band-gap, have attracted great attention owing to broad application in photovoltaic devices and H2 evolution under visible light irradiation. In this contribution, Cu_2SnS_3 nanostructures were successfully synthesized by microwave-assisted solvothermal route in a short time, using $CuCl_2.2H_2O$, $SnCl2.2H_2O$ and thiourea as starting chemicals. The influence of solvent on structure, morphology and optical properties of the as-prepared samples were characterized by using X-ray diffraction (XRD), scanning electron microscopy (SEM), UV-vis diffuse reflectance spectroscopy, and Raman spectroscopy. The morphology of products can be tuned from flower-like to sphere-like by using diethyleneglycol instead of ethyleneglycol as a solvent, while the cubic crystal structure remain unchanged.

Keywords: Microwave, solvothermal, synthesis, Cu_2SnS_3, nanostructure

1. INTRODUCTION

In recent years, Cu_2SnZnS_4 (CTZS), a member of qarternary metal chalcogenides group, has received a lot of attention due to its low band gap energy and high absorption coefficient, which makes it suitable candidate for application as an absorbing layer in thin film solar cells (TFSC) [1,2]. The renew interest stems from an increased pressure towards sustainable and safe manufacture of TFSC. In this respect, Cu_2SnZnS_4 (CTZS) has emerged as a promising alternative to prevailing $Cu(In,Ga)(S,Se)_2$. Whereas Indium, Galium and Tellur are rare elements thus limited and expensive, Copper, Tin, Zinc and are naturally abundant, relatively cheap and environmentally benign elements. CTZS is structurally closely similar to CIGS, maintaining the octet rule when replacing the trivalent In/Ga with a bivalent Zn and IV- valent S [3,4]. However, the synthesis of CZTS is challenging task as it shows rather complex structure and requires very controlled growth conditions in order to suppress the formation of zinc blend (ZnS) and Cu_2SnS_3 (CTS) secondary phases. CTS is a p-type semiconductor with a direct band gap in the range 0.95- 1.3 eV depending on crystal structure and level of impurities, and absorption coefficient greater than 10^4 cm^{-1}. Various physical, chemical, or physico-chemical synthesis routes have been applied for preparation of CTS in either thin film form, or other solid forms such as polycrystalline microparticles and nanocrystals [5-8]. Herein, we present facile and green route for preparation of CTS adopting microwave-assisted solvothermal synthesis method. By using simply chemicals and solvents, various polycrystalline architectures were successfully synthesized in 10 minutes.

2. EXPERIMENTAL PART

2.1. Materials and Methods

Copper chloride, ($CuCl_2.2H_2O$), Tin chloride, ($SnCl_2.2H_2O$) were both purchased from Penta (Czech Republic). Thiourea (CH_4N_2S) was purchased from Sigma Aldrich All chemicals were used as received without any further purification. Diethyleneglycol (DEG) and Ethylene (EG) (Penta, Czech Republic) were used as solvents. In a typical synthesis, 0.2 mmol of $CuCl_2.2H_2O$, 0.1 mmol of $SnCl_2.2H_2O$, and 0.3 mmol of Thiourea were dissolved in a 50 mL of either DEG or EG, respectively. Then, prepared solutions were mixed

together in a 250 mL reaction bottle flak, transferred into the microwave oven cavity (microwave open vessel system MWG1K-10 RADAN, Czech Republic; 1.5 kW, 2.45 GHz; operated in a continuous mode with the temperature monitored by an industrial contactless thermometer) and exposed to microwave radiation for 10 minutes. After that, the system was switched off and left cools down naturally. Resulted black precipitate was washed thoroughly with distilled water, collected by filtration and dried in a vacuum oven at 60 °C overnight.

2.2. Characterization Techniques

Crystalline phases of prepared powders were characterized by the X-ray diffractometer X´Pert PRO X-ray (PANalytical, The Netherlands) with a Cu-Kα X-ray source (λ = 1.5418 Å) and the operation voltage and current maintained at 30 kV and 20 mA, respectively, in the diffraction angle range 20-90° 2θ. The morphology was investigated by scanning electron microscope Nova NanoSEM (FEI Company) at accelerating voltage 5 kV. Optical properties of prepared materials were characterized by lambda 1050 spectrophotometer (Perkin Elmer) in reflectance mode, in the range from 0.6 to 4.2 eV. Specularly and diffusely reflected light were recorded using integrating sphere with the diameter of 150 mm.

3. RESULTS AND DISCUSSION

Fig. 1. shows powder X-ray diffractograms of samples prepared in DEG and EG. For both samples, diffraction peaks at angles 2θ = 28.45°, 32,97°, 47.31°, 56.13°, 58.87°, 69.14°, 76.39°, 78.75°, and 88.05°, corresponding to the (111), (200), (220), (311), (222), (400), (331), (420), (422), and (511) planes can be found. CTS has been reported to exist in a number of crystal structures including cubic, tetragonal, monoclinic, or triclinic. In our study, experimental data matched well with standard file pdf-2-entry 01-089-2877 for cubic Cu2SnS3 crystal structure. No peaks characteristic for secondary phases or impurities were observed.

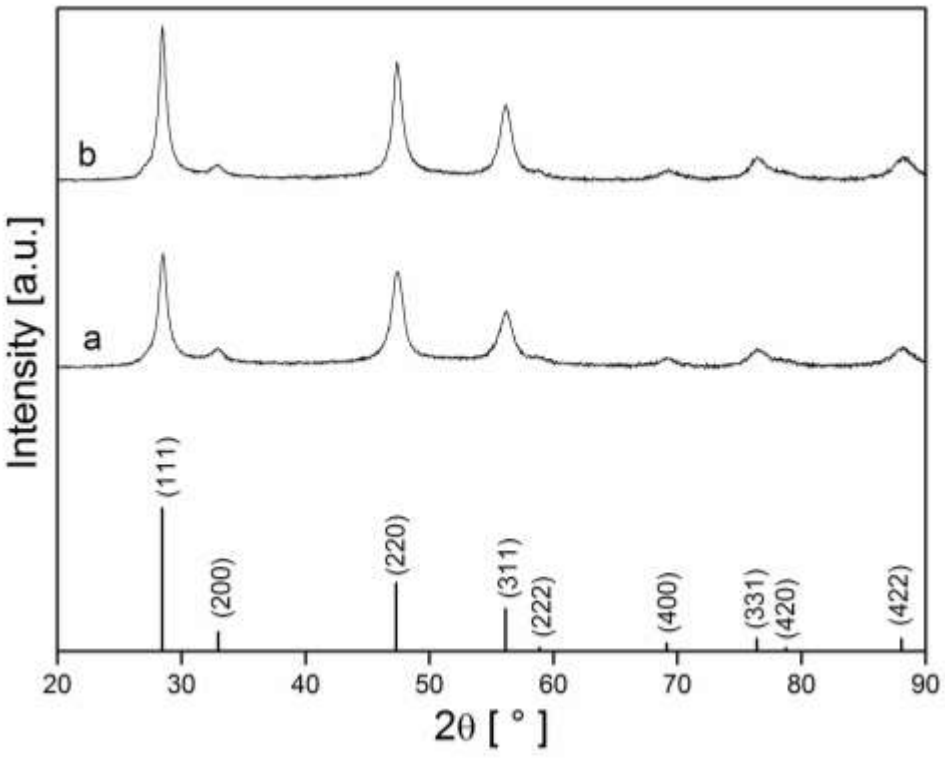

Fig. 1 XRD patterns of prepared Cu2SnS3 in DEG (a) and EG (b) as well as standard data for the pure phase of cubic structure (pdf-2-entry 01-089-2877)

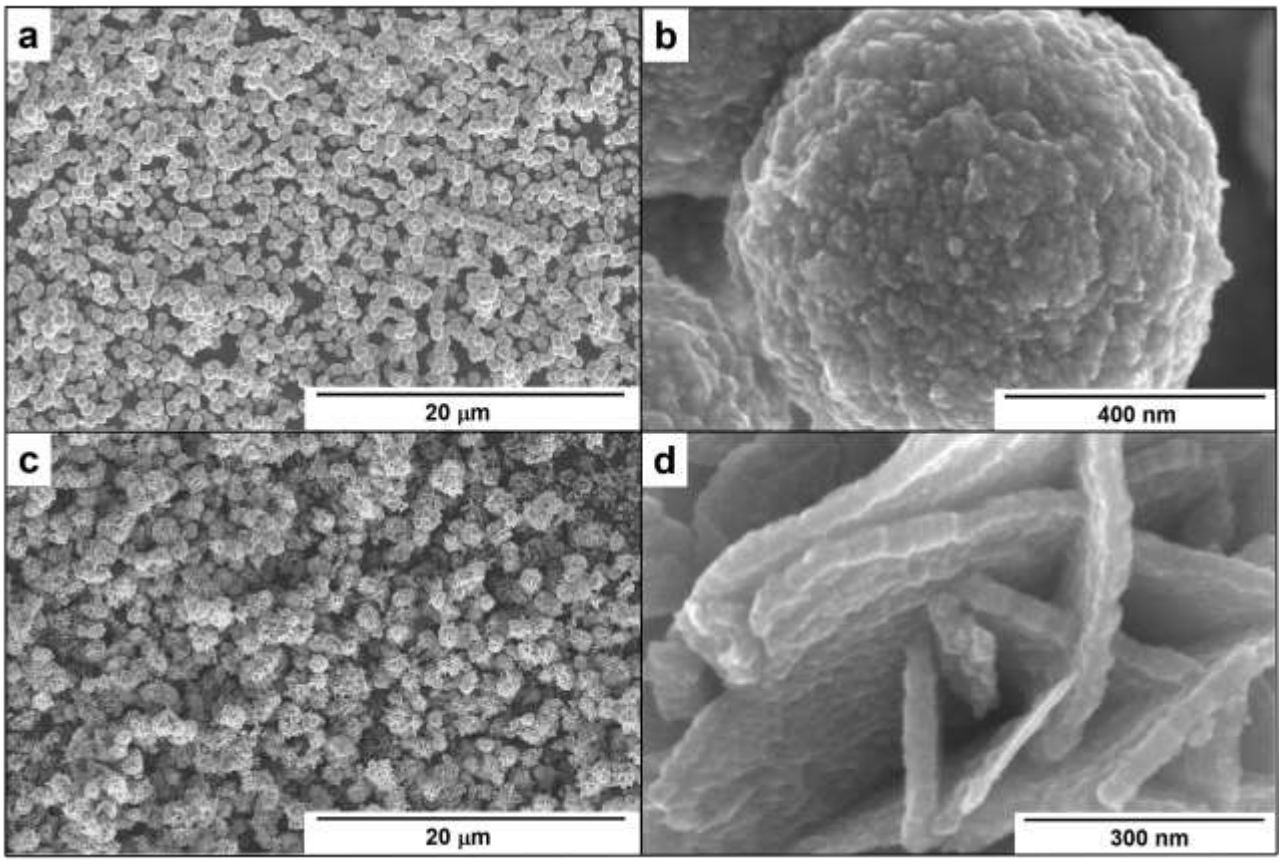

Fig. 2 Morphologies of Cu_2SnS_3 as observed in SEM. Sphere-like morphology (a,b) obtained using DEG and flower-like morphology (c,d) obtained using EG as the solvent.

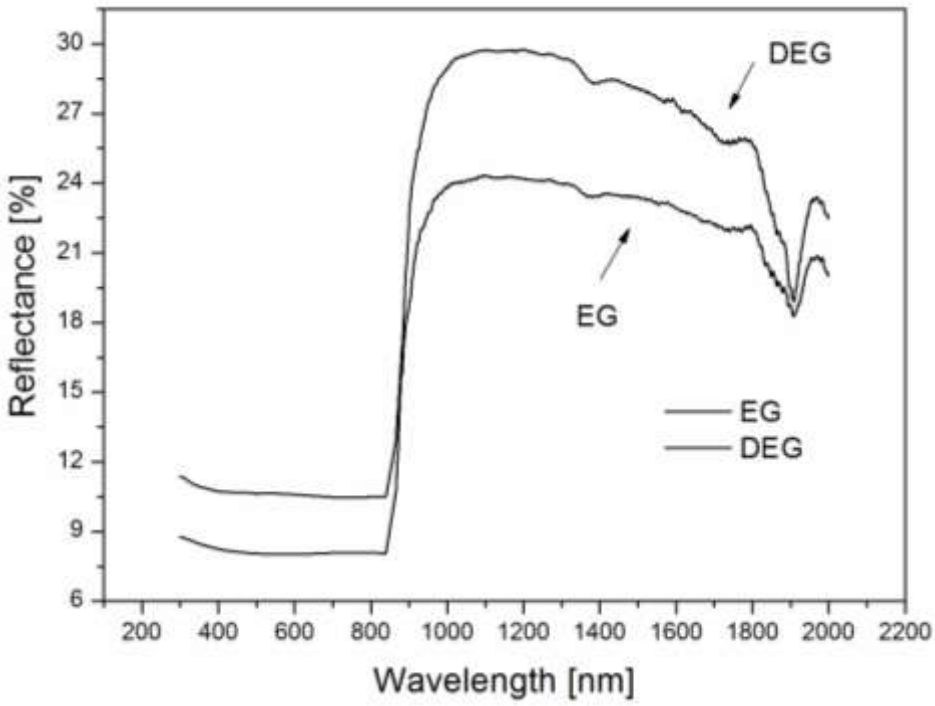

Fig. 3 UV-vis diffuse reflectance spectra of Cu_2SnS_3 samples synthesized in DEG and EG

The morphology of samples as observed by SEM is shown in Fig. 2. It can be clearly seen, that morphology of powders change significantly with solvent used. Uniform sub-micron spheres (Fig. 2a) were formed when DEG was used as a solvent. High resolution image (Fig. 2b) reveals, that these spheres are aggregation of nanocrystals. However, when used DEG as the solvent instead of EG, flower-like morphology was obtained as shown in Fig. 2c. These flowers composed of entangled sheets with thickness of about 30 nm as can be seen from high resolution image in Fig. 2d. UV-vis diffuse reflectance spectroscopy was used to reveal the energy structure and properties of the as prepared Cu_2SnS_3 samples (Fig. 3.). It can be seen that both structures have steep absorption edge in the visible range with a bang gap about 1.35 eV. Moreover, flower-like architecture possesses lower reflectance than its sphere-like counterpart.

4. CONCLUSION

In this work, microwave-assisted solvothermal synthesis route was developed for preparation of Cu_2SnS_3 cubic phase structures in a very short time. By simply changing the solvent from EG to DEG, the morphology of sample changed from flower-like to sphere-like sub-micron polycrystalline aggregates consisting of nanocrystals with dimension of about 20 nm. This can be attributed to increase of synthesis temperature from the 170 °C to the 210 °C due to the different boiling temperature of solvents used. Based on the optical properties measurements, the band gap and absorption coefficient of prepared morphologies are estimated to be 1.35 eV. Preliminary results suggests, that as prepared nanostructured Cu_2SnS_3 architectures are potential candidates for application as absorbing layer in thin films solar cells.

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