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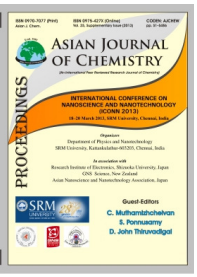

Synthesis of Cu_2ZnSnS_4 Nanopowder by Hydrothermal Method†

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Quaternary compound Cu_2ZnSnS_4 a promising, low cost and highly efficient absorber material in solar cells have been synthesized through hydrothermal method in this study. This method employs simple as well as an inexpensive process using less environmental polluting precursors. The synthesized Cu_2ZnSnS_4 powder had been studied using X-ray diffraction method (XRD). X-ray diffraction pattern reveals that the prepared Cu_2ZnSnS_4 material exhibits kesterite structure and the average grain size has been found to be 17 nm. The compositional analysis carried out using energy dispersive X-ray analysis (EDS) revealed that Cu, Zn, Sn and S are present in the sample. The optical studies indicated the presence of direct optical band gap with a value 1.45 eV.

Key Words: Cu_2ZnSnS_4 nano powder, Hydrothermal method, Solar cell absorber material.

INTRODUCTION

Colloidal semiconductor nanocrystals are a remarkable material set that can be synthesized and processed as a material with high yield while exhibiting optical and electronic properties that are size-dependent[1]. Applications ranging from biolabeling to photocatalysis and photovoltaics that exploit either the discrete or collective properties of these size controlled crystals have emerged in recent years[2].

As on the other side the energy crisis has become increasingly serious, research on high efficiency, low cost solar cells has become more important.

Among numerous type of solar cells, the $CuIn_xGa_{1-x}S(Se)_2$ (CIGS) thin film solar cell has attracted great interest due to its high power conversion efficiency and stability. However, the low availability and toxicity of indium and gallium increases the production costs and hinders the development of $CuIn_xGa_{1-x}S(Se)_2$ thin film solar cells. For years, scientists have been attempting to find a substitute for $CuIn_xGa_{1-x}S(Se)_2$ that avoids using high cost elements. Cu_2ZnSnS_4 which is a structural analogue to $CuIn_xGa_{1-x}S(Se)_2$ has drawn much attention because it is composed of readily abundant materials[3,4]. Also Cu_2ZnSnS_4 is an I2-II-IV-VI4 quaternary compound semiconductor obtained by substituting the selenium with sulfur and the rare metal indium with zinc and tin in the $CuIn_xS(Se)_2$ (CIS) ternary compound. Each component of Cu_2ZnSnS_4 is abundant in the earth's crust (Cu: 50 ppm, Zn: 75 ppm, Sn: 2.2 ppm, S: 260 ppm) and possesses extremely low toxicity[5-8].

Kesterite, Cu_2ZnSnS_4, $Cu_2ZnSnSe_4$ and their alloys $Cu_2ZnSn(S,Se)_4$, are regarded as promising absorber materials for future photovoltaic systems on a terra-watt scale[9-11]. These materials have band gap energies ranging from 1.0 eV to 1.5 eV[12-14], which matches well with the optimal spectral range of solar radiation required for solar cell. The high absorption coefficients of these materials ($>10^4$ cm^{-1})[3,12] assures the absorption of the entire incident photon flux in an absorber layer as thin as a few microns. The latest conversion efficiency of 11.1 %[15] has encouraged numerous investigations to search for more feasible and low-cost production methods for large-scale employment of kesterite solar cells.

The performance of the solar cell is very sensitive to the optical and electrical properties, which mainly depend upon the crystal structure and composition of the absorber material. Hence it is very important to understand and optimize the growth and phase formation of the photovoltaic material in order to achieve the desired stoichiometry. Being quaternary compound, Cu_2ZnSnS_4 often contains other binary and ternary phases and it is difficult to control the stoichiometry. Thus, it requires a very good control over synthesis parameters in order to obtain the desired phase of the material.

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According to the literature, the shapes and dispersion of Cu_2ZnSnS_4 particles in solvent have great influences on the crystalline and morphology of the final *p*-type absorption layer Cu_2ZnSnS_4[16]. However, most researchers used thio-urea as the sulfur source, which is reported to have a contribution to the irregular shape of the Cu_2ZnSnS_4 precursor nanoparticles[17-19]. To the best of our knowledge, we see few synthesis techniques towards the preparation of Cu_2ZnSnS_4 nanocrystals. Wei *et al.*[20] have synthesized spindle-like kesterite Cu_2ZnSnS_4 nanoparticles using thiourea as sulfur source by hot junction method. Shinde *et al.*[21] and Mali *et al.*[22] had discussed the preparation of Cu_2ZnSnS_4 absorbing layer by SILAR method, but up to our knowledge there is almost no reports on synthesis of Cu_2ZnSnS_4 material by hydrothermal method. Among all other methods, hydrothermal synthesis of nano crystals is a promising approach due to its simple process, fast reaction velocity, low cost and size controllable nature. In the present study Cu_2ZnSnS_4 nano particles have been prepared by hydrothermal method and their structural and optical properties have been studied.

EXPERIMENTAL

All the chemicals used in the present study were analytical reagent (AR) grade and used without further purification. Cu_2ZnSnS_4 has been synthesized by hydrothermal method. Stoichiometric amounts of $CuCl_2$, $ZnCl_2$, $SnCl_4$ were dissolved in 30 mL deionized water, the solution was stirred and Na_2S was added to the mixture and the stirring was continued for for 3 h to ensure homogeneity of the mixture, 3-4 pH of 1 N H_2SO_4 was added drop wise into the solution and the stirring was continued for two more hours. The resultant mixture was transferred into an autoclave and kept at 90 ºC for 12 h. The obtained precipitates were centrifuged at 5,000 rpm for 5 min and rinsed several times in deionized water, further it was dried at 70 ºC for 24 h and calcined at 500 ºC for 1 h.

The structural properties of the prepared powders were studied using X-ray diffractometer SHIMADZU (Model 6000) with CuK_α radiation (k_α = 1.54056 Å) in the diffraction angle range of 10 to 90 º at the scanning rate of 10 º/min. Surface morphology and compositional study of the powders were carried out using scanning electron microscopy, (JEOL, JSM-6360, Japan) attached with an energy dispersive X-ray analysis (EDAX) analyzer. Optical properties were studied using the absorbance spectra recorded using UV-VIS-NIR spectrophotometer in the wavelength range of 200-1000 nm (Jasco V-570).

RESULTS AND DISCUSSION

Fig. 1 shows the X-ray diffraction pattern of the Cu_2ZnSnS_4 powder annealed at 500 ºC. Peaks were obtained at the 2θ positions of 28.26º, 47.28º and 55.24º for the annealed powders which corresponds to the (1 1 2), (2 2 0), (3 1 2) planes of Cu_2ZnSnS_4 and they are characteristic of tetragonal type kesterite structure of Cu_2ZnSnS_4 (JCPDS, Card No. 26-0575). The grain size of the annealed Cu_2ZnSnS_4 powders was calculated using Scherer's equation:

$$D = \frac{K\lambda}{\beta Cos\theta}$$

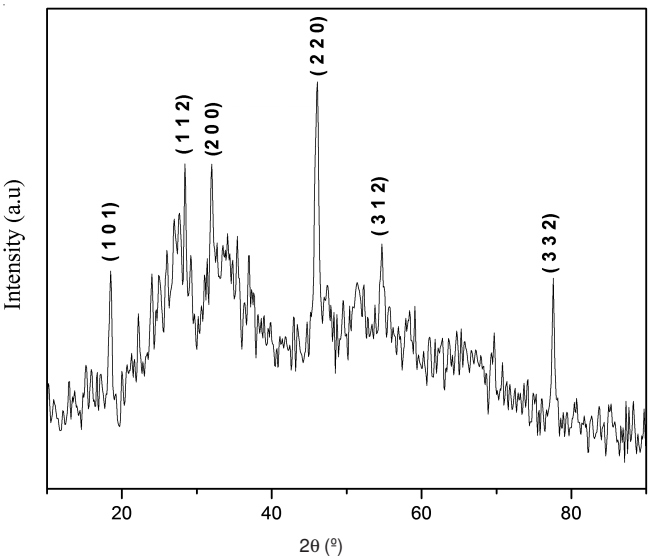
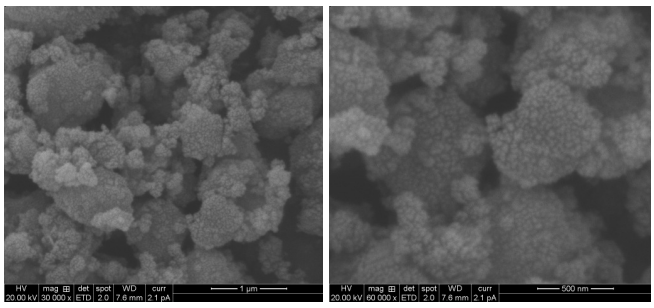


Fig. 1. X-ray diffraction pattern of Cu_2ZnSnS_4 annealed powder at 500 ºC

where λ is the wavelength of X-ray radiation, β is the FWHM and θ is the angle of diffraction. The average grain size was found to be 17 nm. The obtained lattice constants were in good agreement with reported lattice parameters for the JCPDS, Card No. 26-0575. Peaks corresponding to the other binary phases like Cu_2S and ZnS are not present in the diffraction pattern revealing the formation of Cu_2ZnSnS_4.

Fig. 2 shows the SEM images of Cu_2ZnSnS_4 powder taken at 1 μm and 500 nm magnifications respectively. Fig. 2b shows that the annealed powder consists of spherical particles formed as clusters.



(a) (b)

Fig. 2. (a,b) SEM images of annealed Cu_2ZnSnS_4 powder at different magnifications

The elemental composition of Cu_2ZnSnS_4 powder was determined by energy dispersive X-ray analysis and the spectra is shown in Fig. 3. The chemical composition of the powder is Cu - 13.70 wt %, Zn -12.1 wt %, Sn -20.72 wt %, S- 42.7% wt %.

The absorbance spectra of the Cu_2ZnSnS_4 powder is shown in Fig. 4. The absorption coefficient of the Cu_2ZnSnS_4 powder was found to be the order of 10^4 cm^{-1}. The band gap of Cu_4ZnSnS_4 has been determined using the relation:

$$\alpha = A(h\nu - E_g)^{1/2}$$

where, α is the absorption coefficient, A is the constant, E_g is the energy gap and hν is the incident photon energy. The optical band gap is deduced by extrapolating the straight line portion of the $(\alpha h\nu)^2$ *vs.* (hν) plot shown in Fig. 5. The band

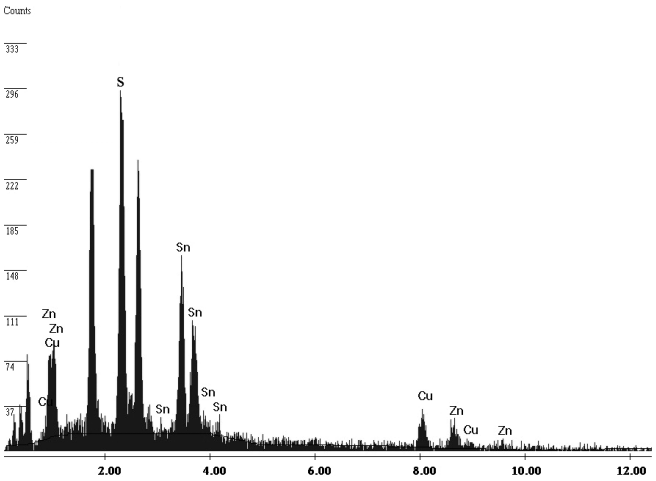


Fig. 3. EDAX spectrum of Cu_2ZnSnS_4 powder

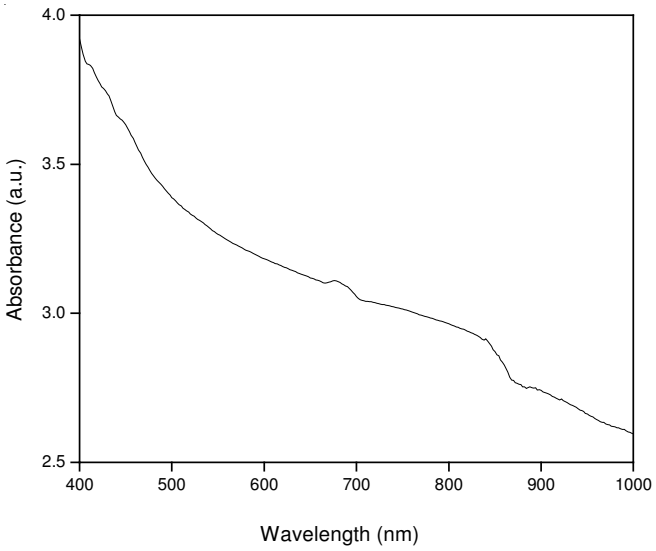


Fig. 4. Absorption spectra of annealed Cu_2ZnSnS_4 powder

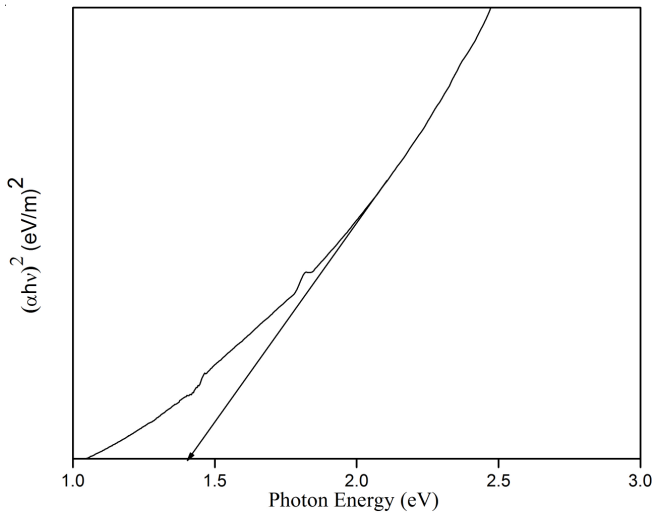


Fig. 5. Plot of $(\alpha h\nu)^2$ *versus* $h\nu$ of annealed Cu_2ZnSnS_4 powder

gap energy was found to be 1.45 eV, which is in good agreement with previously reported values[17,20]. This band gap value is quiet close to the optimum band gap required for a solar cell absorber layer material.

Conclusion

Cu_2ZnSnS_4 nano particles have been synthesized by hydrothermal method. The X-ray-diffraction pattern of the annealed powders revealed the formation of tetragonal type kesterite structure Cu_2ZnSnS_4 material. Surface morphology of the powders revealed the formation of particle with spherical nature and the compositional analysis reveals that the sample contains Cu, Zn, Sn and S respectively. The optical studies show that the nano crystalline Cu_2ZnSnS_4 powder has a direct band gap of 1.45 eV.

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