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Original Research Article

Growth of single phase CZTS by hydrothermal method

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ABSTRACT
Cu_2ZnSnS_4 (CZTS) has emerged as a highly desirable material for use in thin-film solar cells. CZTS materials have exceptional absorber qualities along with the advantages of abundance in the Earth's crust, an ideal band gap that aligns well with the solar spectrum 1.4 – 1.6 eV, a high absorption coefficient of ~ 10^4 cm^{-1}, non-toxicity, and low-cost components. Because of these exceptional characteristics, CZTS is considered a promising material for use in inorganic photovoltaic devices. This study successfully synthesized CZTS nanoparticles using the hydrothermal method. Phase-pure CZTS nanoparticles synthesized with Cu(II), Zn(II), Sn(II) inorganic metal salts and thiourea as a sulfur source in distilled water solution as a precursor are described. The presence of binary or ternary phase impurities at different temperatures is explained. The XRD peaks are observed in CZTS-140, CZTS-160, and CZTS-180 samples at 2θ values of 28.5°, 32.9°, 47.4°, and 56.3°, corresponding to (112), (200), (220), and (312) of the tetragonal crystal Kesterite CZTS phase, respectively along with the presence of SnS_2 binary phase. In addition, the less intense peak observed at 2θ = 50° corresponds to (110) for the SnS_2 phase along with the CZTS phase at reaction temperatures of 140°C and 160°C. The CZTS nanoparticles exhibited crystallite sizes of 13.8 nm, 10.3 nm, and 11.7 nm corresponding to (112) peak, for CZTS-140, CZTS-160, and CZTS-180,respectively. Synthesized CZTS nanomaterials can be used for solar device fabrication.

1. Introduction

The energy issue is one of the most important problems that people are facing in the 21st century. The primary aim of research in this field is the development of affordable and environmentally friendly forms of renewable energy [1]. There are multiple renewable resources, such as sunshine, tides, wind, and geothermal heat, that are safer, cleaner, and more sustainable than fossil fuels, which are environmentally destructive. Solar energy is the most preferred among all investigated green/renewable energy sources [2]. Solar energy is a highly abundant form of energy and is the most prevalent source of renewable energy. Solar energy can be transformed into electricity using a Photovoltaic (PV) system, which is a significant advantage. The solar energy conversion efficiency is comparatively better than that of other energy resources.

It is essential to greatly increase this fraction before fossil fuels run out to protect future generations from the energy crisis. Hydrogen (H_2) is considered the most auspicious clean energy alternative with the capacity to supplant fossil fuels due to its lack of carbon emissions, sustainability, and renewability [3]. The compound Cu_2ZnSnS_4 (CZTS) is a quaternary semiconductor that demonstrates great potential as a material for solar cell absorbers [4]. Copper, zinc, tin, and sulfur are the elements that constitute CZTS. These elements are all nontoxic and extremely common in the earth's crust [5]. CZTS has optimal optical and electrical characteristics, including an ideal bandgap, conductivity, and immediate fabrication throughput. CZTS, a semiconductor with p-type conductivity, shows potential as a solar absorber because of its elevated coefficient of absorption (>10^4 cm^{-1}) and versatile optical band gap (1.45-1.65 eV), which is well-matched to the solar spectrum [6].

Research on CZTS primarily focuses on its synthesis and photovoltaic performance, but it has also gained interest for photoelectron-chemical and photocatalytic applications, suggesting it could be a cost-effective material for organic pollutantdegradation [7]. CZTS material has been synthesized using a range of physical and chemical procedures, including sputtering, pulsed laser deposition, ultrasonic spray pyrolysis, spray pyrolysis, thermal evaporation, electrochemical deposition, microwave synthesis, and sol-gel spin coating [8, 9]. The hydrothermal approach is highly attractive for large-scale semiconductor nanoparticle synthesis.

In this report, we present a low-cost, environmentally friendly hydrothermal synthesis method for CZTS nanoparticles at different reaction temperatures. The method uses thiourea as the reacting agent, as well as $CuCl_2$, $ZnCl_2$, and $SnCl_2.2H_2O$ as the metal salts.The structural and optical characteristics have been explored in detail.

2. Materials and methods

2.1 Materials

Copper (II) chloride ($CuCl_2$), tin (II) chloride dihydrate ($SnCl_2.2H_2O$), thiourea (CH_4N_2S), zinc (II) chloride ($ZnCl_2$), ethanol, and de-ionized water were used as precursors for the synthesis of CZTS nanoparticles. All of the chemicals were obtained and utilized without subjecting them to purification.

2.2 Methods

CZTS was prepared by dissolving 0.10M $CuCl_2$, 0.06M $ZnCl_2$, 0.06M $SnCl_2.2H_2O$, and 0.36M thiourea in 60 mL of deionized water. The mixture was stirred magnetically for 3 hours at a temperature of 45℃. Subsequently, the entire precursor solution was then put into a 100 mL (70% filled) Teflon-coated stainless-steel autoclave. The autoclave was subjected to different temperatures of 140℃, 160℃, and 180℃ for 24 hours, after which it was allowed to cool down to the ambient temperature. The precipitate was subjected to centrifugation and subsequently washed several times with deionized water and ethanol to eliminate any by-products. The ultimate outcome was subjected to a drying process at a temperature of 80℃ for the duration of one night (Figure 1). As synthesized CZTS nanoparticles kept in the autoclave at temperatures of 140℃, 160℃, and 180℃ were named CZTS-140, CZTS-160, and CZTS-180, respectively.

Figure 1: Schematic representation of the hydrothermal technique.

2.3 Characterizations

The structural characterization and optical properties of CZTS nanoparticles were analyzed with a Rigaku X-ray diffractometer for X-ray diffraction (XRD) and a Perkin Elmer Lambda 365 UV-visible spectrophotometer for the UV-visible spectrum. The XRD patterns of CZT Snanoparticles were obtained by measuring the angles (2θ) between 20°and 60° using CuK_α radiation with a wavelength (λ = 0.154 nm). The optical characteristics of the CZTS nanoparticle were determined by UV-vis spectroscopy in the range of 500 eV to 1000 eV.

3. Results and discussion

Figure 2 displays the X-ray diffraction (XRD) patterns of CZTS nanoparticles at different temperatures at a reaction time of 24 hours. The diffraction pattern of the CZTS nanoparticle, synthesized using the hydrothermal method, at the temperature of 140℃, 160℃ and 180℃, exhibited distinctive peaks at specific angles. These peaks were observed at 2θ = 28.5°, 32.9°, 47.4°, and 56.3°, corresponding to the crystallographic planes (112), (200), (220), and (312) of the tetragonal CZTS crystal respectively. This crystal structure was identified by the JCPDS No.26–0575 [10]. According to the XRD data, sample CZTS-180 had a single-phase crystalline structure of CZTS (Figure 2), whereas sample CZTS-140 and CZTS-160 had less intense impurity peaks of SnS_2at 2θ= 32°, 50° and 2θ = 50°alone with the CZTS respectively. When the reaction temperature increased from 140℃ to 180℃, no highly intense secondary phases occurred.

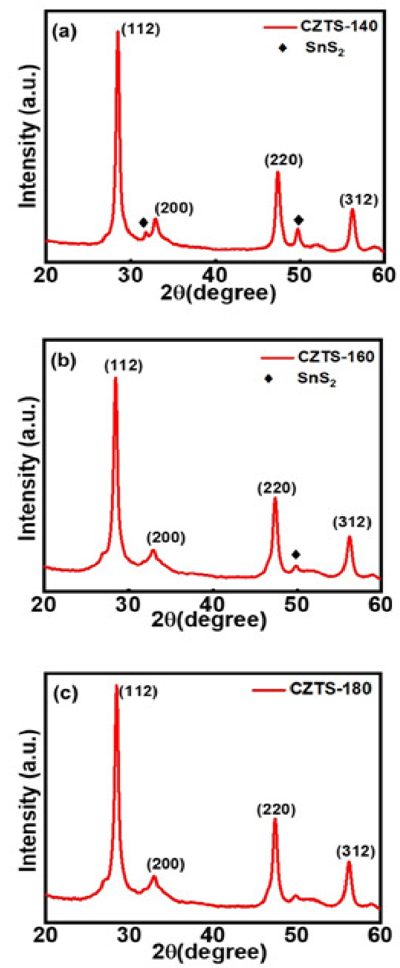

Figure 2: The XRD pattern of CZTS nanoparticles at different temperatures. (a) CZTS-140, (b) CZTS-160, and (c) CZTS-180

The size of CZTS nanoparticles, known as crystallite size (*d*), was determined by using Debey-Schere's formula (Equation 1).

$$d = \frac{K\lambda}{\beta \cos\theta} \quad (1)$$

where λ ($\lambda_{Cu\text{-}K\alpha}$ = 1.54 Å) is the X-ray wavelength, *K* is Schere's constant (0.94), d is the crystallite size, β is the full-width half maxima, and θ is the Bragg angle [11]. The CZTS nanoparticles synthesized at 140℃, 160℃, and 180℃ yielded crystallite sizes of 13.8 nm, 10.3 nm, and 11.7 nm corresponding to (112) peak respectively.

Figure 3 exhibits the ultraviolet-visible (UV-vis) absorption spectra of the hydrothermally produced CZTS nanoparticles at a temperature of 180℃. The spectra show that the CZTS exhibited significant absorption in both the UV and visible regions. The plot of $(\alpha h\nu)^2$ vs. $h\nu$ (Figure 4) is extrapolated to calculate the band gap of the materials.

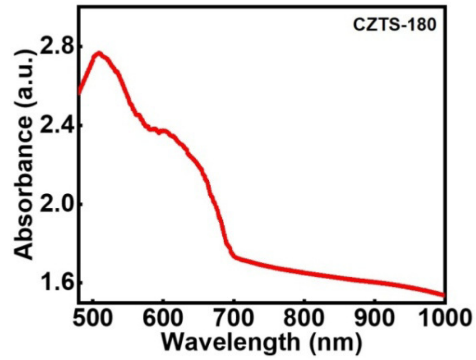

Figure 3: Optical absorption spectrum of CZTS nanoparticle at 180 °C.

Table 1: Experimental conditions and results of the CZTS samples.

Sample	Precursors ratio (Cu: Zn: Sn: S)	Time (Hours)	Temperature (°C)	Products	crystallite size (nm)
CZTS 140	(1.6:1:1:6)	24	140	CZTS,SnS_2	13.8
CZTS 160	(1.6:1:1:6)	24	160	CZTS,SnS_2	10.3
CZTS 180	(1.6:1:1:6)	24	180	CZTS	11.7

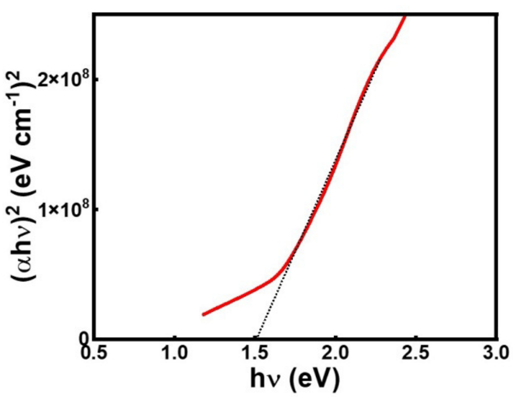

Figure 4: Variation of $(\alpha h\nu)^2$ versus hν for the CZTS nanoparticle at 180 °C shows a band gap of ~1.5 eV.

$$(\alpha h\nu)^{\frac{1}{n}} = B(h\nu - E_g) \quad (2)$$

Here, α is the absorption coefficient, *h* is Planck's constant, *B* is a constant, E_g is band gap, ν represents frequency, and *n* may have values of 1/2 or 2 corresponding to allowed direct and indirect transitions, respectively. The linear component of the curve was extrapolated to determine the optical band gap of CZTS. The estimated value of the band gap obtained was 1.5 eV.

4. Conclusions

A monophasic CZTS nanoparticle was synthesized via the hydrothermal technique that uses deionized water as a surfactant. The effect of reaction temperatures (140°C, 160°C, and 180°C) on the structural properties of CZTS nanoparticles has been studied. The crystallite sizes of the CZTS nanoparticles synthesized at different reaction temperatures of 140℃, 160℃, and 180℃ were 13.8 nm, 10.3 nm, and 11.7 nm respectively. The CZTS nanoparticle, which was synthesized at a reaction temperature of 180℃ has a wide absorption spectrum in the visible region. The extrapolation reveals that the hydrothermally synthesized CZTS has a band gap of 1.5eV.

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