Structural and Optical Properties of Chemically Synthesized Cu$_2$ZnSnS$_4$ (CZTS) Nanoparticles

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Abstract The structural and optical properties of Cu$_2$ZnSnS$_4$ nanoparticles prepared by an affordable chemical route were investigated with the aim of determining suitability of the nanoparticles for photovoltaic applications. XRD characterization indicates phases that exhibit kesterite structure of CZTS. The crystallite sizes calculated for both CZTS nanoparticles specimen were comparable to those reported in literature. The absorbance was found to be considerably high within the visible region of the electromagnetic radiation while the transmittance was very low. Theoretical band-gap was calculated to be between 1.55 eV and 1.92 eV which are the ideal band-gap for solar cell absorber for high conversion efficiency.

Keywords: Nanoparticles, Characterization, Grain size.

Introduction

In the nearest future, thin film solar cells will be the dominant p-n junction device in the photovoltaic market. The reason is simply their affordability and high conversion efficiency, which has led to the scientific community focusing their attention on developing thin film photovoltaics. Recently, attention has shifted to copper zinc thin sulfide (Cu$_2$ZnSnS$_4$ or (CZTS)) quaternary semiconductor [1,2,3] due to its eligibility as earth abundant, non-toxic and cheaper alternative absorber layer to the popular cadmium telluride (CdTe) and copper indium gallium selenide (CIGS) which has reached commercial levels in the photovoltaic market [3,4]. Cadmium telluride contains toxic elements that have been found to be

carcinogenic and the CIGS system contains rare indium elements [5]. CZTS has a direct optical band gap of 1.4-1.5 eV which is the optimum value band gap for high efficiency solar cells, it has p-type conductivity with large absorption coefficient, over $10^4 cm^{-1}$, lowering usage of materials. A 32.2% light to power conversion efficiency can be reached using CZTS as absorber according to Schockley-Queisser photon balance calculations. An impressive efficiency of 11% has been achieved by Todorov and his group [6] by using a process involving hydrazine solution to fabricate CZTS thin films. The performance of a solar cell device is heavily dependent on the structural, optical and electrical properties of the semiconductor material which is influenced by its stoichiometric composition and crystal structure. Therefore, understanding the growth and formation of photovoltaic material is highly necessary. Stoichiometry is difficult to control in CZTS due to its quarternary phase leading to formation of secondary phases such as ZnS, Cu_2S and Cu_2SnS_3 [7]. These phases are one of the factors limiting the efficiency of CZTS solar cells as they act as centres of non-radiative recombination. Formation of secondary phases can be controlled by tuning photovoltaic material synthetic conditions. Several synthetic processes have been developed for preparation of CZTS nanoparticles and thin films, both vacuum [8,9,10] and non-vacuum [11,12,13] processes. These processes involve very high temperatures (above 350 ^{o}C), high quality substrates and very expensive precursors. A simple approach based on a non vacuum method known as solvothermal has been used in this work to prepare CZTS nanoparticles. This

method has been used extensively by many authors to prepare CZTS nanoparticles [13-17]. Solvothermal technique has an advantage of low temperature (less than 250 ^{o}C) over other methods; hence, it is a suitable alternative. CZTS nanoparticles synthesized by solvothermal method could be used in roll-to-roll fabrication of CZTS solar cells by dispersing the nanoparticles in appropriate solvents. The ink can then be printed onto a substrate for use as absorber layer.

Methods

The precursors of copper, zinc, tin and sulfur used in this work are analytical grade reagents, all of them above 99.0% in purity. A precursor mixture was obtained by dissolving 0.025 M of copper(II) acetate monohydrate $(Cu(CH_3COO)_2.H_2O)$, 0.025 M of zinc acetate dihydrate $(ZnC_4H_6O_4.2H_2O)$, 0.025M of tin(IV) chloride pentahydrate $(SnCl_4.5H_2O)$ and 0.2 M of water soluble organic compound thiocarbamide $(CS(NH_2)_2)$ in 70% deionized water and 30% ethanol. The solution was stirred continuously until a clear solution was obtained. The solution was placed inside an oven and it was maintained at 200 ^{o}C. The black precipitate formed were later removed from the oven, washed in ethanol and filtered. The resulting nanoparticles was oven-dried at 60 ^{o}C for three hours and classified as specimen *CZTS*. A similar mixture was prepared using ethylene glycol monoethyl ether as solvent with final product obtained by following experimental procedure similar to that of CZTS prepared from deionized water as solvent. The product was classified as specimen *CZTS (EG)*. The structural characterization of CZTS nanoparticles was carried out by a Bruker (model ECO D8 Advance) x-ray diffractometer

with a lynx eye detector using copper target (Cuα,1.5418 Å). All x-ray diffraction (XRD) data for the specimens were recorded at current and acceleration voltages of 25mA and 40 kV respectively. Morphological and grain growth analysis of CZTS nanoparticles were carried out by using Hitachi scanning electron microscope (SEM) and optical characterization was done using UV- vis spectrophotometer of JENWAY (model 6800). The infrared spectra of CZTS nanoparticles were recorded using a Shimadzu IRtracer-100 spectrophotometer in the wavenumber range 4000-400 cm^{-1}.

Results and Discussion
XRD Analysis
The XRD patterns of CZTS nanoparticles prepared by solvothermal method are shown in Figure 1. It can be noticed that all the patterns exhibit diffraction peaks at 2θ equal to 28.58^0, 47.33^0 and 56.26^0 corresponding to the (112), (220), (312) and (332) reflection

planes of CZTS which is in agreement with the JCPDS card number (26-0575). The tetragonal and cubic phases are signatures of the kesterite structure of prepared CZTS nanoparticles. Broad peaks can be observed in both specimen which is an evidence of their nanocrystalline nature. It can be observed that the 2θ position for (112) direction shifts to higher values in *CZTS (EG)*. The average crystallite size for both specimens was calculated using the Scherer formula expressed as:

$$D = \frac{0.9\lambda}{\beta cos\theta} \quad\quad (1)$$

Where λ is the x-ray wavelength for CuK_α radiation, β is the full width half maximum and θ is the angle of diffraction. The calculated average crystallite sizes are 10 nm and 6 nm for *CZTS* and *CZTS (EG)* respectively. We observed that there is a remarkable agreement between our crystallite size and previously reported experimental work [7].
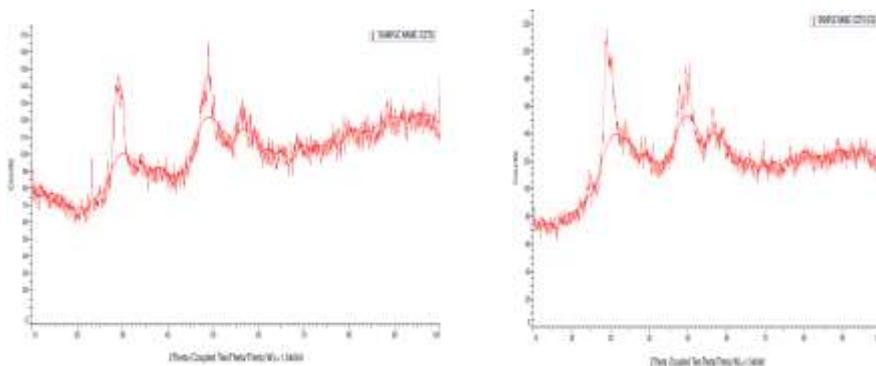

Figure 1. XRD patterns of CZTS nanoparticles

SEM Analysis
Figure 2 shows the SEM images of CZTS nanoparticles. Densely packed

and homogeneous sphere-like nanoparticles can be observed in the images with little porosity and voids.
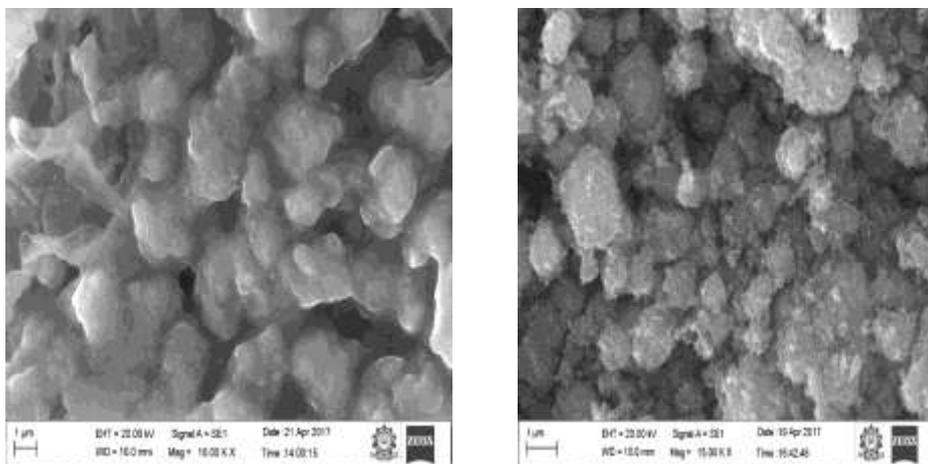
Figure 2. SEM micrographs of CZTS nanoparticles specimen *CZTS (EG)* and *CZTS*

FITR studies

For better identification of volatile compounds lost during the solvothermal process, an FTIR spectroscopy was performed on the specimens. FTIR response for specimen CZTS is shown in figure 3. The peak at 3,424 cm^{-1} can be attributed to OH vibrational band of H_2O or symmetric and asymmetric NH stretching vibrational band of thiourea [18]. Absorption at 2,925.71 cm^{-1} can be attributed to S-H thiol functional class; 2353 cm^{-1} peak is within the O-C-O vibrational band of CO_2 [19]. Peaks at 2074.28 cm^{-1} and 1648.76 cm^{-1} can be attributed to alkyne and alkene functional groups respectively [19]. The peak at 783 cm^{-1} is a characteristic infrared band of diatomic inorganic molecules indicating a very strong presence of metals. The FTIR spectra of specimen CZTS (EG) is also shown in figure 3. NH amine groups indicating presence of thiourea complexes can be seen at 3400.50 cm^{-1} and 3292.48 cm^{-1}. The lower bands ranging from 570.93 cm^{-1} to 410.84 cm^{-1} can be attributed to metal-chloride compounds.
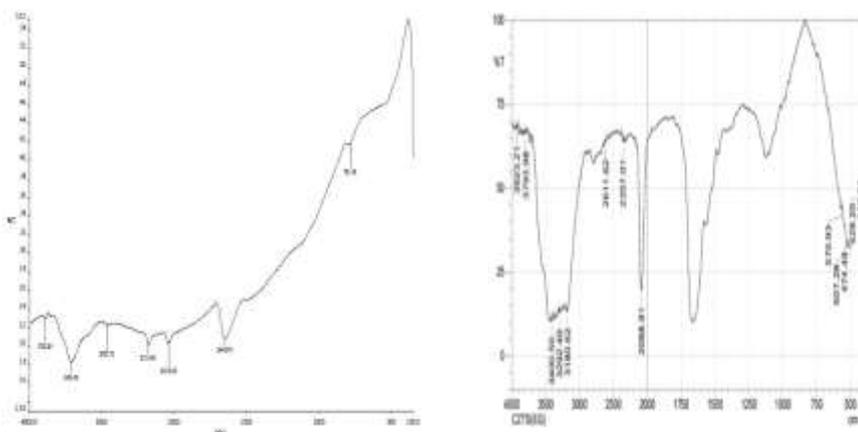

Figure 3. FTIR spectra of CZTS nanoparticles specimen *CZTS* and *CZTS (EG)*
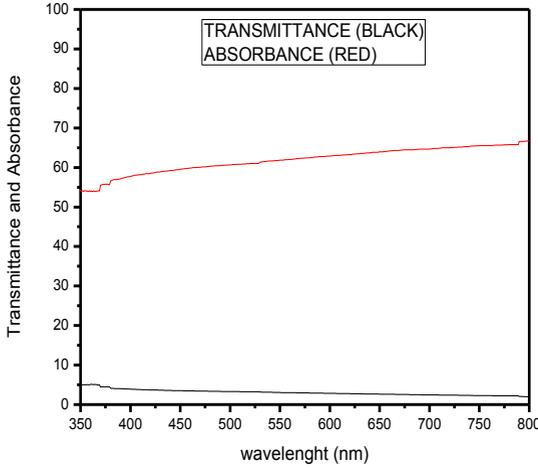
Optical Characterization

Figure 4. Transmittance and Absorbance Spectra of CZTS Nanoparticles

It was observed from figure 4 that the prepared CZTS nanoparticles have a high absorbance and low transmittance of electromagnetic radiation within the visible region. This makes it a promising good material as an absorber layer in fabricating thin film solar cell, which is of more advantage than the already widely used cadmium telluride which is toxic.

Fig. 5 shows the $(\alpha hf)2$ versus hf plots for the films. The plot is derived from the expression

$$(\propto hf)^{1/n} = A(hf - E_g) \qquad (2)$$

where α is the absorption coefficient, h is the Planck's constant, f is the photon frequency, Eg is the band-gap and A is a constant of proportionality. n depends on the nature of radiative transition and is given as n = ½ for directed allowed band-gap [19]. The optical band gap energies are determined by extrapolating the linear portion of $(\alpha hf)2$ versus hf curve to $(\alpha hf)2 = 0$. The band-gaps of the CZTS nanoparticles specimen CZTS and CZTS (EG) are estimated to be 1.55 eV and 1.93 eV respectively. These values are appropriate band-gap energy of solar cell absorber layer for high solar to electrical power conversion efficiency as they can absorb photons consisting of visible and infrared rays [20].
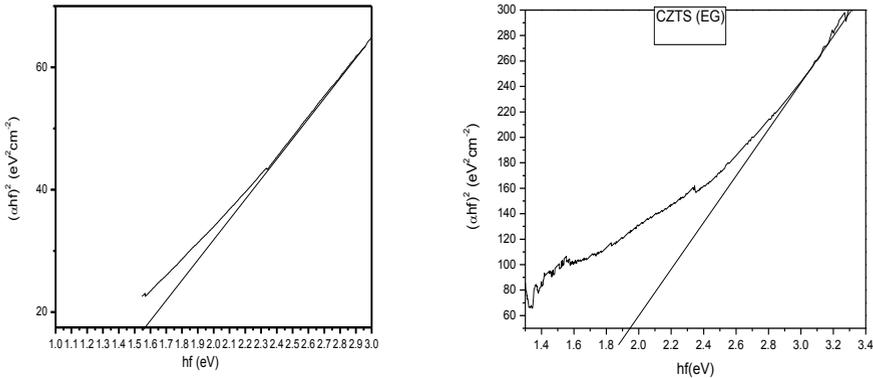
Figure 5. Optical absorption coefficient of CZTS nanoparticles specimen *CZTS* and *CZTS (EG)*

Conclusion

Eco-friendly Cu_2ZnSnS_4 nanoparticles have been synthesized by a very efficient chemical route. The Structural and optical properties of CZTS nanoparticles have been investigated. XRD characterization of nanoparticles reveals the tetragonal and cubic phases confirming the kesterite structure of CZTS. SEM images showed sphere-like nanoparticles with closely packed distribution. The band-gap of the CZTS nanoparticles has been estimated to be between 1.55 eV and 1.92 eV, suitable for photovoltaic applications.

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