

## Structural and Optical Properties of $\text{Cu}_2\text{ZnSnS}_4$ Nanoparticles for Solar Cell Applications

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The  $\text{Cu}_2\text{ZnSnS}_4$  (CZTS) nanoparticles were successfully synthesized by Chemical co-precipitation method with different synthesis temperatures. The synthesized nanoparticles were characterized by X-ray diffraction, Raman Spectroscopy, Scanning electron microscopy, Energy dispersive spectroscopy and UV-VIS-NIR spectrophotometer. XRD and Raman studies revealed that the CZTS nanoparticles exhibited Kesterite Structure with preferential orientation along the (112) direction. The CZTS nanoparticles synthesized at a temperature 150 °C exhibited near stoichiometry. On further increasing the synthesis temperature sulphur composition was decreased due to volatile nature of the sulphur. The synthesized nanoparticles exhibited an optimum band gap of 1.4 eV.

**Keywords:** CZTS, Nanoparticles, Solar cell.

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### 1. INTRODUCTION

Nanoparticles have been very much attracted the researchers in the field as the transition from micro-particles to nanoparticles was seen to lead to huge changes in the physical and chemical properties of a material. Nanotechnology is used in many fields of Science and Technology including photovoltaics. Photovoltaic research and development will continue intense interest in new materials, cell designs and novel approaches to solar material and product development. The price of photovoltaic power will be competitive with traditional sources of electricity. Chalcopyrite materials like CIGS solar cells exhibited conversion efficiency of 20 % [1]. However, the materials like In and Ga are rare in the earth's crust and the selenium is toxic nature. It is observed that CIGS is a preceding runner of the next generation absorber layer of the solar cell. The quaternary semiconductor copper zinc tin sulphide (CZTS) is the best alternative to the CIGS. The constituent elements of CZTS are easily available, low cost, pollution free and non-toxic [2]. CZTS has direct band gap energy 1.5 eV which is optimum value and also have a large absorption coefficient  $> 10^4 \text{ cm}^{-1}$  [3, 4]. Theoretical conversion efficiency CZTS solar cell is 32.2 % [5]. The solar cells based on CZTS already shown a conversion efficiency of 10 % [6]

In the last decades, a plenty of techniques have been reported on synthesis of CZTS films such as spray pyrolysis deposition [7], pulsed laser deposition [8-10], electro-deposition [11], co-evaporation [12], electron beam evaporation [13], RF magnetron sputtering deposition [3], hybrid sputtering [14], atom beam sputtering [15], hot injection [16-19], photo chemical deposition [20]. However, these techniques have some disadvantages such as expensive, complicated vacuum techniques, complicated apparatus and toxic byproducts. In the present study, CZTS nanoparticles are synthesized by Chemical co-precipitation method which can yield very low cost, low power consumption and effective control of the size and shape of nanoparticles. In last few years,

researchers have been devoted to the preparation of high quality CZTS nanoparticles for effective use in the formation of thin films and study their properties.

### 2. EXPERIMENTAL

To synthesis CZTS nanoparticles the chemicals used were  $(\text{C}_5\text{H}_8\text{O}_2)_2\text{Cu}$ ,  $(\text{C}_5\text{H}_8\text{O}_2)_2\text{SnBr}_2$ ,  $(\text{CH}_3\text{COO})_2\text{Zn}\cdot 2\text{H}_2\text{O}$  and  $\text{H}_2\text{N}\cdot\text{CS}\cdot\text{NH}_2$ . All the chemicals were purchased from Sigma Aldrich in the purest form available and were used without further purification. CZTS nanoparticles have been synthesized through chemical co-precipitation technique. In a typical experimental process, 1.5 mmol of  $(\text{C}_5\text{H}_8\text{O}_2)_2\text{Cu}$ , 0.75 mmol of  $(\text{C}_5\text{H}_8\text{O}_2)_2\text{SnBr}_2$ , 0.75 mmol of  $(\text{CH}_3\text{COO})_2\text{Zn}\cdot 2\text{H}_2\text{O}$  and 3 mmol of  $\text{H}_2\text{N}\cdot\text{CS}\cdot\text{NH}_2$  were dispersed in 40 ml of oleylamine. The solution was stirred for 4 hours with various synthesis temperatures such as room temperature (27 °C), 100 °C, 150 °C and 200 °C. The precipitate was washed several times with excess ethanol to remove byproducts and annealed at 100 °C. Finally black coloured nanoparticles were collected by grinding the precipitate.

X-ray Diffraction was used as the major tool for identification of the phases of CZTS nanoparticles. This analysis was done with a Seifert 3003 TT X-ray diffractometer with Cu  $\text{K}\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ). Raman Spectroscopic studies of the as prepared samples were carried out using LabRam HR800 Raman Spectrometer. The surface morphology of the nanoparticles was characterized by scanning electron microscope (SEM) of model EVO MA 15 manufactured by Carl Zeiss. The compositional analysis of the nanoparticles were studied by energy dispersive spectroscopy (EDS) attached with SEM of model Oxford instruments Inca Penta FET x3. In order to study optical properties of the nanoparticles, the absorption measurements were carried out by using a Perkin Elmer Lambda 950 UV-VIS-NIR spectrophotometer with a wavelength resolution better than  $\pm 0.2 \text{ nm}$  at room temperature.

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### 3. RESULTS AND DISCUSSION

#### 3.1 Structural Studies

X-ray diffraction patterns of the CZTS nanoparticles at various synthesis temperatures are shown in Fig. 1. The diffraction peaks at  $2\theta$  values  $28.59^\circ$ ,  $33.09^\circ$  and  $47.44^\circ$  are indexed as (112), (200) and (220) corresponding to that of Kesterite structure of CZTS (JCPDS 26-0575). The lattice constants were calculated and were found to be  $a = 5.427 \text{ \AA}$  and  $c = 10.848 \text{ \AA}$ , which are good agreement with the previous reported data of stoichiometric CZTS with tetragonal phase [16-18]. The intensity of peaks increased with increasing the synthesis temperature up to  $150^\circ\text{C}$  indicating improvement in crystallinity. Further increasing the stirring temperature, the intensity of the peaks decreased and an impurity peak was observed at  $2\theta = 43.12^\circ$  corresponding to copper (JCPDS 85-1326). From the XRD studies we confirmed that, stoichiometric CZTS nanopowder was observed at a synthesis temperature of  $150^\circ\text{C}$ .

However, XRD studies alone cannot confirm the exact structure of this quaternary nanoparticles, it requires additional characterization. Fig. 2 shows Raman scattering data at various synthesis temperatures.

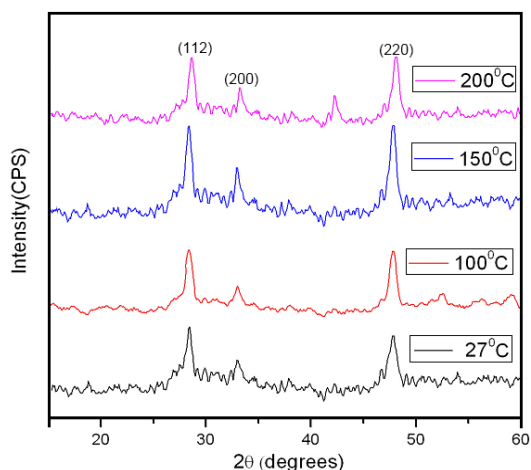


Fig. 1 – X-ray diffraction patterns of the CZTS nanoparticles at various synthesis temperatures

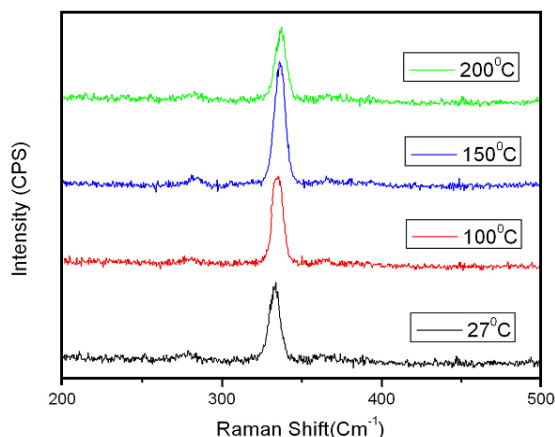


Fig. 2 – Raman scattering spectra of CZTS nanoparticles

The Raman shift at  $334 \text{ cm}^{-1}$  was due to CZTS structure. This peak aggregate with the bulk CZTS peak at  $338 \text{ cm}^{-1}$  [21, 22]. Peak intensity was increased with increasing the synthesis temperature up to  $150^\circ\text{C}$  and decreased further increasing the temperature. From Raman studies we concluded that single phase CZTS nanopowder was observed at a synthesis temperature of  $150^\circ\text{C}$ . The observed reports were similar to XRD results.

#### 3.2 Compositional and Microstructural Studies

Typical elemental composition of the CZTS nanoparticles synthesized at  $150^\circ\text{C}$  is shown in Fig. 3. The CZTS nanopowders synthesized up to the temperature of  $150^\circ\text{C}$  exhibited near stoichiometry. Sulphur deficiency was observed for the samples synthesized at higher temperatures. This might be due to volatile nature of the sulphur.

In order to study the surface morphology of the as grown CZTS nanoparticles, SEM micrographs were taken at all the temperatures (Fig. 4).

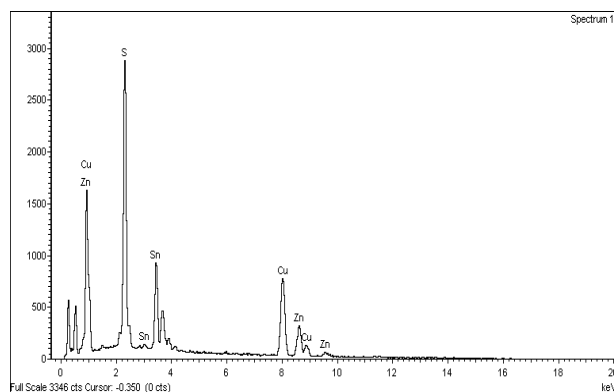


Fig. 3 – EDS spectra of CZTS nanoparticles synthesized at  $150^\circ\text{C}$

From the SEM images, it was noticed that nanoparticles shown distinct grains with round shape and uniformly distributed for the sample with synthesis temperatures of  $100^\circ\text{C}$  and  $150^\circ\text{C}$ . The particle size of the CZTS nanoparticles is about 8 nm. The surface morphology was smeary for the sample with synthesis temperatures below and above of these temperatures.

#### 3.3 Optical Properties

Optical band gap of CZTS nanoparticles were deduced from  $(\alpha h\nu)^2$  vs photon energy, by extrapolating the straight line portion of the graph in the higher absorption region. Where  $\alpha$  and  $h\nu$  are absorption coefficient and photon energy respectively. Fig. 5 shows the band gap of the sample with synthesis temperatures  $27^\circ\text{C}$ ,  $100^\circ\text{C}$ ,  $150^\circ\text{C}$  and  $200^\circ\text{C}$ .

All the nanopowders exhibited direct transitions and the observed band gap varied from 1.6 to 1.35 eV with increasing the synthesis temperature. The band gap of the samples synthesized at temperatures of  $100^\circ\text{C}$  and  $150^\circ\text{C}$  was found to be 1.5 eV and 1.4 eV which are in good agreement with the reported values of CZTS [23]. The change in band gap may be due to variations in the particle size.

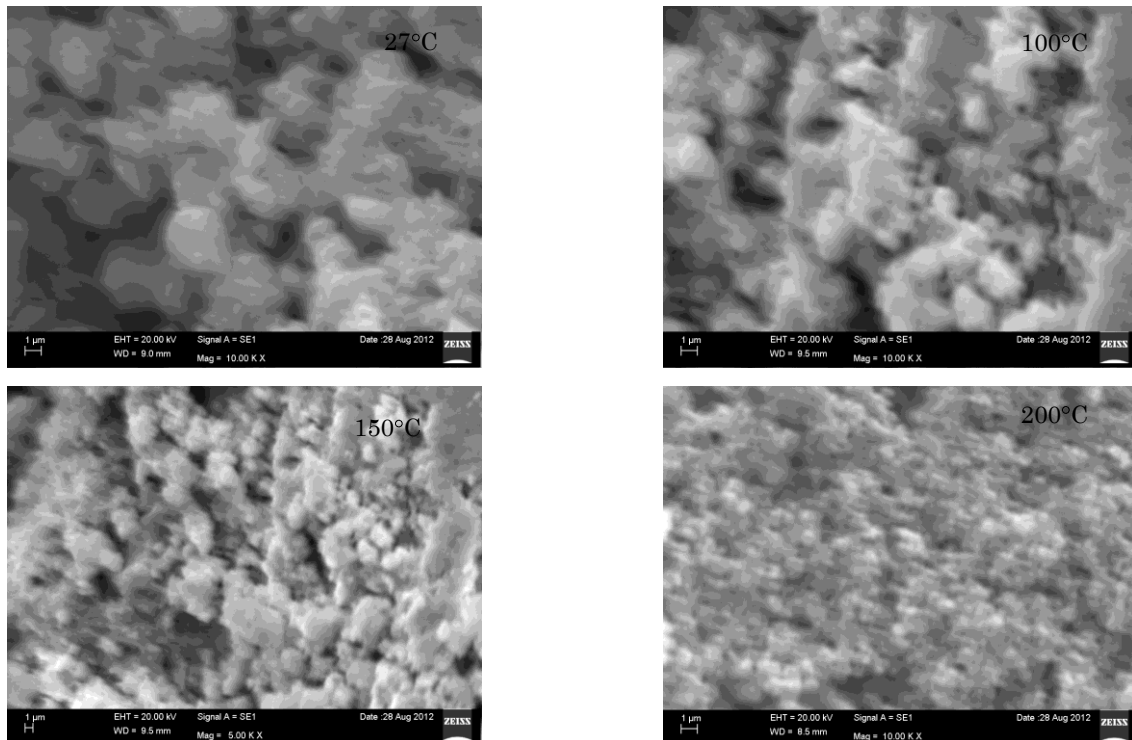


Fig. 4 – SEM images of CZTS nanoparticles at various synthesis temperatures

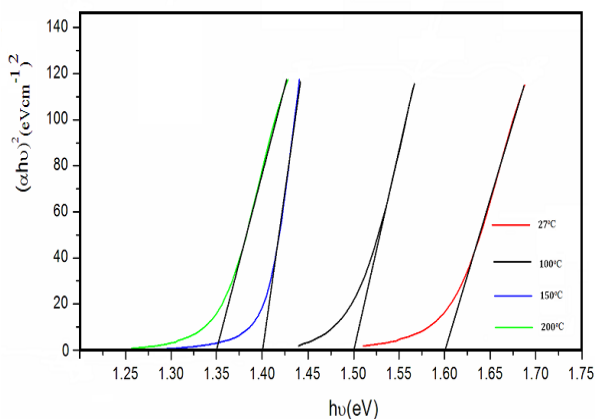


Fig. 5 – The band gap images of the sample with synthesis temperatures 27 °C, 100 °C, 150 °C and 200 °C

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## 4. CONCLUSIONS

CZTS nanoparticles have been successfully synthesized by Chemical co-precipitation method by using purest form of chemicals such as  $(\text{C}_5\text{H}_8\text{O}_2)_2\text{Cu}$ ,  $(\text{C}_5\text{H}_8\text{O}_2)_2\text{SnBr}_2$ ,  $(\text{CH}_3\text{COO})_2\text{Zn} \cdot 2\text{H}_2\text{O}$  and  $\text{H}_2\text{N} \cdot \text{CS} \cdot \text{NH}_2$ . The CZTS nanopowders synthesized at 150 °C exhibited Kesterite structure with near stoichiometry. The particle size varied with varying the synthesis temperature. The direct band gap of the CZTS is 1.4 eV to 1.5 eV. The lattice parameters were found to be  $a = 5.427 \text{ \AA}$  and  $c = 10.848 \text{ \AA}$ . The obtained results were suitable for solar cell applications.

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