

## Effects of Annealing on Structural Properties of Copper Zinc Tin Sulphide (CZTS) Material

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Copper Zinc Tin Sulphide compound was synthesized from its elemental precursors using simple solid state method. Being quaternary material, there is a large probability of formation of secondary phases like SnS, ZnS, CuS during the material growth process and it requires a detail investigation on the effects of synthesis parameters on the composition and structural properties of the CZTS compound. Here we report the study of effects of annealing on the synthesized compound. The annealing was performed at two different temperatures in the presence of Sulphur. The structural and compositional properties of the as-grown and annealed samples were examined by X-ray diffraction (XRD) and Energy Dispersive Analysis of X-Ray (EDAX). The formation of Kesterite CZTS phase was confirmed by Raman Spectroscopy.

**Keywords:** Synthesis, Structural properties, Stoichiometry.

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### 1. INTRODUCTION

Low cost, high efficiency and less environmental pollution have been regarded as the requirements of the next generation thin film solar Photovoltaics (PV). Chalcopyrite semiconductors such as CdTe and Cu-InGaSe<sub>2</sub> (CIGSe) have already been commercialized materials as absorbers in thin film solar cells. The performance of CIGSe based solar cells have also improved remarkably over the past decade with the power conversion efficiency as high as 20.3 % [1]. However, the toxicity of Cadmium as well as steep hikes and fluctuations in the prices of Indium and Gallium have motivated research community to search for an alternative material with low toxicity, low cost and sufficient availability of resources. Copper Zinc Tin Sulphide (CZTS) is one of such promising materials which is formed by replacing Indium and Gallium with Zinc and Tin. CZTS has sparked tremendous research due to its less toxicity and earth-abundant constituents. It is a p-type quaternary compound semiconductor with kesterite crystal structure, high absorption coefficient of the order of  $10^4 \text{ cm}^{-1}$  and direct band gap of about 1.5 eV which makes it one of the most suitable material for low cost thin-film solar PV [2-3].

In 1966, R. Nistche et al. [4] reported synthesis of CZTS material by Iodine vapour transport method. Nearly 2 decades later, in 1988, K. Ito and T. Nakazawa reported the photovoltaic effect in CZTS based hetero diode for the first time [5]. Since then various groups have studied CZTS material with different techniques. These include solvothermal [6], hot injection method [7] and solid state methods [8]. The CZTS has also been investigated extensively as a thin-film absorber material in solar cells using variety of deposition methods based on vacuum and non vacuum techniques such as co-evaporation [9], e-beam evaporation [10], pulsed laser deposition [11], sputtering [12], spray pyrolysis [13], and electrodeposition [14]. However, being quaternary compound, the control over the composition, stoichiometry and consequently the structural and optical properties of the material is very challenging. This is clearly evi-

dent from the vast gap, that exists between the values of Shockley-Queisser efficiency limit for a single junction cell based on CZTS (~ 30 %) and the highest efficiency of CZTS based solar cell achieved so far (10.1 %) [15]. Thus it requires a detail systematic study of the fundamental structural and compositional properties of the material and its dependence on the synthesis parameters in order to narrow-down the gap. Here we report the effects of annealing on the structural and compositional properties of CZTS material synthesized by a simple solid state method.

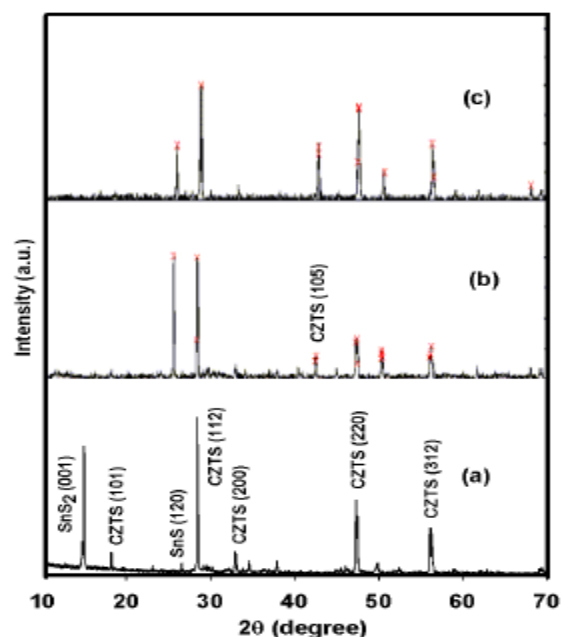
### 2. EXPERIMENTAL

The elemental precursors, Cu:Zn:Sn:S, were weighted in atomic stoichiometric proportion of 2:1:1:4 and sealed in a evacuated quartz ampoule at a base pressure of  $10^{-5}$  mbar. The ampoules were heated in electrical arc furnace from room temperature to 670 K at the rate of 4 K/min and then up to 1030 K at the rate of 2 K/min, where it was kept for 24 hours to ensure homogenous crystallization. It was cooled down up to 670 K at the rate of 4 K/min and then up to room temperature naturally. The solid ingot was then powdered by mechanical grinding. To study the effects of annealing, the synthesized as-grown sample (S1) was then sealed in two different evacuated quartz ampoules with 25 % excess sulphur and sealed with the base pressure of  $10^{-5}$  mbar. One ampoule was then heated to anneal the compound at 1073 K, whereas the other ampoule was heated at 773 K. The annealing was done for one hour at constant temperatures. The heating and cooling was done with the same ramp-up and ramp-down rate as mentioned above. The other two samples, "S2" and "S3", were prepared by mechanical grinding of solid ingots taken out from the ampoules heated at 1073 K and 773 K, respectively.

### 3. RESULTS AND DISCUSSION

The structure of the synthesized powder was studied using X-ray Diffraction (XRD) made by PANalytical

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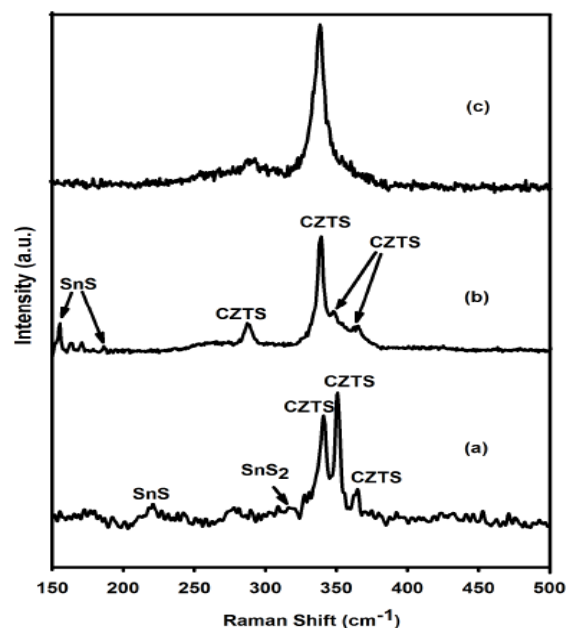


**Fig. 1** – XRD profiles (a) S1 (b) S2 ( sample S1 annealed at 1073 K) (c) S3 (sample S1 annealed at 773 K)

X'pert Pro (Cu K $\alpha$ ). The XRD profiles of CZTS powder samples S1, S2 and S3 are shown in Fig. 1.

Diffractogram of the sample S1 shows sharp peaks at  $2\theta$  values of  $18.3^\circ$ ,  $28.5^\circ$ ,  $32.9^\circ$ ,  $47.4^\circ$  and  $56.1^\circ$ , which are identified as the diffractions from (101), (112), (200), (220) and (312) planes of the CZTS crystal respectively. The diffractions from (112), (220) and (303) planes were observed clearly in all the samples indicating the formation of Kesterite CZTS phase. The lattice parameters calculated for the CZTS samples from XRD analysis come out to be  $a = 5.427 \text{ \AA}$  and  $c = 10.854 \text{ \AA}$ , which are in good agreement with the reported values [16]. However, as discussed earlier, the CZTS is quaternary compound; the presence of secondary phases is always expected in the compound synthesized by solid state method. Here, as seen from Fig. 1, the peaks at  $15^\circ$  and  $26.4^\circ$  indicate the diffraction from (001) plane of SnS<sub>2</sub> [17] and (120) plane of SnS [18], clearly revealing the presence of these secondary phases in the as-grown compound. For sample S2 and S3 diffraction patterns also show peaks at  $43.3^\circ$ , which corresponds to (105) plane of CZTS [16]. The peak from (120) plane of SnS enhances in both the annealed samples, S2 and S3. However, the peaks from CZTS are prominent in both these samples. This indicates that in both annealed samples, the SnS phase co-exists with the dominant CZTS phase.

Apart from SnS, another probable phase which could be present in the samples is  $\beta$ -ZnS. However, the XRD profile of CZTS and that of  $\beta$ -ZnS are identical and the angle differences in the major peaks are within the instrument accuracy. Hence, for the investigation of presence of  $\beta$ -ZnS phase in the sample, Raman Scattering Spectroscopy was performed on samples using JOBIN YVON HR800 with an excitation wavelength of 514.5 nm. Fig. 2 shows the Raman spectra of the samples.



**Fig. 2** – Raman spectra of (a) S1 (b) S2 ( sample S1 annealed at 1073 K) (c) S3 (sample S1 annealed at 773 K).

As shown in Fig. 2, the Raman spectrum of sample S1 also depicts the presence of other binary phases such as SnS and SnS<sub>2</sub>, which are in agreement with the results of XRD [19]. For sample S2 and S3 two major peaks are observed at  $287 \text{ cm}^{-1}$  and  $337 \text{ cm}^{-1}$ . The strongest peak at  $337 \text{ cm}^{-1}$  along with the presence of peak at  $287 \text{ cm}^{-1}$  is attributed to the A<sub>1</sub> symmetry of Kesterite CZTS [20]. The A<sub>1</sub> modes are pure anion modes which correspond to the vibration of sulphur atoms surrounded by motionless neighbouring atoms. A shoulder peak of the main peak at  $349 \text{ cm}^{-1}$  and a broad peak at about  $368 \text{ cm}^{-1}$  were also observed, which is in agreement with the reported results for CZTS [19]. The shoulder peak at  $349 \text{ cm}^{-1}$  and the other peak at  $368 \text{ cm}^{-1}$  are attributed to the Transverse optical (TO) modes and Longitudinal Optical (LO) mode of Kesterite CZTS phase respectively. Absence of peak at  $277 \text{ cm}^{-1}$ , which is a characteristic peak of Stannite phase in CZTS in sample S2 and S3, indicates that the CZTS phase formed in the annealed samples exhibit dominant Kesterite phase [20], which is favourable for its application as an absorber in the solar PV. Thus, the presence of these four peaks i.e.  $287 \text{ cm}^{-1}$ ,  $337 \text{ cm}^{-1}$ ,  $349 \text{ cm}^{-1}$  and  $368 \text{ cm}^{-1}$  in the Raman spectra confirms the formation of Kesterite CZTS phase in the compound. Sharp and strong major peak indicates the good crystalline quality of the compound. More importantly, the absence of strong peak at  $352 \text{ cm}^{-1}$  and  $271 \text{ cm}^{-1}$  denies the presence of  $\beta$ -ZnS phase [8, 19]. The Raman spectra results are in good agreement with the XRD findings for samples S1 and S2. But, for sample S3, no clear peak corresponding to SnS phase is detected in the Raman spectrum. This might be either due to the very small amount of SnS phase in the sample or because of a little inhomogeneity in the compound. Overall, the Raman spectrum eliminates the possibility of presence of  $\beta$ -ZnS phase and confirms the formation of dominant CZTS phase in the sample S3, annealed at temperature 773 K.

The atomic stoichiometry and compositional analysis of the synthesized compounds were performed by Energy Dispersive Analysis of X-Ray (EDAX) using Philips make scanning electron microscope ESEM, XL-30. The atomic stoichiometry of the constituent elements with the ratio of the Zinc to Tin and S to Metals are given in Table 1.

**Table 1** – Chemical composition of CZTS samples

Sample	Cu (%)	Zn (%)	Sn (%)	S (%)	$\frac{[Zn]}{[Sn]}$	$\frac{[S]}{[Cu]+[Zn]+[Sn]}$
S1	28.19	24.54	09.78	37.48	2.50	0.59
S2	26.74	15.83	10.90	46.54	1.45	0.87
S3	29.23	13.42	11.08	46.28	1.21	0.86

All the samples were found to be Zn-rich and Sn-poor, which can be due to the poor incorporation efficiency of Sn as well as the loss of Sn in form of its secondary binary sulphide phase as observed in XRD profiles and raman spectra of the samples. Some of this secondary phase may evaporate out of CZTS at high temperature and get accumulated at cooler surfaces near the end of the ampoule making the samples Sn-poor.

However, it is also to be considered that the Zn-rich material shows better properties as an absorber layer in CZTS based solar cells. The results reveal that sample S1 shows very poor stoichiometry for the CZTS. But, after annealing in presence of Sulphur, better stoichiometry is achieved for both S2 and S3 samples.

Moreover, Sulphur is highly volatile in nature and melting point of Sulphur is very low. So Sulphur-content in sample S1 is very less, as expected. The annealing of the sample in presence of Sulphur created the Sulphur-environment in the ampoule and enhances the Sulphur incorporation, which leads to the improved stoichiometry of the material.

#### 4. CONCLUSION

We have investigated the synthesis of CZTS powder from its constituent elements viz. Copper, Zinc, Tin and Sulphur using simple solid state method. Structural properties of material were studied by XRD, Raman spectroscopy and EDAX. The XRD profiles in tandem with Raman spectra confirms the formation of dominant Kesterite CZTS phase in all the samples. The as-grown sample S1 was found to have secondary phases such as SnS and SnS<sub>2</sub> present in the compound. The material also shows Tin- and Sulphur-deficient stoichiometry. Sample S2 annealed at 1073 K and S3 annealed at 773 K in presence of Sulphur show better stoichiometry as compared to that of as-grown sample. Sample S2, annealed at higher temperature than the growth temperature, indicates dominant CZTS phase along with considerable presence of SnS, whereas sample S3, annealed at lower temperature than the growth temperature, shows significantly strong signature of formation of a good quality CZTS phase.

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