



## Solvothermal Synthesis of Secondary Phase Free Copper Zinc Tin Selenide (CZTSe) Nanoparticles for Thin Film Fabrication

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### ABSTRACT

The current study provides an effective solvothermal synthesis of copper zinc tin selenide (CZTSe) nanoparticles for thin film fabrication. CZTSe nanoparticles were synthesized via a solvothermal route and were allowed to cool at room temperature with different cooling durations ranging from 24 to 96 hours. The results obtained from the X-ray diffraction analysis and Raman spectroscopy revealed that the synthesized CZTSe which are allowed to cool for 72 hours shows the highest quality of sample without any impurities. The results show that the 72 hours is the optimum period to allow proper solution reaction to occur. The morphological properties and chemical components of the CZTSe nanoparticles were equally presented.

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### INTRODUCTION

Copper Zin Tn Selenide (CZTSe) based photovoltaic cell, made of readily available earth-bound materials is one of the semiconductor material examples that factors in safety, affordability and considerable performance efficiency with its core properties. CZTSe made from copper (Cu), zinc (Zn), tin (Sn) and selenium (Se) as its precursor materials, will act as an absorber layer which possesses an absorption coefficient of approximately  $10^4 \text{ cm}^{-1}$ , and a band gap energy of between 1.0 eV – 1.5 eV (Delgado-Sanchez & Lillo-Bravo, 2022), (Hasan & Chowdhury, 2018). These properties place it around the same league as copper indium gallium diselenide (CIGS)-based solar cells, which so far have the highest conversion efficiency of 23.35% (Nakamura et al., 2019).

CZTSe-based solar cells have the advantage of having cheaper and more readily available materials than CIGS. With a recent highest conversion efficiency of 12.6% (Liang et al., 2022), the CZTSe is quite disadvantaged when compared with CIGS in terms of performance efficiency. This relatively low

performance of the CZTSe photovoltaic cell needs urgent optimization and hence improvement during the fabrication process to meet the requirements for commercial manufacturing. Hence, ensuring proper crystallinity, limiting secondary phases such as ZnSe and Cu<sub>2</sub>Se, manipulating the band gap energy, and reducing defects is important to improve the performance of the CZTSe photovoltaic during the fabrication process. CZTSe nanoparticles have been synthesized by several techniques such as microwave-assisted synthesis (Vallejo et al., 2016), solvothermal route (Wu et al., 2016), hot injection method (Engberg et al., 2015), and solvent-thermal reflux technique (Wang et al., 2014).

The formation of multiple secondary phases vastly increases with the increase in number of compounds used in the synthesis of chalcogenide and kesterite nanoparticles (Just et al., 2016). CuSn, ZnSe, Cu<sub>2</sub>Se and SnSe are some of the secondary phases exhibited along with the CZTSe phase after synthesis (Simya et al., 2020). There is always a tendency to form the CuSe phase during the formation of chalcogenide

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and kesterite compounds (Ahmadi et al., 2012; Lee et al., 2013; Zhou et al., 2015). While the presence of certain secondary phases may not be innocuous to the overall performance of kesterite-based photovoltaic cells, it is pertinent that impurity phases are eliminated as they hinder the proper transport of photogenerated electron-hole pair (Zhang et al., 2022). This study presents a facile solvothermal synthesis procedure that results in secondary phase free CZTSe nanoparticles that can be applied for thin film fabrication, focusing on the room temperature cooling duration which eliminates secondary phases.

### EXPERIMENTAL DETAILS

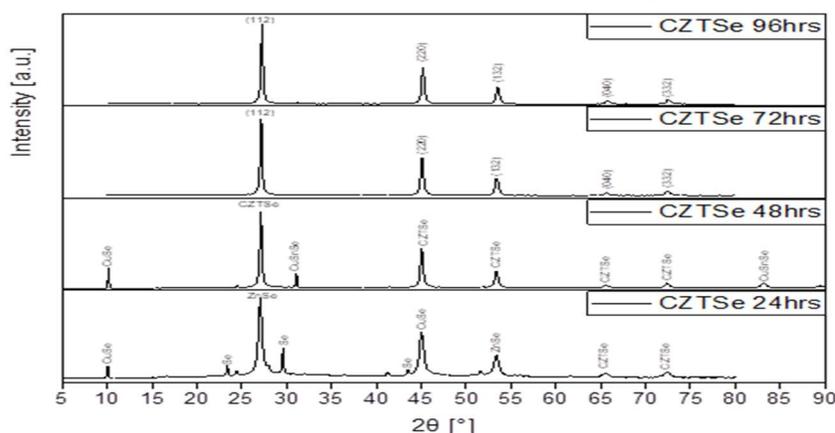
CZTSe powder was synthesized via solvothermal method, following the procedure reported by (Du et al., 2012). All precursors used for the synthesis process are of analytical grade and require no further purification. Specifically, 0.4738 g of Selenium metal powder was added to 30 ml of ethylenediamine to form 0.2 M of solution A. The solution was stirred for 2 hrs to reduce the selenium into selenium ions. Added into solution A, in the following sequence, were 0.1 M of copper chloride dihydrate (0.51 g), 0.05 M of zinc acetate (0.3293 g), 0.05 M of tin chloride pentahydrate (0.528 g), and 0.4 g of CTAB as a catalyst. The new solution was stirred for another 1 hr to obtain a homogenous solution. The solution was poured into the steel autoclave, transferred to a furnace and heated to a temperature of 250 °C for 24 hrs.

The product solution was allowed to cool at room temperature with different time intervals (24 hrs – 96 hrs). The product formed was centrifuged at 3,000 rpm for 10 mins to separate the precipitate from the byproduct. The black precipitate was washed 3 times with deionized water and another 3 times with ethanol and allowed to dry in an oven at 60°C for 12 hrs. The dried black powder was grinded with a mortar to obtain a uniform powder which was stored in a sealed sample bottle for characterization.

The purity and structure of all samples were analyzed and identified with the Philips X'Pert pro Panalytical PW3040 MPD X-Ray Diffractometer, Raman Spectroscopy (WITec Alpha 300R) to confirm the sample purity. Morphological characterization of all samples was determined by Field Emission Scanning Electron Microscopy (FESEM) with the Zeiss GeminiSEM 500. Energy Dispersive Spectrometer (EDS) (Oxford Instrument X-Max 80) was equipped with the FESEM to measure the elemental composition of the samples. Finally, the Anton Paar Litesizer 500 to measure sample Zeta potential and particle size.

### RESULTS AND DISCUSSION

The XRD patterns for the powdered CZTSe samples allowed to cool at different hours, ranging from 24 hrs to 96 hrs presented in Figure 1. Secondary peaks were gradually eliminated as the duration of cooling at room temperature increased indicating purer CZTSe nanoparticles.



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Figure 1: XRD patterns of synthesized CZTSe cooled for different durations respectively

All XRD patterns of the samples showed peaks corresponding to CZTSe with ICSD reference code 98 – 006 – 7242 as their primary peaks, however, samples cooled for 24 to 48 hrs all indicated secondary (impurity) peaks that are from one form of secondary phase or the other. CZTSe sample cooled for 24 hrs showed impurity peaks at  $2\theta = 9.695^\circ$  and  $42.738^\circ$  corresponding to CuSe,  $27.025^\circ$  and  $53.280^\circ$  corresponding to ZnSe, and  $23.387^\circ$ ,  $29.564^\circ$ , and  $41.194^\circ$  corresponding to CuSnSe. The patterns of CZTSe cooled for 48 hrs indicated minor peaks at  $2\theta = 9.695^\circ$  and  $31.279^\circ$ , all consistent with structures of CuSe and CuSnSe respectively.

The XRD patterns for the CZTSe sample allowed to cool for 72 hrs indicated that the sharp diffraction peaks are located at  $27.156^\circ$ ,  $45.076^\circ$ ,  $53.392^\circ$ ,  $65.701^\circ$  and  $72.367^\circ$   $2\theta$ , corresponding to (112), (220), (132), (040) and (332) respectively, with no other noticeable minor peaks, which are consistent with that of the kesterite tetragonal structure of the CZTSe (ICSD reference code 98 – 006 – 7242) and lattice constants  $a = 5.6880 \text{ \AA}$  and  $c = 11.3380 \text{ \AA}$ . These

peaks are similar to those reported by Matsushita et al. (2000), K. Liu et al. (2014) and Wu et al. (2016) equally and the lattice parameters are in agreement with Olekseyuk et al. (2002). Further allowing the sample to cool for 96 hrs did not present any significant difference with the sample allowed to cool for 72 hrs, indicating that 72 hrs is sufficient for the CZTSe compound to be fully formed in the reaction. It is clear that solvothermally synthesized samples need adequate room temperature cooling time to allow the complete reaction of the compounds to manifest.

XRD patterns alone are not sufficient enough to determine the phase purity of the CZTSe compound, as the crystal structure and often the lattice constants have certain similarities with compounds such as CuSe, CuSnSe etc. Hence, Raman spectroscopy was carried out to confirm the purity of the CZTSe sample cooled for 72 hrs. The Raman shift of the CZTSe powder was performed at an excitation wavelength of 633.073 nm as presented in Figure 2.

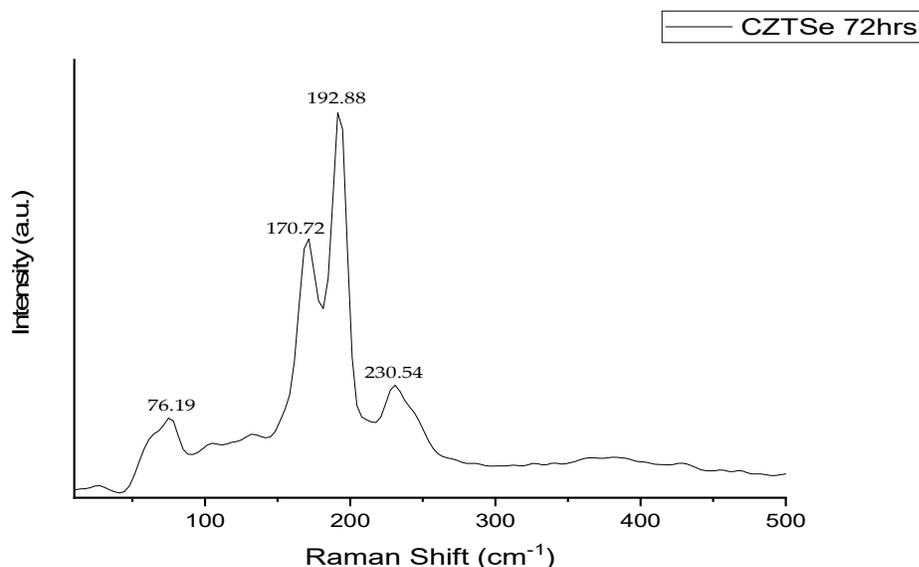


Figure 2: Raman spectra of the CZTSe powder cooling at 72 hrs

As can be seen from Figure 2, the Raman shift of the CZTSe powder reveals a

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composition of 4 modes, two main peak modes at  $170.72\text{ cm}^{-1}$ , and  $192.88\text{ cm}^{-1}$ , which are of A symmetry, and two weaker modes at  $76.19\text{ cm}^{-1}$  and  $230.54\text{ cm}^{-1}$ . These values are roughly consistent with results obtained experimentally by Djemour et al. (2013) and Chandel et al. (2018),

hence confirming the formation of pure CZTSe nanoparticles. The composition of elements and their weight percentage for the CZTSe sample cooled for 72 hrs is shown by the EDS spectra in Figure 3.

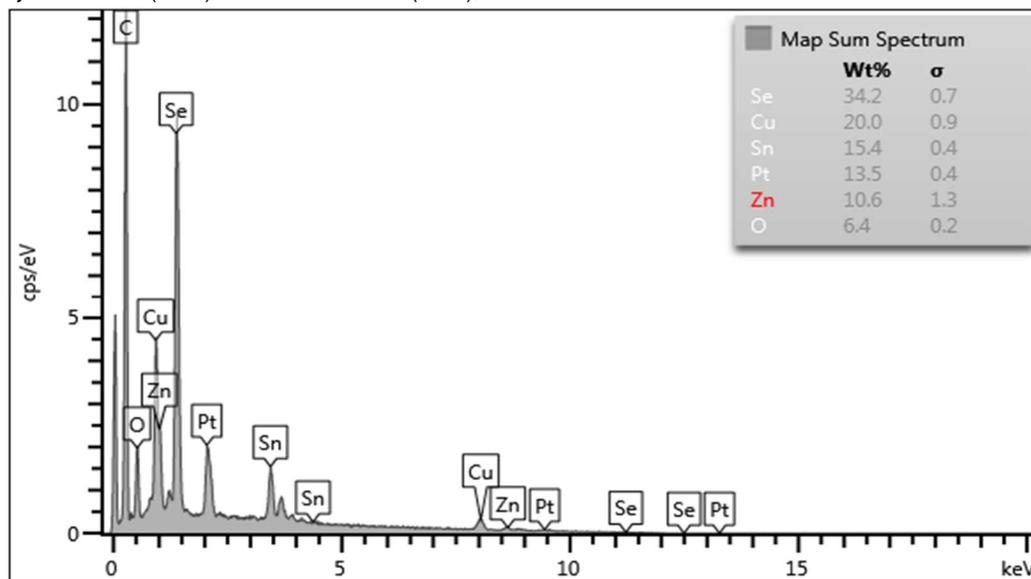


Figure 3: The EDX spectrum of the CZTSe powder cooled for 72 hrs.

Figure 3 shows the weight percentage of all the elements found during the EDS analysis. It can be seen that Se, Cu, Sn, Pt, Zn, and O each with weights 34.2%, 20.0%, 15.4%, 13.5%, 10.6% and 6.4% are the compounds traced in the CZTSe cooled at 72 hrs. However, the Pt displayed in the results is from the coatings made before placing

samples in the chamber to avoid charging effects in imaging. Moreover, it is the atomic weight percentage that is used to obtain the stoichiometric ratio of the compound is presented in Table 1.

Table 1: The atomic weight percentage of the CZTSe powder cooled at 72 hrs.

Element	At % Composition	$\frac{[Cu]}{[Zn] + [Sn]}$	$\frac{[Zn]}{[Sn]}$
Cu	30.27%		
Zn	15.59%	1.08	1.25
Sn	12.48%		
Se	41.66%		

Table 1 shows the atomic weight percentage of the synthesized CZTSe sample cooled at 72 hrs, and the values of the  $\frac{[Cu]}{[Zn] + [Sn]}$

and  $\frac{[Zn]}{[Sn]}$  compositional ratio. The above results show that the sample has a stoichiometric ratio (Cu: Zn:Sn:Se) of 2:1.03:0.83:2.75. This seems to be away from the initial elemental composition

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ratio of  $\text{Cu}_2\text{ZnSnSe}_4$  (2:1:1:4) that was used for the synthesis, with a visible reduction in the Se ratio. The morphology of the CZTSe powder

cooled for 72 hrs is presented in the FESEM images as shown in Figure 4.

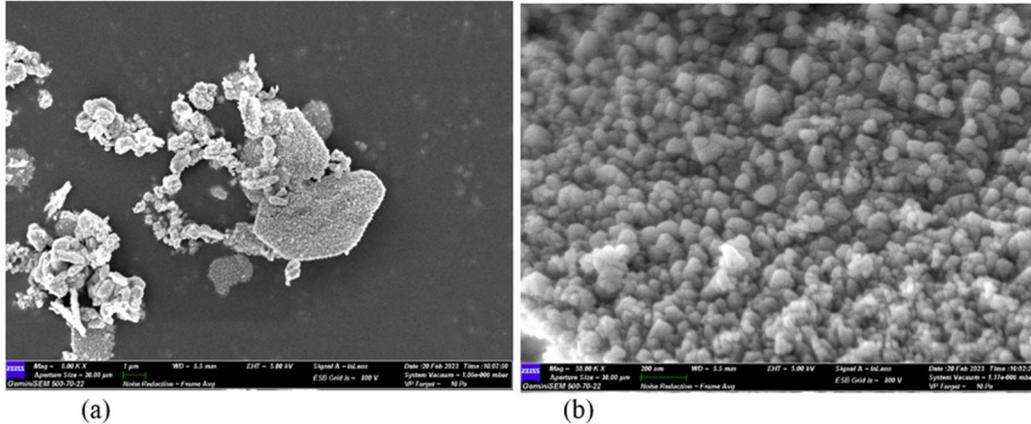


Figure 4: FESEM images of the CZTSe cooled for 72 hrs at (a) 5.0 KX magnification (b) 50.0 KX magnification.

In Figure 4 (a), it can be seen that the CZTSe powder is made up of mainly irregular hexagonal-shaped flakes. At higher magnification as shown in 4 (b) reveals that the CZTSe is made of many small-sized irregular hexagonal-shaped particles (nanocrystals). These images are in

close agreement with Du, Zhou, et al. (2012) and Liu et al. (2014).

The zeta potential and particle size of the CZTSe powder cooled for 72 hrs are shown in the Figure 5.

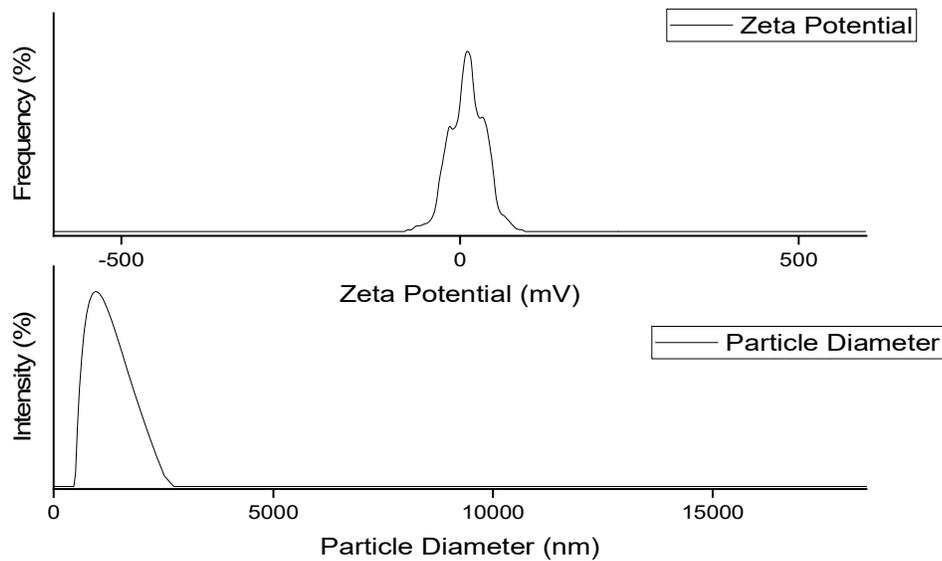


Figure 5: The Zeta potential (top) and Particle size (bottom) of the CZTSe powder cooled at 72 hrs.



The mean zeta potential of the CZTSe as presented in Figure 5 is  $-5.25$  mV. This value indicates that the synthesized CZTSe powder cooled for 72 hrs is unstable and highly susceptible to flocculation (Raja & Barron, 2022). This means that the powder is not suitable to be used as a colloid, hence thermal evaporation will be the better technical for deposition on thin film. The negative polarity of the value indicates that the CZTSe powder has possible traces of  $\text{Se}^{2-}$  ions on its surface (Nag et al., 2011). The average hydrodynamic diameter of the CZTSe powder cooled for 72 hrs is 915 nm, indicating that the particles are in the nano range.

## CONCLUSION

CZTSe nanoparticles free of secondary phases were successfully synthesized via solvothermal route. The XRD, Raman, EDS, FESEM and Zeta potential results confirmed their structure, purity, chemical composition, morphology and stability respectively. To investigate the influence of cooling duration at room temperature, the synthesized nanoparticles were allowed to cool at room temperature for a duration of 24 to 96 hours. It was revealed that to prepare CZTSe nanoparticles that are free from secondary phases, the synthesized solution should be allowed to cool for at least 72 hours at room temperature. Raman shifts of the CZTSe nanoparticles allowed to cool for 72 hours proved the nanoparticles contained only kesterite phase of CZTSe. The stoichiometry of the CZTSe nanoparticles cooled at 72 hrs showed a Se poor composition, and zeta potential revealed the nanoparticles will not be suitable for colloidal use.

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