

## Cu<sub>2</sub>ZnSnS<sub>4</sub> Agglomeration Nanoparticles Study by TEM

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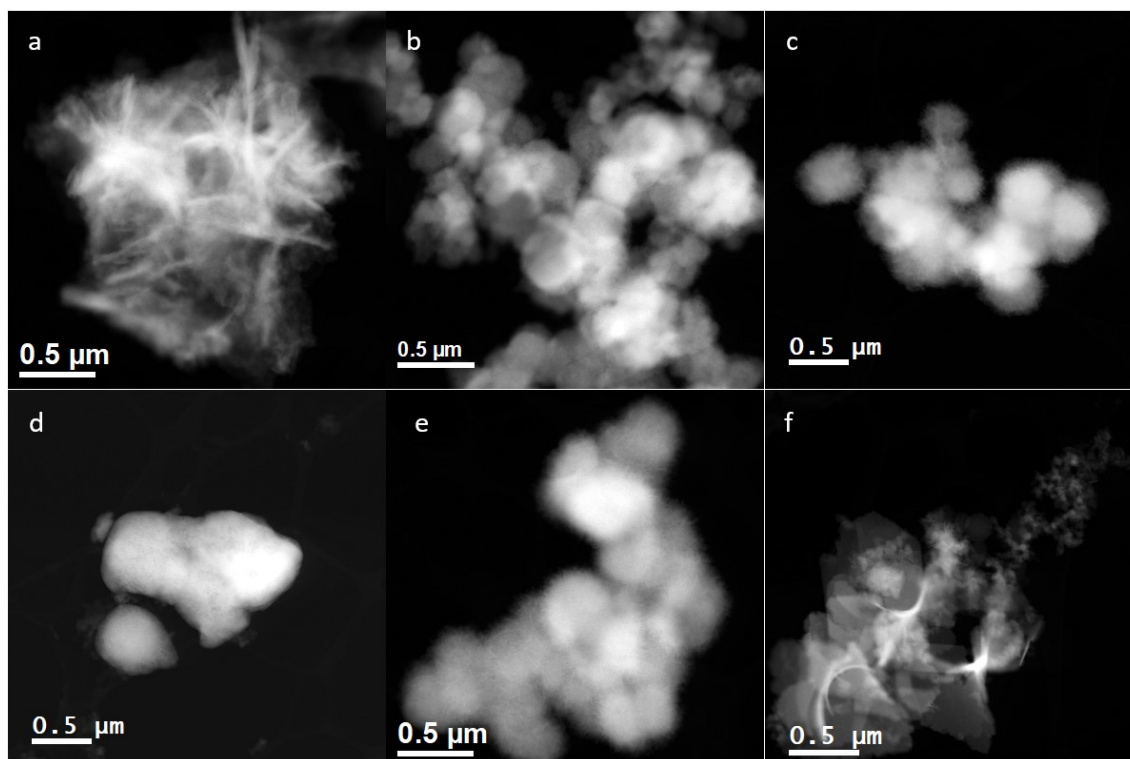
The study of the microstructure and morphology of materials is very important, due to the properties linked to them. The photoelectric properties of semiconductors depend on the morphology of the synthesized material [1]. There are different methods of synthesis and conditions; one of the simplest and fastest ways to obtaining the semiconductor with a high purity is through the hydrothermal method assisted by microwaves [2]. In this work, the influence of polyvinylpyrrolidone (PVP) on the synthesis of (Cu<sub>2</sub>ZnSnS<sub>4</sub>) CZTS nanoparticles is studied by TEM and XRD.

The synthesis of CZTS nanoparticles was carried out in the following way: different quantities PVP (1.28, 0.64, 0.32, 0.16, 0.04 g) were dissolved in 80 mL of HOCH<sub>2</sub>CH<sub>2</sub>OH, then the following reagents starting with 0.137 g of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 0.270 g of CuSO<sub>4</sub>, 0.276 g of SnCl<sub>2</sub>·2H<sub>2</sub>O and 0.383 g of CH<sub>4</sub>N<sub>2</sub>S were added into it, this solution was maintained at 70 °C for 30 min with constant stirring. Then the solution was heated at 200°C by microwave reactor MicrowavePro Anton Paar, with ramp rate 15 °C/min for 1 hour. The different sizes of the agglomerations in the materials are the result of the variation in weight of the PVP in the synthesis process. The materials were characterized by XRD, TGA, RAMAN, SEM and HRTEM techniques. Materials name are related according to the PVP quantity content CZTSP1.28, CZTSP0.64, CZTSP0.32, CZTSP0.16 and CZTSP0.04.

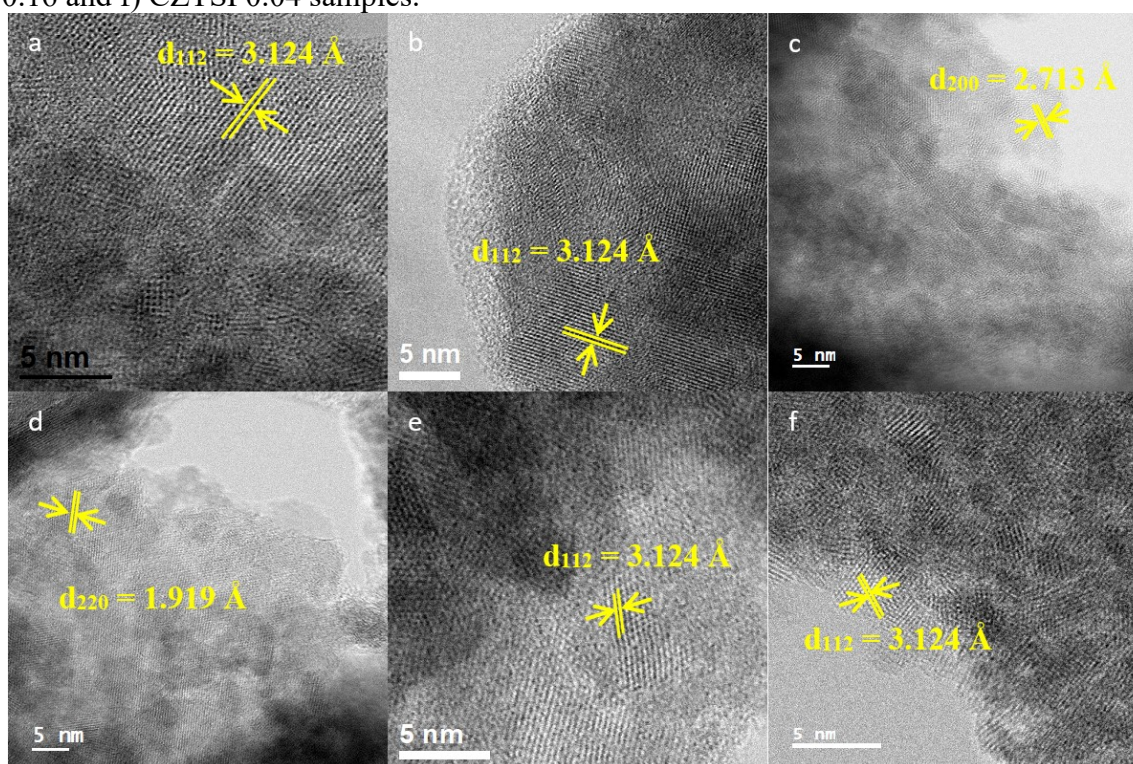
Three characteristic peaks of the CZTS corresponding to (112), (220) and (312) planes which were identified by XRD (not showed). The morphology and microstructure variation of particles were studied by TEM and STEM mode techniques. Figure 1a shows the agglomeration size of about 1650 nm for CZTS material without PVP, the materials synthesized in the presence of PVP appeared as spherical agglomerates with average sizes of 350, 450, 550, 560 and 210 nm for CZTSP1.28, CZTSP0.64, CZTSP0.32, CZTSP0.16 and CZTSP0.04, respectively (other figures). Each agglomerate content crystalline nanoparticles with average diameter of ~5 nm, as seen in the HRTEM images (Fig. 2). These images show the corresponding d-spaces corroborate by JCPDS card. This study was carried out to understand the behavior of the agglomerate in the synthesized materials when introducing different quantities of PVP in the synthesis process. Small agglomeration was obtained by lowest content of PVP.

### References:

- [1] K Tanaka et al., *Solar Energy Materials & Solar Cells* **95** (2011), p. 838.
- [2] R Saravana Kumar et al., *Materials Letters* **65** (2012), p. 174.



**Figure 1.** HAADF micrographs for a) CZTS, b) CZTSP1.28, c) CZTSP0.64, d) CZTSP0.32, e) CZTSP0.16 and f) CZTSP0.04 samples.



**Figure 2.** High resolution TEM micrographs for a) CZTS, b) CZTSP1.28, c) CZTSP0.64, d) CZTSP0.32, e) CZTSP0.16 and f) CZTSP0.04 samples.