

Solution Synthesis and Aerosol Deposition of $\text{Cu}_2\text{ZnSnS}_4$ Nanoparticles

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Introduction:

Copper zinc tin sulfide (CZTS) is being studied as an absorber material for thin film solar cells and as an alternative to copper indium gallium selenide (CIGS), which is expensive to produce because it contains the rare element indium. CZTS is an ideal absorber material due to its optimal band gap (1.5 eV), high absorption coefficient ($> 10^4 \text{ cm}^{-1}$), abundant/cheap materials, nontoxicity, and adaptability to various growth techniques [1].

Aerosol deposition (AD) is a type of powder spraying utilizing nanoparticles and is a cheap alternative deposition method to those requiring vacuum. Upon impact with the substrate, the nanoparticles' kinetic energy converts into thermal energy and a rise in temperature at the impact point promotes particle-particle/particle-substrate bonding to produce a dense film. Advantages of AD include high deposition rate, high density resultant films, low process temperature, scalability for mass production, and low cost equipment [2].

From this background, this work aims to synthesize CZTS nanoparticles via solution method appropriate for thin film AD. Advantages of solution synthesis include non-vacuum, single-step processing, utilization of inexpensive equipment/precursors, and scalability for mass production.

Experimental Procedure:

Solution Synthesis. CZTS powder was synthesized by a solution deposition process. Precursor powders, according to reaction $2\text{Cu(s)} + \text{Zn(s)} + \text{Sn(s)} + 4\text{S(s)} \rightarrow \text{Cu}_2\text{ZnSnS}_4$, were put into a reaction vessel with tetraethylene glycol (TetraEG) as a solvent. The precursors reacted at the solvent boiling temperature (317°C). This process was optimized by varying precursor chemicals, precursor/solution ratio, and reaction time (Table 1). Some samples were prepared using copper, tin, or zinc chloride salts instead of metallic precursors.

Two amounts of solvent (200/100 mL) were examined for effect of solubility and synthesis varied between 19–48 hours to determine sufficient reaction time. In a second variation, nanoparticles were grown onto a copper sheet, also serving as a source of copper for the reaction. Post-synthesis, the nanoparticles were centrifuged to separate from the solvent.

Characterization. Crystalline phases in the synthesized powders were identified by x-ray powder diffraction (XRD). Phase identification was done by referring to literature reporting XRD pattern of CZTS (kesterite-type structure) [3] and ICDD files. Chemical composition of synthesized powder was analyzed by means of energy dispersive x-ray (EDX) analysis. Particle size distribution in the resultant powder was determined by laser scattering.

Results and Conclusions:

X-Ray Diffraction. The crystal structure and XRD patterns for many of the residual phases and CZTS were very similar, so exact phase identification based solely on XRD was difficult. The possibilities were narrowed down to a few probable phases based on the best match between reference ICDD files and experimental peaks (Table 1).

The XRD pattern of sample 100715 corresponded most closely to kesterite and was also most similar to that of kesterite reported in literature (Figure 1). XRD peaks labeled 'Mo' in the reference pattern were from a molybdenum substrate used in the reference, which are absent in our results because we used glass as a substrate. CZTS phase was also produced in synthesis 100726 and 100802, though

Sample	Time [hours]	Cu source	S Source	Zn source	Sn Source	TEG [mL]	XRD	
							Main Phase	Possible 2nd Phases
100629	19	Cu powder	S powder	Zn powder	Sn powder	200	CuS, CuxSy, Sn, Zn	
100706	20	Cu powder	S powder	Zn powder	Sn powder	200	CuS, Zn, Sn	CuxSy
100715	24	CuCl	S powder	Zn powder	Sn powder	200	CZTS	CuxSy, ZnS, Cu3SnS4
100726	24	CuCl	S powder	Zn powder	Sn powder	100	ZnS, CZTS	CuxSy, ZnS, Cu3SnS4
100802	48	CuCl	S powder	Zn powder x 2	Sn powder	200	ZnS, CZTS	Cu3SnS4, CuxSy
100818	24	Cu sheet & CuCl	S powder	Zn powder	Sn powder	200	CuxSy, ZnS	
100823	24	Cu sheet	S powder	ZnCl2	SnCl2	200	ZnS	
100824	24	Cu powder	S powder	ZnCl2	SnCl2	200	Cu3SnS4	CZTS, ZnS

Table 1: Summary of conditions for CZTS nanoparticle solution synthesis.

the amount of residual phase was much higher than in 100715. These results indicated a tendency for syntheses with CuCl instead of metallic Cu to form CZTS.

Chemical Composition. Results of EDX analyses (Figure 2) indicate that sample 100715 had the composition closest to ideal CZTS, consistent with results that sample 100715 is almost pure CZTS from XRD. Formation of CZTS was confirmed by XRD in synthesis 100726 and 100802, and consequently, compositions of those samples were also closer to ideal. Thus, it is clearly indicated that usage of CuCl as precursor enhanced formation of CZTS. Comparison of three samples prepared using CuCl also indicated that the amount of solvent is a crucial parameter for successful synthesis of CZTS. Chemical composition of 100726 deviated from the ideal composition, although the precursor composition was the same as that used in 100715.

Grain Size Distribution. Grain size distribution had three maximums. Peak 1 (0.7 nm) corresponded to an unknown source. Peak 2 (100-400 nm) corresponded to grain size, while peak 3 (~5 μm) corresponded to agglomerated grain size. Looking at synthesis 100715 where almost pure CZTS was obtained, grain size was 200 nm, a little smaller than the ideal size of 500 nm for AD. However, agglomerated size of 100715 was 5.7 μm which indicates that obtained grains were composed of primary particles.

Summary:

Based on XRD, EDX, and laser scattering, sample 100715 was the most successful synthesis, producing nanoparticles of the kesterite phase of CZTS with near stoichiometric composition and approaching ideal particle size. The combination of CuCl, Zn, Sn, and S powders appears to be the most promising precursors for producing kesterite nanoparticles. Increased synthesis time may enlarge grain size.

Future Work:

We hope to improve phase purity of CZTS by further optimization of precursor composition, solvent/precursor fraction, and particle size distribution by increasing primary grain size and dispersing grains to prevent agglomerations. We would also like to perform photoelectrical characterization to determine valence band structure and Fermi level with XPS, band gap with optical absorption, and concentration of carriers and mobility with Hall measurements.

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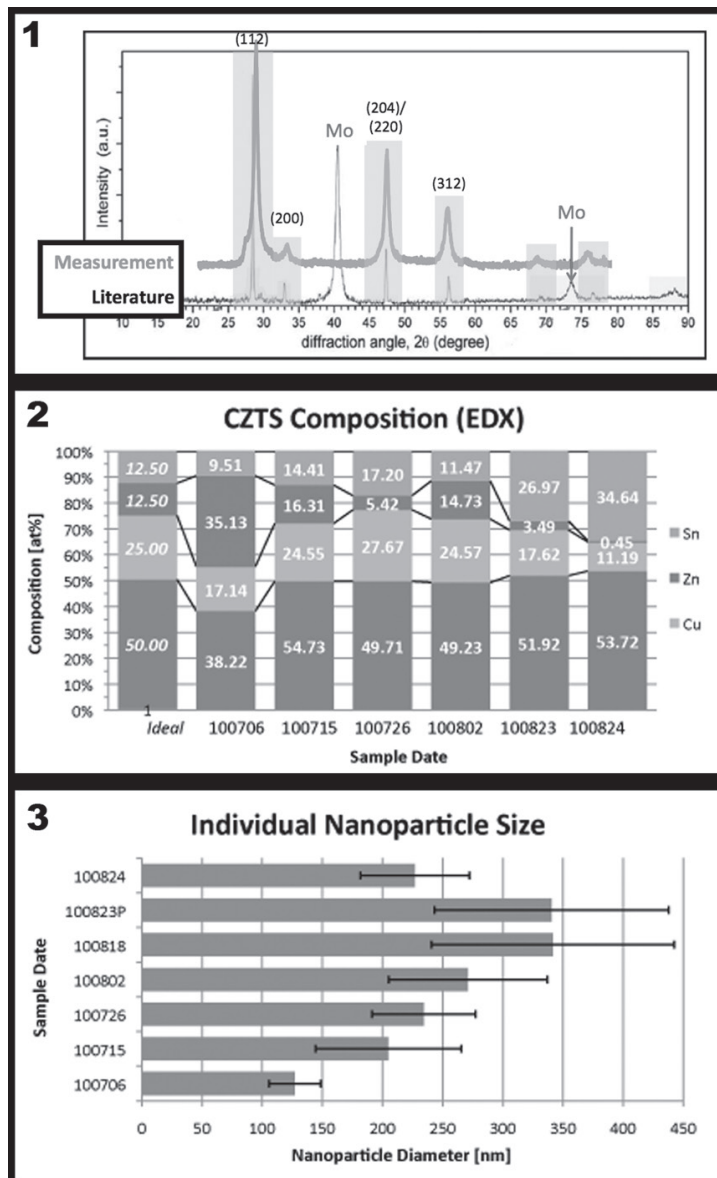


Figure 1: XRD spectra of sample 100715 compared to literature spectra for kesterite phase of CZTS [1].

Figure 2: Composition of syntheses from energy dispersive x-ray (EDX).

Figure 3: Size of primary grains of CZTS.

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References:

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