Supporting Information Controlling Cu₂ZnSnS₄ (CZTS) phase in microwave solvothermal synthesis

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Rietveld refinement procedure

All the Rietveld refinement was performed using the software XPert HighScore Plus. The wurtzite structure (space group $P6_3mc$, #186) was simulated using a = 0.38353 nm, b = 0.38353 nm, c = 0.63008 nm, α = 90°, β = 90°, γ = 120°. Wyckoff positions of the Cu, Zn, Sn, and S used in the simulations are given in Table S1.

Table S1. Wyckoff position of the Cu, Zn, Sn, and S used to simulate wurtzite CZTS, space group P6₃mc (#186).

Element	Wyckoff Position	x	У	Z	sof	Biso
Cu	2b	1/3	2/3	0	0.333	0.500
Zn	2b	1/3	2/3	0	0.333	0.500
Sn	2b	1/3	2/3	0	0.333	0.500
S	2b	1/3	2/3	0.375	1	0.500

The kesterite structure was simulated according to the cif file Cu_2ZnSnS_4 ICSD 262388 from the Inorganic Crystal Structure Database (ICSD). Starting with this information the kesterite and wurtzite crystalline structures were refined using, the following steps in this order:

- 1) Scale Factors for kesterite and wurtzite structures were refined at the same time.
- 2) The 4 first background parameters were refined.
- 3) Zero Shift was refined.
- 4) The a and b lattice parameters for one phase were refined, followed by the refinement of a and b lattice parameters for the other phase.
- 5) The c lattice parameter for one phase was refined, followed by the c lattice parameter for the other phase.
- 6) After refining all lattice parameters (a, b, c) for both phases, the lattice parameters (a, b, c) for both phases were kept constant, while profile parameter U was refined first for one of the phases followed by the other phase.
- 7) The parameter peak shape 1 for one phase was refined followed by the other phase. The profile parameter U and peak shape 1 are the parameters related to the peak width.

The fraction (percentage) of wurtzite, and kesterite phases and the Goodness of Fit (GoF) for each refinement are shown in Table S2. The values presented in Table S2 were used to produce Figure 1b of the main text. Three results for each nanocrystal product were calculated and averaged and their standard deviation calculated, producing the error bars shown in Figure 1 b.

Fraction of wurtzite and kesterite phases in the product synthesized at 160 °C using various S:M ratios

S:M	Wurtzite (%)	Kesterite (%)	GoF
	64.4	35.6	2.82
1.9	44.4	55.6	2.27
	74.2	25.8	2.09
	64.0	36.0	1.83
	50.3	49.7	2.44
Average	59.5	40.5	
Std Dev	10.7	10.7	
	52.8	47.2	4.29
2.7	34.9	65.1	2.60
	63.8	36.2	2.81
	48.0	52.0	1.89
	48.0	52.0	1.89
Average	49.5	50.5	
Std Dev	9.3	9.3	
	49.5	50.5	4 67
3.2	62.7	37.3	2.87
0.2	33.7	66 3	2.67
	49.3	50.7	4.61
	49.5	50.2	3 92
	49.0	51.0	5.52
Std Dev	9.2	9.2	
Stuber	47.0	53.0	1 77
3.6	62.3	37.7	3.02
5.0	35 5	64.5	2.02
	3/1 1	65.9	1.62
	32.5	67.5	1.02
	12.3	57.7	1.52
Std Dev	11.2	11.2	
Stubev	11.2	 	2 40
45	25 5	64 5	2.49
4.5	33.5 25.2	74.9	1.96
	25.2	74.8	1.00
	25	75	2.10
Average	21.5	76.7	1.65
Std Dov	23.7	70.5	
Stu Dev	12.0	26.2	4.22
5.2	13.0 12 /	00.Z 0C.C	4.23
5.5	13.4	80.0	4.21
	39.5	60.5	0.93
	22.0	77.4	2.94
A	20.4	79.6	2.37
Average	21.9	/8.1	
Std Dev	9.5	9.5	
6.2	24.5	/5.5	1.74
6.2	13.5	86.5	3.41
	28.7	71.3	2.51
	15.4	84.6	1.81
	26.2	73.8	1.74
Average	21.7	78.3	
Std Dev	6.0	6.0	

Table S2. Fractions (in %) of wurtzite and kesterite phases and Goodness of Fit (GoF) for five trials of the product synthesized at 160 °C using various S:M ratios Cu(II)_Sn(II)_Tu_S:M_160 °C.

Crystallite size estimate using the Scherrer equation for Cu(II)_Sn(II)_Tu_S:M_160 °C

Table S3. Crystallite size estimates for Cu(II)_Sn(II)_Tu_S:M_160 °C. Sizes were calculated using the Scherrer equation, a shape factor of 0.9 and the peak at $2\theta \approx 32^\circ$, (112) of the wurtzite and the (002) of the kesterite phases. Deviation from a spherical shape and differences in the shapes of kesterite and wurtzite nanocrystals in multiphase mixtures may change these estimates slightly.

S:M	Size (nm)
1.9	6.4
2.7	5.0
3.2	4.1
3.6	4.4
4.5	4.3
5.3	3.7
6.2	3.7

TEM Images of Cu(II)_Sn(II)_Tu_1.9_160 °C nanocrystals



Figure S1. (a) TEM image (same as Figure 3a) of Cu(II)_Sn(II)_Tu_1.9_160 °C nanocrystals with boxes around the oblate nanocrystals. (b) Higher magnification TEM images from another region of the same sample, where the oblate nanocrystals can be seen more clearly.

STEM-HAADF elemental mapping of the Cu(II)_Sn(II)_Tu_1.9_160 °C and Cu(II)_Sn(II)_Tu_6.2_160 °C samples



Elemental Composition of Cu(N)_Sn(L)_Tu_S:M_160 °C

Table S4. Elemental composition determined from SEM-EDS for nanocrystal products synthesized using Cu and Sn precursors with different oxidation states and S:M ratios, i.e., $Cu(N)_Sn(L)_Tu_S:M$, for N= I or II, L= II or IV, and S:M = 1.9 or 6.2. All nanocrystals were synthesized at 160 °C. Compositions are given with respect to S, where the sulfur EDS intensity was normalized to 4.

Sample	Cu	Zn	Sn	S
Cu(I)_Sn(II)_1.9_Tu_160 °C	2.7	1.4	1.0	4.0
Cu(I)_Sn(II)_6.2_Tu_160 °C	1.6	0.8	0.9	4.0
Cu(II)_Sn(II)_1.9_Tu_160 °C	2.6	1.2	1.0	4.0
Cu(II)_Sn(II)_6.2_Tu_160 °C	2.3	1.1	1.1	4.0
Cu(I)_Sn(IV)_1.9_Tu_160 °C	3.2	0.4	1.0	4.0
Cu(l)_Sn(lV)_6.2_Tu_160 °C	2.0	1.1	1.1	4.0
Cu(II)_Sn(IV)_1.9_Tu_160 °C	2.8	1.1	0.9	4.0
Cu(II)_Sn(IV)_6.2_Tu_160 °C	2.4	1.2	1.1	4.0

Microwave Synthesis of CZTS using other excess sulfur sources

To verify if the presence of thiourea is necessary to form phase pure CZTS, we performed experiments without using thiourea. Instead, we used either L-cysteine or thioglycolic acid as the only source of sulfur, varying the tin oxidation state and fixing the S:M ratio equal to 1.9 with the final temperature 160 °C. The XRD patterns of these samples are presented on Figure S4. Figure S4 shows that CZTS could not be detected in any of the products, regardless of the tin oxidation state or the sulfur source. These results reveal that thiourea is necessary.



Infrared Spectroscopy of the Samples Cu(II)_Sn(II)_Tu_S:M_160 °C

Since the wurtzite to kesterite product ratio depends on S:M ratio, we considered the possibility that the S:M ratio might affect the surface chemistry of the product and hence also the product phases. The adsorption of surfactant molecules could serve to alter the relative surface energy of different facets, which could result in the formation of a metastable phase. Accordingly, we collected and examined infrared (IR) spectra from nanocrystals synthesized using different S:M ratios to determine if these nanocrystals exhibited differences in ligands that cap their surfaces. These IR spectra showed that the surface of the nanocrystals were capped with ethylene glycol regardless of the S:M ratio used in the synthesis. For example, Figure S3 shows the IR spectra of nanocrystals synthesized using two different S:M ratios (Cu(II)_Sn(II)_Tu_S:M_160 °C, where S:M=1.9 or 6.2) before they were washed with ethanol

and dried. Infrared spectra of ethylene glycol and thiourea are also shown for comparison. The IR spectra of nanocrystals Cu(II)_Sn(II)_Tu_S:M_160 °C with S:M equal to 1.9 and 6.2 show bands at 882, 1033, 1086, and 3329 cm⁻¹. The first band is assigned to stretching of C-C-O groups, the next two to stretching of C-O groups, and the last one to the stretching of O-H groups in ethylene glycol, respectively. The sharp and intense band at 1601 cm⁻¹ present in thiourea spectra, which is characteristic of in-plane deformation of N-H group, is absent in both Cu(II)_Sn(II)_Tu_S:M_160 °C spectra. These observations are consistent with the presence only of ethylene glycol on the nanoparticle surface.

Since there is no obvious difference in the surface ligands when S:M=1.9, and S:M=6.2 we also rule out the possibility that the wurtzite stabilization is due to changes in the surface energies of different crystal facets under these two synthesis conditions. This leaves the possibility that the preferential synthesis of one phase over another may be related to the differences in their formation mechanism at different S:M ratios.



Effect of S:M ratio and Sn oxidation state, and excess sulfur source on phase composition

Figure 5 of the main text shows the XRD patterns of the CZTS samples prepared from Cu(II), different S:M ratios, different tin oxidation states (Sn(II) or Sn(IV)), and different excess sulfur excess sources, such as thiourea, L-cysteine, thioglycolic acid and 3-mercaptopropionic acid. In order to complement the data presented in Figure 5, Table S5 presents the quantitative phase percentages estimated by Rietveld Refinement. Table S5 confirms the trend that when the sulfur excess is provided by a molecule without an NH₂ group wurtzite is formed as the major phase, regardless of the S:M ratio and tin oxidation state. On the other hand, when the sulfur excess source contains an NH₂ group, mostly wurtzite is formed when tin has the oxidation state +2 and mostly kesterite formed when tin has the oxidation state +4, regardless of the S:M ratio.

Sample	Wurtzite	Kesterite
Cu(II)_Sn(II)_Tu_1.9_160 °C	59.4 ± 10.7	40.6 ± 10.7
Cu(II)_Sn(II)_Tu_3.6_160 °C	49.0 ± 9.2	51.0 ± 9.2
Cu(II)_Sn(IV)_Tu_1.9_160 °C	34.5 ± 5.1	65.5 ± 5.1
_Cu(II)_Sn(IV)_Tu_3.6_160 °C	31.5 ± 6.8	68.5 ± 6.8
Cu(II)_Sn(II)_Cyst_1.9_160 °C	76.2 ± 6.7	23.8 ± 6.7
Cu(II)_Sn(II)_Cyst_3.6_160 °C	81.0 ± 5.3	19.0 ± 5.3
Cu(II)_Sn(IV)_Cyst_1.9_160 °C	29.4 ± 4.3	70.6 ± 4.3
_Cu(II)_Sn(IV)_Cyst_3.6_160 °C	47.8 ± 6.8	52.2 ± 6.8
Cu(II)_Sn(II)_TGacid_1.9_160 °C	67.8± 6.3	32.2 ± 6.3
Cu(II)_Sn(II)_TGacid_3.6_160 °C	81.4 ± 3.8	18.6 ± 3.8
Cu(II)_Sn(IV)_TGacid_1.9_160 °C	62.0 ± 5.3	38.0 ± 5.3
_Cu(II)_Sn(IV)_TGacid_3.6_160 °C	69.9 ± 4.8	30.1 ± 4.8
Cu(II)_Sn(II)_MCPacid_1.9_160 °C	62.8 ± 7.5	37.2 ± 7.5
Cu(II)_Sn(II)_MCPacid_3.6_160 °C	78.6 ± 7.5	21.4 ± 7.5
Cu(II)_Sn(IV)_MCPacid_1.9_160 °C	78.8 ± 5.3	21.2 ± 5.3
Cu(II)_Sn(IV)_MCPacid_3.6_160 °C	68.7 ± 3.3	31.3 ± 3.3

Table S5 Quantitative phase percentages estimated by Rietveld Refinement.

Synthesis of Zn-Sn intermediates at room temperature

A white powder formed when the synthesis was conducted at 25 °C with Cu(II) and Sn(II) precursors and thiourea (e.g. products Cu(II) Sn(II) Tu S:M 25 °C). Formation of this powder persists at low temperature but is converted to CZTS at higher temperatures (see main text). This white powder contains Zn and Sn, and we refer to it as the Zn-Sn intermediate or Zn-Sn glycolate intermediate in the text. The XRD pattern from this product is shown in the main text. An extensive search on Cambridge Structural Database (CSD) was carried out, looking for Zn or Sn coordination compounds containing thiourea and glycolate groups. Although the search did not reveal any compound that matches completely with the XRD pattern obtained for from our white powder, it resembled XRD patterns that could originate from a mixture of the compounds thioureatin(II) chloride (Sn(NH₂CSNH₂)Cl₂) (CSD code: CAPWEV) and catena-((m2-Succinato-O,O')-bis(thiourea-S)-zinc) (CSD code: FELXEA). Figure S5 shows the XRD pattern from these compounds and the white powder product of Cu(II)_Sn(II)_Tu_1.9_25 °C. The similarity of the XRD pattern of this zinc succinate thiourea complex and the Zn-Sn intermediate prompted us to hypothesize that the intermediate is a mixture of the complex thioureatin(II) chloride and complex containing glycolate and thiourea ligands, where the glycolate ligands would be able help form polymeric units. Moreover, the composition of this white powder product (i.e. Cu(II) Sn(II) S:M 25 °C) always had 1:1 Zn:Sn ratio and did not contain any detectable copper (Figure S6, see the data point at 25 °C).



Figure S5. a) XRD pattern from Cu(II)_Sn(II)_Tu_1.9_25 °C product and XRD patterns for coordination compounds of Zn and Sn that matched the best. b) Molecular Structure of the compounds possibly present in the Zn-Sn intermediate.



In order to see if the other sulfur excess sources, besides thiourea, could produce the same Zn-Sn intermediate, the room temperature synthesis was carried out either with Sn(II) or Sn(IV) and with 3.4×10^{-3} mol of cysteine, thioglycolic acid, or mercaptopropionic acid added as the excess sulfur source, in addition to the stoichiometric amount of thiourea (4.0×10^{-3} mol), to reach S:M=1.9. Figure S7 shows the XRD pattern from products synthesized using different sulfur excess sources and Sn initial oxidation state at 25 °C. When the sulfur excess is provided by L-cysteine and Sn initial oxidation state is +2 (*e.g.,* Cu(II)_Sn(II)_cyst_1.9_25 °C), the same Zn-Sn intermediate forms. The XRD pattern is the same as that obtained from the product formed using thiourea (*e.g.,* Cu(II)_Sn(II)_Tu_1.9_25 °C). See Figure 6 of the main text for the latter XRD pattern, also reproduced in Figure S7 for easy comparison. In contrast, when the sulfur source does not contain NH₂ groups, (*e.g.,* 3-mercaptopropionic acid and thioglycolic acid), this Zn-Sn intermediate does not form.



Figure S8 shows an SEM image of the Zn-Sn intermediate formed by the synthesis where L-cysteine was used as the excess sulfur source (*e.g.*, Cu(II)_Sn(II)_cyst_1.9_25 °C). The crystals of this product have the same anisotropic hexagonal rod-like morphology as the Zn-Sn intermediate formed by the synthesis where thiourea was the excess sulfur source (*e.g.*, Cu(II)_Sn(II)_Tu_1.9_25 °C, Figure 7a in the main text).



Experiments varying Sn oxidation state at room temperature

To explore the identity of the Zn-Sn precursor that leads to wurtzite CZTS, the Cu oxidation state was fixed at (II) while the Sn oxidation state was varied between (II) and (IV) for S:M=1.9 or 6.2. Microwave heating was not used in these experiments. After sonication at room temperature, the solid products were collected by centrifugation and characterized. When using the Sn(IV) reagent, a yellow powder was obtained both for S:M=1.9 and S:M=6.2. The XRD pattern for both samples matched the XRD pattern for elemental sulfur (Figure S9). When the solid product of the synthesis with Cu(II) and Sn(IV) reagents with S:M=1.9 at 25 °C (*i.e.*, Cu(II)_Sn(IV)_Tu_1.9_25 °C) was analyzed, it was found that it consisted only of sulfur (Table S6). The production of elemental sulfur can be explained by the decomposition of thiourea in acidic media, according to the following reaction:

$$SC(NH_2)_{2(I)} + H^+ \rightarrow NH_{3(g)} + H^+ + HCN_{(g)} + 1/8 S_{8(s)}$$

Table S6. Composition of the product synthesized with Cu(II) and Sn(IV) reagents, thiourea, and S:M=1.9 at 25 °C (*e.g.*, Cu(II) Sn(IV) Tu 1.9 25 °C). Elemental values are in atom %.

Element	Spectra	Std Dev									
	1	2	3	4	5	6	7	8	9	10	
Cu	0.44	0	0	0.83	0.36	0	0	0.99	0	0.85	0.4
Zn	0	0	0	0	0	0	0	1.31	0	0	0.4
Sn	0	0.67	0	0	0.59	0	0	1.61	0	0	0.5
S	99.56	99.33	100	99.17	99.05	100	100	96.08	100	99.15	1.1

Effect of temperature on the morphology of products Cu(II)_Sn(II)_Tu_1.9_T and Cu(II)_Sn(II)_Tu_6.2_T

Figure S10 shows the SEM images of the products whose XRD patterns are shown in Figure 6 of the main text. Figure S10a shows that synthesis with S:M=1.9 at 75 °C produces only hexagonal prisms. At higher temperatures, 100 and 130 °C, these hexagonal prisms are still present but are now mixed with smaller spherical particles. Synthesis with S:M=6.2 at 75 °C produces small spherical particles mixed with the hexagonal plates. Synthesis with S:M=6.2 at 100 and 130 °C produces primarily spherical particles. These results are in agreement with the XRD results presented in Figure 6 of the main text, which shows that the Zn-Sn intermediates persist until 130 °C for S:M=1.9, whereas, for S:M=6.2, the Zn-Sn glycolates (associated with the hexagonal morphology) are present only until 75 °C, and the phase pure CZTS kesterite is obtained starting from 100 °C. It appears that higher sulfur concentration transforms the glycolates into CZTS at lower temperature and hexagonal glycolates persist to higher temperatures only when S:M is low.

The elemental analysis by SEM-EDS of the white powder, the Zn-Sn precursor synthesized with S:M=1.9 and S:M=6.2 at room temperature, revealed that it does not contain detectable Cu, and the Zn to Sn ratio is 1 (see Figure S6). This confirms that the white precipitate at room temperature is the Zn-Sn intermediate. The powder synthesized with S:M=6.2 had a larger amount of sulfur than the powder synthesized with S:M=1.9 (see Fig. S5). By 75 °C, fractions of Zn and Sn decrease in both products synthesized with S:M=1.9 and S:M=6.2. This decrease is accompanied by the appearance of Cu, approximately 15% in the product synthesized at 75 °C. At and above 100 °C, the product synthesized with S:M=6.2 has a composition very close to that expected for CZTS. In contrast, with S:M=1.9 the amount of sulfur increases more slowly, getting close to the expected CZTS composition only at 160 °C.

These results corroborate the hypothesis that, at room temperature, only Zn-Sn intermediates are formed, while copper remains in solution without incorporation into the solid. As the temperature increases, copper incorporates into the glycolates and the glycolates transform into CZTS. Also, as described in the main text, the intermediates synthesized with S:M=6.2 have a higher amount of sulfur than the intermediates with S:M=1.9, which accelerates the transformation to CZTS, lowering the



(c) Cu(II)_Sn(II)_Tu_1.9_160 °C (d) Cu(II)_Sn(II)_Tu_6.2_160 °C (e) Cu(I)_Sn(IV)_Tu_1.9_160 °C (f) Cu(I)_Sn(IV)_Tu_6.2_160 °C (g) Cu(II)_Sn(IV)_1.9_Tu_160 °C (h) Cu(II)_Sn(IV)_Tu_6.2_160 °C.

temperature CZTS is formed to 100 $^\circ C$ for S:M=6.2.

Elemental Analysis of the Product Cu(II)_Sn(IV)_TGacid_1.9_100 °C

As shown in Figure 8b in the main text, the sample Cu(II)_Sn(IV)_TGacid_1.9_100 °C forms a crystalline compound identified as copper sulfide by XRD. This product was placed onto Au TEM grids and elemental analysis by TEM-EDS was performed. The results are presented in Table S7.

Table S7. TEM-EDS analysis of the product Cu(II)_Sn(IV)_TGacid_1.9_100 °C. Elemental composition is in atom %. Composition from three locations are shown.

	Spectrum	Spectrum	Spectrum		
Element	1	2	3	Average	Std Dev
Cu	89.1	57.6	89.7	78.8	15.0
Zn	0	0	0	0	0.0
Sn	0	0	0	0	0.0
S	10.9	42.4	10.3	21.2	15.0



.Cu(II) Sn(II) Tu 1.9 130 °C.

Influence of the water on the CZTS phase composition

Considering that the syntheses were carried out using the following reagents: Copper (II) acetate monohydrate ($CuAc_2 \cdot H_2O$), copper (I) acetate (CuAc), zinc acetate dehydrate ($ZnAc_2 \cdot 2H_2O$), tin (II) chloride ($SnCl_2$), tin (IV) chloride pentahydrate ($SnCl_4 \cdot 5H_2O$), and thiourea (CH_4N_2S), it is necessary to ask whether the water present in the starting reagents influences the CZTS crystalline phase produced in the synthesis. Table S8 summarizes the results presented in Figure 4 of the main text, and lists the total

amount of water introduced in the synthesis via the reagents. To check if this difference in the hydration water amount has some influence on the crystalline phases produced in the synthesis, we conducted a synthesis (specifically, Cu(II)_Sn(II)_1.9_160 C) while including an additional 5 mmols of deionized water in ethylene glycol, to bring the total water level to 9 mmol of H₂O. As shown in Figure S12, the product was comprised mostly of wurtzite, identical to the XRD pattern obtained when no additional water was included in the synthesis (e.g., product Cu(II)_Sn(II)_Tu_1.9_160 C in Figure 4. We conclude that water introduced through starting reagents has no influence on the CZTS crystalline phases produced.

Sample	Number of mols of hydration H₂O (mmols)	Phase Composition
Cu(I)_Sn(II)_S:M_160 C	2	Wurtzite (S:M = 1.9), Kesterite (S:M = 6.2)
Cu(I)_Sn(IV)_S:M_160 C	7	Mostly Kesterite, regardless S:M ratio
Cu(II)_Sn(II)_S:M_160 C	4	Wurtzite (S:M = 1.9), Kesterite (S:M = 6.2)
Cu(II)_Sn(IV)_S:M_160 C	9	Mostly Kesterite, regardless S:M ratio

