Supporting Information

Synthesis of Cu₂(Zn_{1-x}Co_x)SnS₄ Nanocrystals and Formation of Polycrystalline Thin Films from Their Aqueous Dispersions

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Measurement and Control of Co fraction, x in Nanocrystals



Figure S1. Comparison of the nominal Co fraction, x in $Cu_2(Zn_{1-x},Co_x)SnS_4$, with the Co fraction, X, measured using ICP-MS (blue triangles) and SEM-EDS (red squares). The measured cobalt fraction, X is defined as $X=C_{Co}/(C_{Zn}+C_{Co})$, where C_i is the concentration of species *i* (Co or Zn). The nominal Co fraction, x, is the Co fraction in the precursor solutions calculated from the ratio of the moles of CoAc₂ to the sum of the moles of CoAc₂ and ZnAc₂ (*i.e.*, [CoAc₂]/[CoAc₂ + ZnAc₂]). The elemental composition determined by ICP-MS and SEM-EDS reveal the $C_{Co}/(C_{Zn}+C_{Co})$ ratio is very close to expected x value in $Cu_2(Zn_{1-x}Co_x)SnS_4$, as shown in the Figure S1.

Ritveld Refinement and XRD Simulation Details

Rietveld refinement was performed using the software XPert HighScore Plus. The wurtzite structure (space group P6₃mc, #186) was simulated using an initial guess of a = 3.8353 Å, b = 3.8353 Å, c = 6.3276 Å while keeping $\alpha = 90^{\circ}$, $\beta = 90^{\circ}$, $\gamma = 120^{\circ}$ and. For Cu₂ZnSnS₄ (x=0) and Cu₂CoSnS₄ (x=1). The Wyckoff positions of the atoms are given in Table S1. For the solid solutions Cu₂(Zn_{1-x}Co_x)SnS₄, the occupational parameter (sof) was adjusted according to the relative amounts of Zn and Co present in each sample (*i.e.*, x). The Rietveld refinement was carried out in the following order: (1) Scale factors were refined; (2) the 4 first background parameters were refined; (3) zero shift was refined; (4) the a and b lattice parameters were refined; (5) the c lattice parameter refined; (6) the profile parameter, U, was refined; (7) the peak shape parameter, peak shape 1, was refined; (8) the profile parameter, V, was refined; (9) the peak shape parameter peak shape 2 was refined.

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 (1-x)	0.500
Со	2b	1/3	2/3	0	0.333 x	0.500
Sn	2b	1/3	2/3	0	0.333	0.500
S	2b	1/3	2/3	0.375	1	0.500

Table S1. Wyckoff positions and occupational parameters (sof) used in the Rietveld refinement and XRD simulations.

XRD patterns from Cu₂(Zn_{1-x}Co_x)SnS₄Nanocrystals as a function of x on an expanded scale



Figure S2. XRD patterns from $Cu_2(Zn_{1-x}Co_x)SnS_4$ nanocrystals as a function of the nominal Co fraction, x on an expanded scale. Simulated XRD patterns of wurtzite Cu_2ZnSnS_4 and Cu_2CoSnS_4 are shown as stick patterns.

Discussion on Band Gap of Wurtzite Cu₂(Zn_{1-x}Co_x)SnS₄

All the reported measurements for wurtzite CZTS show absorption below the reported band gap values (references 52 and 59 of the main text). For example, while both Singh *et al.* and Kang *et al.* reported a band gap of 1.43 eV (references 52 and 59 of the main text, respectively), the absorption spectra shown in these articles show either a tail or significant absorption well above 1000 nm (*i.e.*, < 1.24 eV). In fact, the absorption shown by Lu *et al.* (reference 41 of the main text) reaches a minimum at 1200 nm ($\sim 1 \text{ eV}$) and begins to rise again above 1200 nm (below 1 eV): the authors do not discuss whether this rise could be due to a plasmon or thin film interference. Depending on the region, we used to extrapolate, we could draw lines through their data to get any band gap value between $\sim 1 \text{ eV}$ and 1.43 eV.

Gillorin *et al.* reported a band gap value of 1.5 eV on "highly crystalline Cu_2CoSnS_4 " though the absorption spectra were not shown (reference 25 of the main text). Zhang *et al.* synthesized wurtzite Cu_2CoSnS_4 nanocrystals and reported a band gap value of 1.58 eV (reference 26 of the main text). Murali *et al.* claimed to have made the wurtzite Cu_2CoSnS_4 phase and reported a band gap of 1.4 eV for films but the their XRD intensity distribution, while showing the wurtzite peaks did not match the intensity distribution expected from a powder diffraction pattern (reference 27 of the main text.) In fact, the diffraction intensity expected from the kesterite phase was the most intense. Thus, these films may have been a mixture of wurtzite and kesterite phases. Again, the $(\alpha hv)^2$ vs. (hv) plot showed a significant tail and extrapolation to determine the band gap was ambiguous.

The absorption edge in our $Cu_2(Zn_{1x}Co_x)SnS_4$ nanocrystal films gradually blue shifts from ~1.1 eV to ~1.35 eV as more Co is substituted for Zn and x increases, the opposite trend reported by Huang *et al.* (reference 31 in the main text.) To our knowledge, there are no reported density functional theory (DFT) calculations for the band gap in wurtzite $Cu_2(Zn_1$. $_{x}Co_{x})SnS_{4}$. Khadka and Kim calculated the band gap in wurtzite $Cu_{2}FeSnS_{4}$ and found that the band gap energy was slightly larger (1.46 eV) than the calculated value for wurtzite Cu₂ZnSnS₄ (1.372 eV); (reference 55 in the main text.) Also, in kesterite $Cu_2(Zn_{1x}Fe_x)SnS_4$ substitution of Fe for Zn increases the theoretical prediction of the band gap slightly from 1.54 eV to 1.74 eV. Since Fe and Co are next to each other and to the left of Zn in the same row of the periodic table, we would expect similar trends for $Cu_2(Zn_{1-x}Co_x)SnS_4$ as $Cu_2(Zn_{1-x}Fe_x)SnS_4$: that is we would expect the band gap energy to increase slightly. This conclusion is consistent with the absorption spectra, which shows a blue shift in the absorption edge as Co substitution for Zn in wurtzite $Cu_2(Zn_{1-x}Co_x)SnS_4$ is increased. There is, however, also the possibility that the nanocrystals become increasingly more quantum confined as their sizes decrease with increasing Co concentration (see Figure 1). While quantum confinement can also blue shift the absorption edge, Khare et al. (reference 61 in the main text) showed that the CZTS nanocrystal sizes must be approximately 3 nm or less to observe this effect: the data from Khare et al. showed that even the nanocrystals that were 5 nm in diameter showed the same band gap value as bulk crystals. In our case, the average $Cu_2(Zn_{1,x}Co_x)SnS_4$ nanocrystals size decreases below 5 nm but only for x > 0.8 and is never as small as 3 nm. Unless the effective carrier masses in wurtzite $Cu_2(Zn_{1-x}Co_x)SnS_4$ or the dielectric constant are significantly different than those in kesterite Cu_2ZnSnS_4 , we do not expect quantum confinement to explain all the shifts in Figure 4 of the main text.



Figure S3. Fast Fourier transform (FFT) images from the HRTEM images shown in Figure 3 (main text). All of the FFT patterns are well matched with the wurtizite structure of $Cu_2(Zn_{1-x}, Co_x)SnS_4$ structure.