Supporting Information (SI)

Tailoring the Thermoelectric and Structural Properties of Cu-Sn Based Thiospinel Compounds [$CuM_{1+x}Sn_{1-x}S_4$ (M = Ti, V, Cr, Co)]

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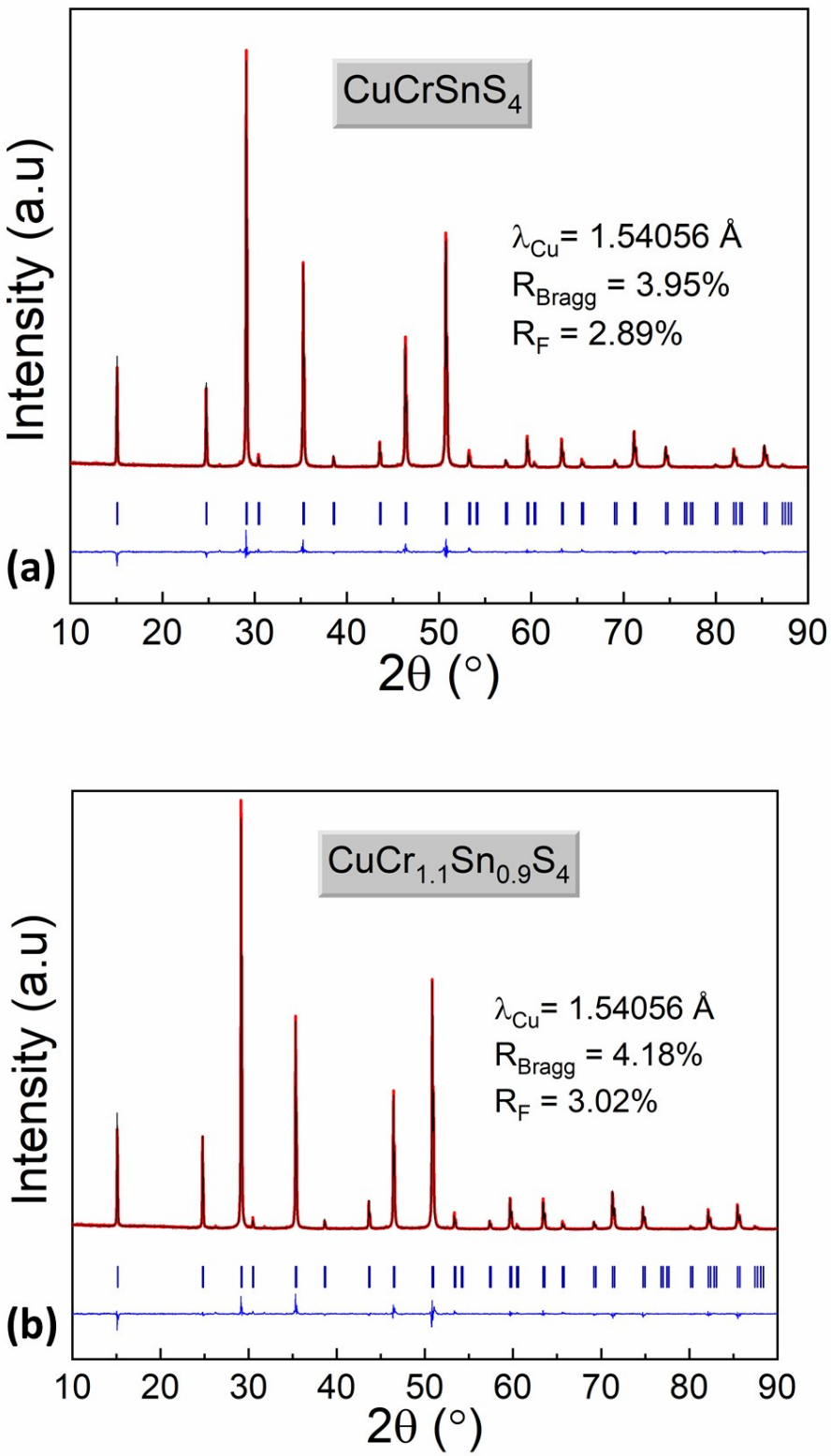


Figure S1. *Rietveld refinement for the (a) $CuCrSnS_4$, and (b) $CuCr_{1.1}Sn_{0.9}S_4$ thiospinel compounds.*

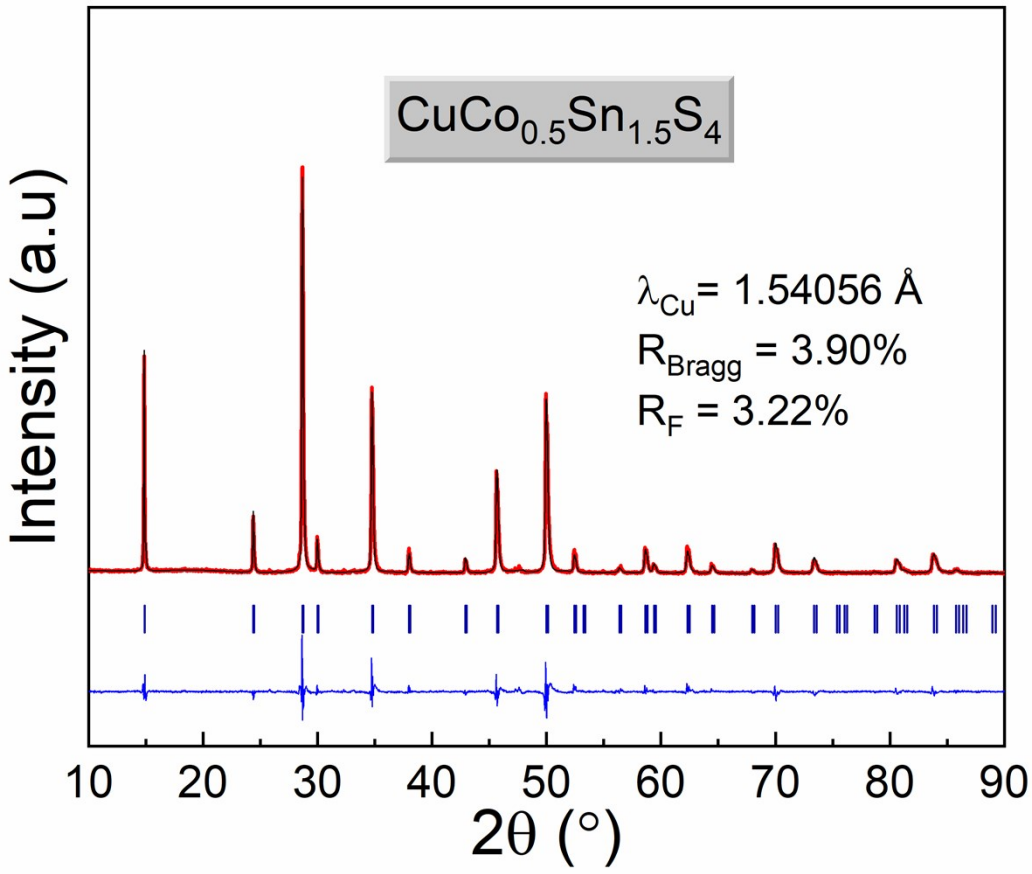


Figure S2. *Rietveld refinement for the $CuCo_{0.5}Sn_{1.5}S_4$ thiospinel compound.*

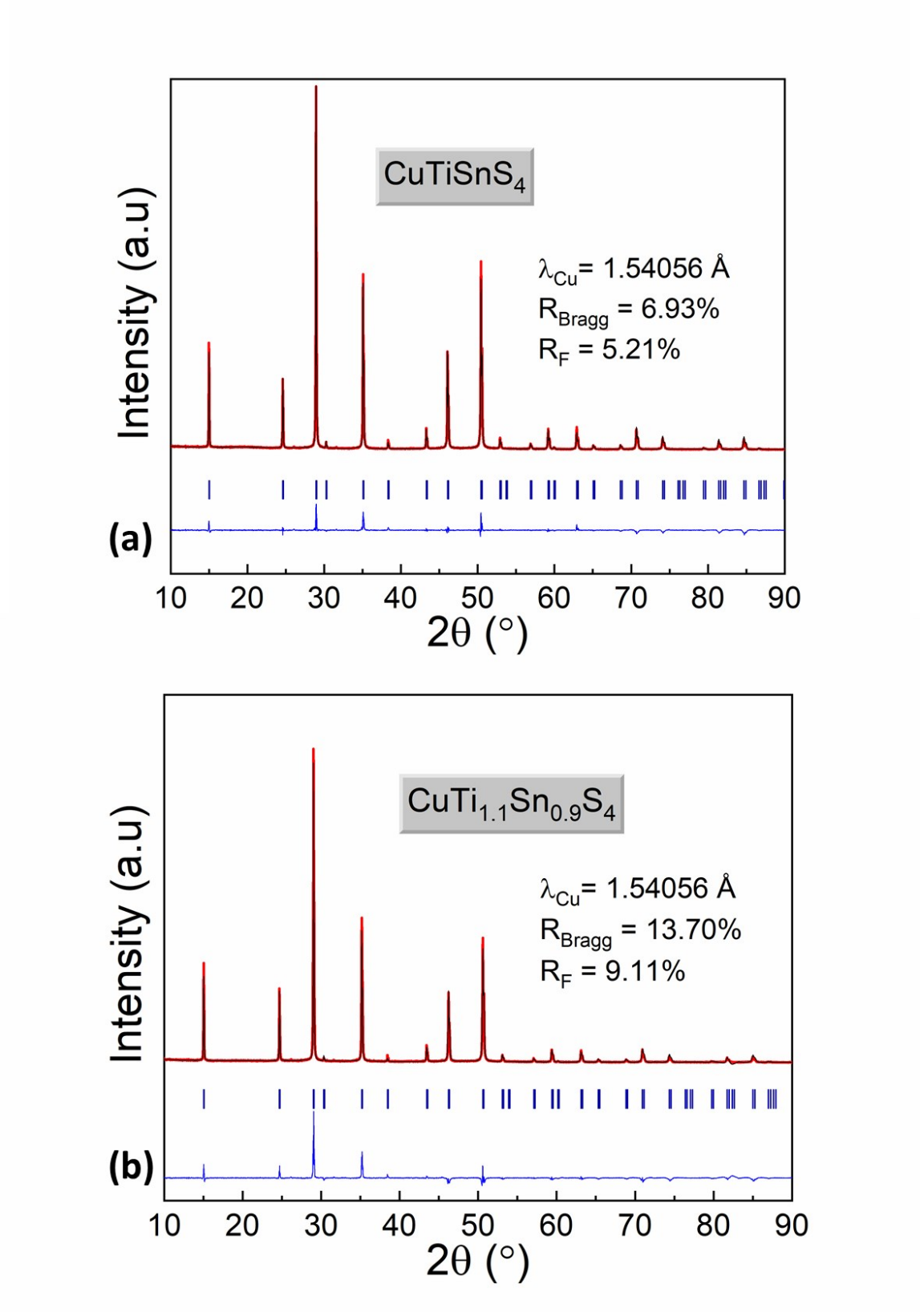


Figure S3. *Rietveld refinement for the (a) $CuTiSnS_4$, and (b) $CuTi_{1.1}Sn_{0.9}S_4$ thiospinel compounds.*

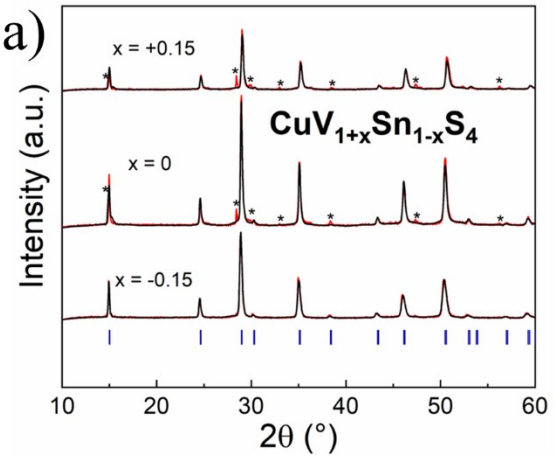
Table S1. *Atomic coordinates and atomic occupancy of the obtained from Rietveld refinement X-ray powder diffraction patterns (λ_{Cu} = 1.5418 Å) of the $Cu(M;Sn)_2S_4$ (M = Co, Ti and Cr) sample after Spark Plasma Sintering at room temperature *These values have been fixed due to too close Z values of metallic atoms and due to the resolution limit of the XRD Rietveld analysis.*

	*Occ. (Cu)	*Biso (Cu)	$Occ._{exp}$ (M)	$Occ._{theo}$ (M)	Occ_{exp} (Sn)	Occ_{theo} (Sn)	*Biso (M/Sn)	*Occ. (S)	x position (S)	*Biso (S)
$CuCo_{0.5}Sn_{1.5}S_4$	1	0.5	0.17	0.25	0.83	0.75	0.5	1	0.2548	0.5
$CuTi_{0.9}Sn_{1.1}S_4$	1	0.5	0.4	0.45	0.6	0.55	0.5	1	0.2404	0.5
$CuTiSnS_4$	1	0.5	0.51	0.5	0.49	0.5	0.5	1	0.2441	0.5
$CuTi_{1.1}Sn_{0.9}S_4$	1	0.5	0.53	0.55	0.47	0.45	0.5	1	0.2418	0.5
$CuCrSnS_4$	1	0.5	0.52	0.5	0.48	0.5	0.5	1	0.2464	0.5
$CuCr_{1.1}Sn_{0.9}S_4$	1	0.5	0.57	0.55	0.43	0.45	0.5	1	0.2457	0.5
$CuCr_{1.2}Sn_{0.8}S_4$	1	0.5	0.61	0.6	0.39	0.4	0.5	1	0.2454	0.5

Table S2*. Computed carrier concentration and effective mass values at room temperature for $CuM_{1+x}Sn_{1-x}S_4$ (x= 0 for M = Ti, Cr, and x = -0.5 for M = Co)[a] with λ = 0.5.*

Computed transport properties (based on band structures)	**$CuCo_{0.5}Sn_{1.5}S_4$**	**$CuTiSnS_4$**	**$CuCrSnS_4$**
Carrier concentration, *n* (cm^{-3})	1.6 x 10^{20}	1.9 x 10^{20}	3.3 x 10^{19}
Effective mass, *m** (m_e)	2.17	0.33	3.36

a)



b)

$CuV_{1+x}Sn_{1-x}S_4$ at 300K	S (μV/K)	ρ (mΩ.cm)	PF (mW/m.K^2)	κ (W/m.K)
x = - 0.15	17.9	18.3	$1.8x10^{-3}$	1.1
x = 0	2.8	6.5	$1.0x10^{-4}$	0.9
x = + 0.15	9.0	16.1	$5.0x10^{-4}$	1.2

Figure S4. *$CuV_{1+x}Sn_{1-x}S_4$ series – (a) XRD patterns, (b) electrical and thermal transport properties at room temperature.*

Table S3. *Specific Sn-S and M-S distances (Å, M = Co, Ti, Cr, V) of* $CuM_{1+x}Sn_{1-x}S_4$ *(x = 0 for M = Ti, V, Cr, and x = -0.5 for M = Co) thiospinel compounds.*

Structural Information	**$CuCo_{0.5}Sn_{1.5}S_4$**	**$CuTiSnS_4$**	**$CuCrSnS_4$**	**$CuVSnS_4$**
Sn-S	2.583 (a) 2.628 (b) 2.660 (c) 2.662 (d)	2.534 (a) 2.555 (b) 2.578 (c) 2.609 (d)	2.517 (a) 2.560 (b) 2.567 (c) 2.594 (d)	2.535 (a) 2.548 (b) 2.558 (c) 2.590 (d)
M-S (M = Co, Ti, Cr, V)	2.466 (a, b, d) 2.623 (b, d, c)	2.511 (a) 2.520 (b) 2.575 (c) 2.601 (d)	2.440 (a) 2.484 (b) 2.495 (c) 2.567 (d)	2.465 (a) 2.480 (b) 2.519 (c) 2.537 (d)

Note: Please refer Figure S5 for a, b, c, and d labeling in Table S3.

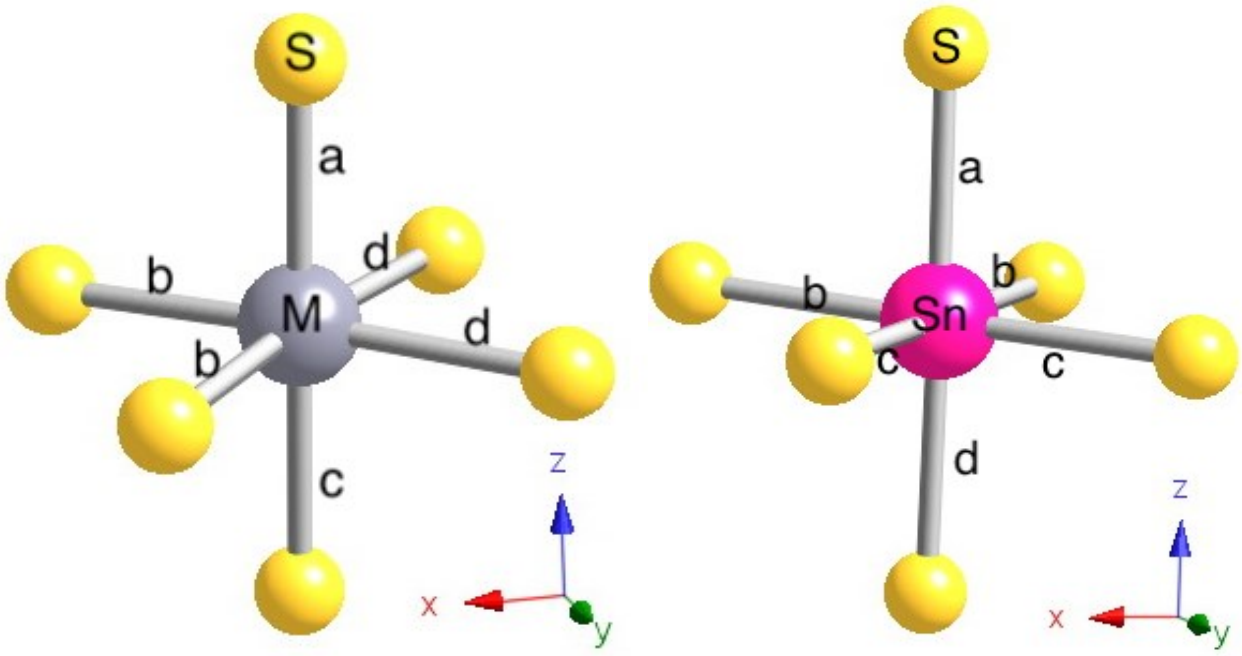


Figure S5. *Distorted octahedral environment of M (M = Co, Ti, Cr, V) and Sn of* $CuM_{1+x}Sn_{1-x}S_4$ *(x = 0 for M = Ti, V, Cr, and x = -0.5 for M = Co) thiospinel compounds.*

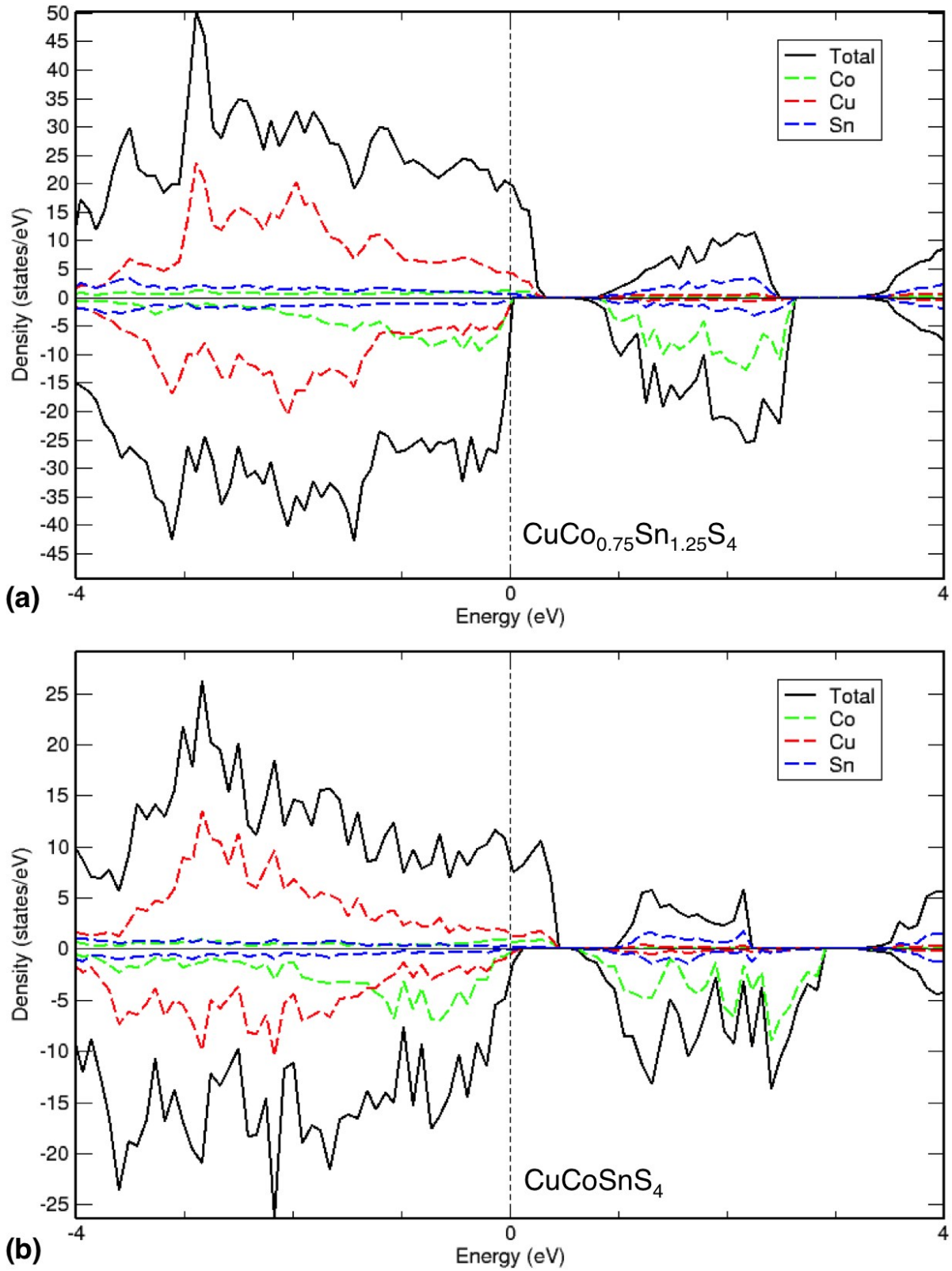


Figure S6. *Spin-polarized density of states (DOS) of (a) $CuCo_{0.75}Sn_{1.25}S_4$, and (c) $CuCoSnS_4$ hypothetical models.*