

Electronic Supplementary Information

Structural and Electronic Evolution in the Cu_3SbS_4 - Cu_3SnS_4 Solid Solution

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Table S1. Compositional analysis of representative samples $\text{Cu}_3\text{SbS}_4(\text{BM})$, Cu_3SbS_4 , $\text{Cu}_3\text{Sb}_{0.3}\text{Sn}_{0.7}\text{S}_4$ and Cu_3SnS_4 . The Cu, Sb and Sn contents were determined by inductively coupled plasma optical emission spectrometry (ICP-OES) and the S content was determined by combustion analysis (LECO).

Sample Name		wt. %				Relative Density
		Cu	Sb	Sn	S	
$\text{Cu}_3\text{SbS}_4(\text{BM})$	Nominal	43.3	27.6	-	29.1	NA
	Actual	43.4	27.2		29.4	
Cu_3SbS_4	Nominal	43.3	27.6	-	29.1	98%
	Actual	43.1	27.4		29.4	
$\text{Cu}_3\text{Sb}_{0.3}\text{Sn}_{0.7}\text{S}_4$	Nominal	43.5	8.3	19.0	29.3	99%
	Actual	43.4	8.2	18.9	29.5	
Cu_3SnS_4	Nominal	43.6	-	27.1	29.3	100%
	Actual	43.2	-	27.3	29.5	

Table S2. Comparison of R-factors in ordered and disordered models for $\text{Cu}_3\text{Sb}_{1-x}\text{Sn}_x\text{S}_4$ (bs = back scattering bank and la = low angle bank).

		x = 0.0	x = 0.4	x = 0.7	x = 1.0
Ordered model Sb/Sn in 2a	Rwp neut bs	0.0227	0.0235	0.0230	0.0228
	Rwp neut la	0.0237	0.0271	0.0264	0.0296
	Rwp X-ray	0.0956	0.0686	0.0704	0.1152
	χ^2	44.37	41.37	41.36	61.57
Disordered model	Rwp neut bs	0.0228	0.0233	0.0230	0.0229
	Rwp neut la	0.0240	0.0268	0.0265	0.0296
	Rwp X-ray	0.1124	0.0948	0.0831	0.1040
	χ^2	45.39	41.47	41.93	61.41

Table S3. Comparison of (a) R-factors, and (b) isotropic thermal parameters (\AA^2) for different cation ordering models in Cu_3SnS_4 (bs = back scattering bank and la = low angle bank).

Atomic positions: 2a = 0, 0, 0; 2b = 0, 0, $\frac{1}{2}$; 4d = 0, $\frac{1}{2}$, $\frac{1}{4}$

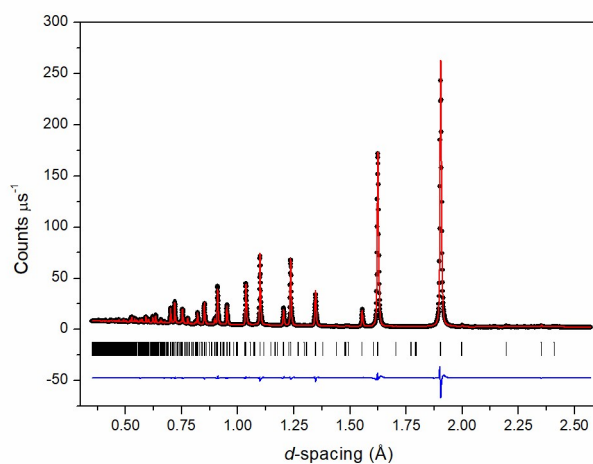
(a)

Model	Rwp neut bs	Rwp neut la	Rwp X-ray	χ^2
2: All Sn in 2a	0.0228	0.0296	0.1152	61.57
3: Sn in all sites varying	0.0228	0.0296	0.1040	61.42
4: All Sn in 2b	0.0228	0.0296	0.1152	61.57
5: All Sn in 4d	0.0228	0.0297	0.1075	61.63
6: Sn in 2a and 2b	0.0228	0.0297	0.1075	61.56
7: Sn in 2a and 4d	0.0227	0.0296	0.1040	61.31
8: Sn in 2b and 4d	0.0227	0.0296	0.1040	61.33
9: Sn in all sites	0.0228	0.0296	0.1040	61.41

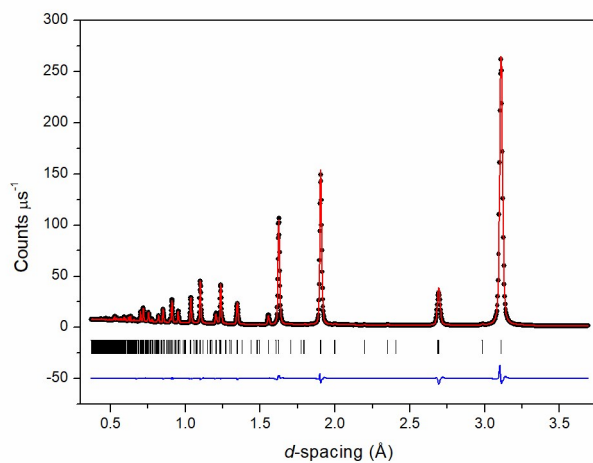
(b)

Model	2a	2b	4d
2: All Sn in 2a	0.00977	0.02894	0.01627
3: Sn in all sites varying	0.01067	0.02099	0.01690
4: All Sn in 2b	0.02927	0.00989	0.01612
5: All Sn in 4d	0.01267	0.01825	0.01982
6: Sn in 2a and 2b	0.01398	0.01613	0.02328
7: Sn in 2a and 4d	0.00940	0.01920	0.02067
8: Sn in 2b and 4d	0.01901	0.00957	0.02063
9: Sn in all sites	0.01045	0.01655	0.02131

(a)



(b)



(c)

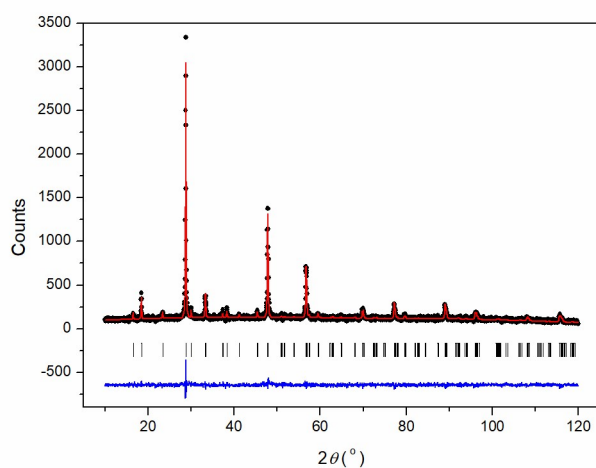
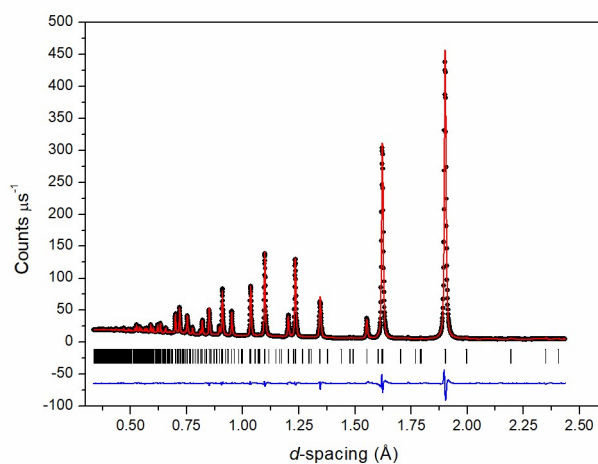
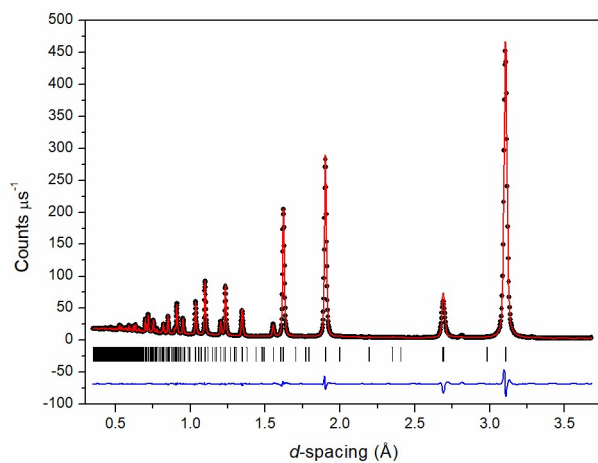


Fig. S1. Fitted diffraction profiles for Cu_3SbS_4 : (a) neutron back-scattering; (b) neutron low-angle; and (c) X-ray data. Observed (circles), calculated (red line) and difference (blue) profiles are shown, with reflection positions indicated by markers.

(a)



(b)



(c)

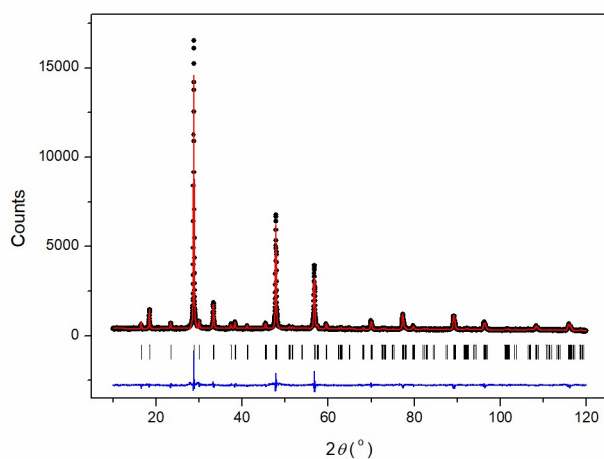
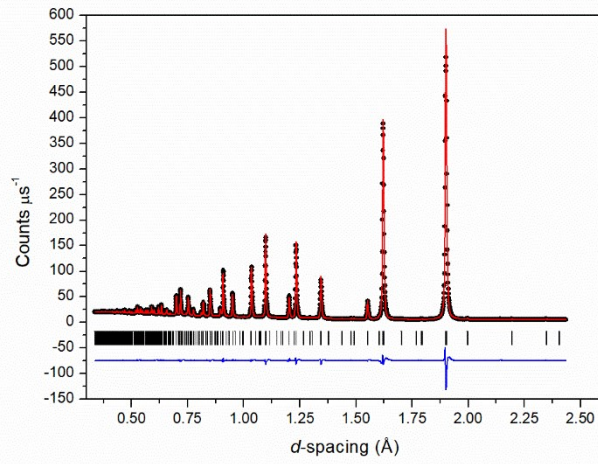
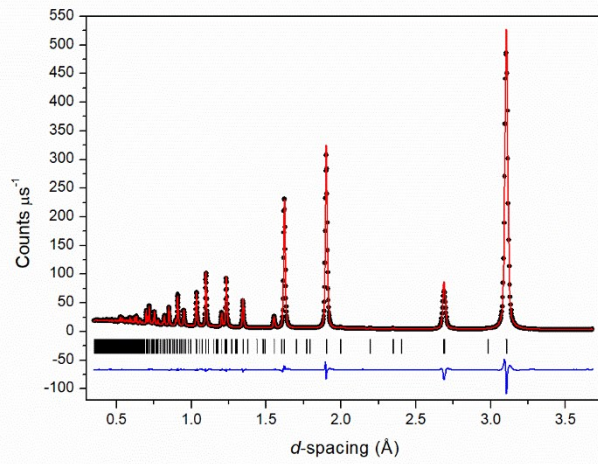


Fig. S2. Fitted diffraction profiles for $\text{Cu}_3\text{Sb}_{0.6}\text{Sn}_{0.4}\text{S}_4$: (a) neutron back-scattering; (b) neutron low-angle; and (c) X-ray data. Observed (circles), calculated (red line) and difference (blue) profiles are shown, with reflection positions indicated by markers.

(a)



(b)



(c)

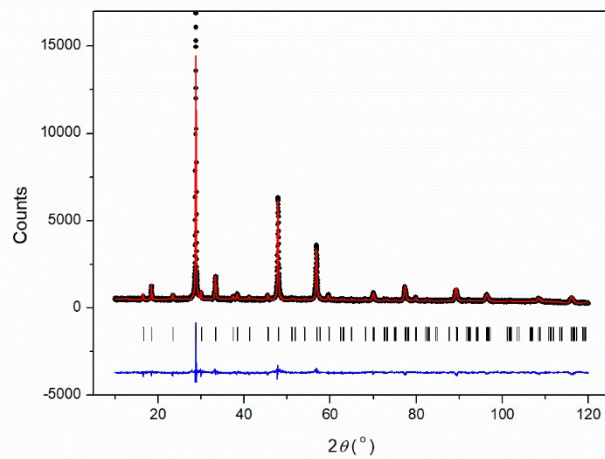
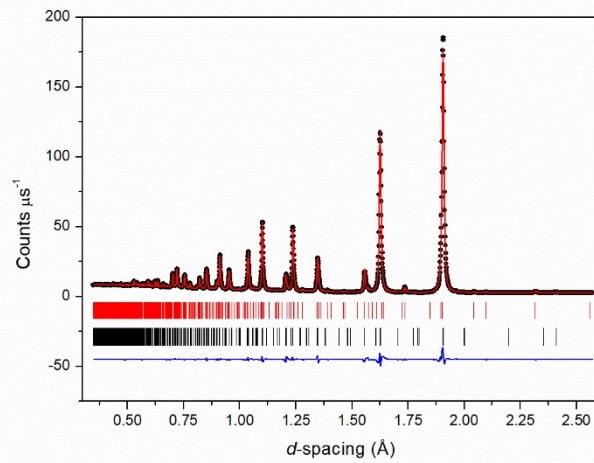
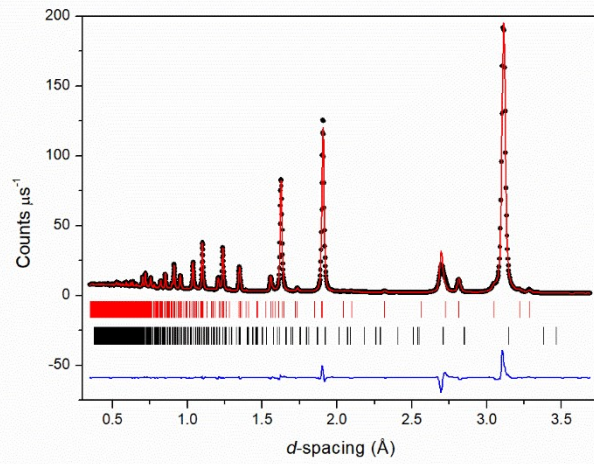


Fig. S3. Fitted diffraction profiles for $\text{Cu}_3\text{Sb}_{0.3}\text{Sn}_{0.7}\text{S}_4$: (a) neutron back-scattering; (b) neutron low-angle; and (c) X-ray data. Observed (circles), calculated (red line) and difference (blue) profiles are shown, with reflection positions indicated by markers.

(a)



(b)



(c)

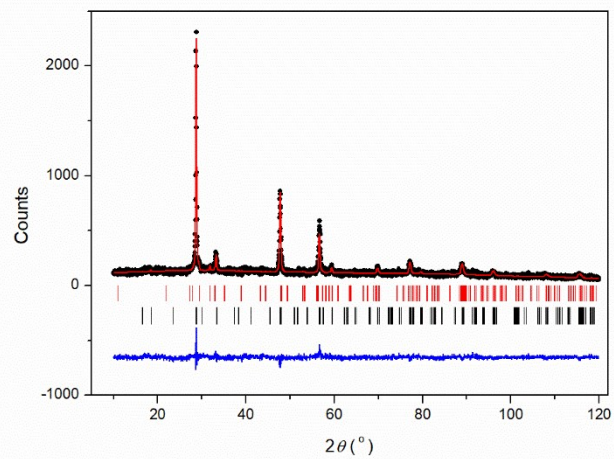


Fig. S4. Fitted diffraction profiles for Cu_3SnS_4 : (a) neutron back-scattering; (b) neutron low-angle; and (c) X-ray data. Observed (circles), calculated (red line) and difference (blue) profiles are shown, with reflection positions indicated by markers Cu_3SnS_4 (black), CuS (red).

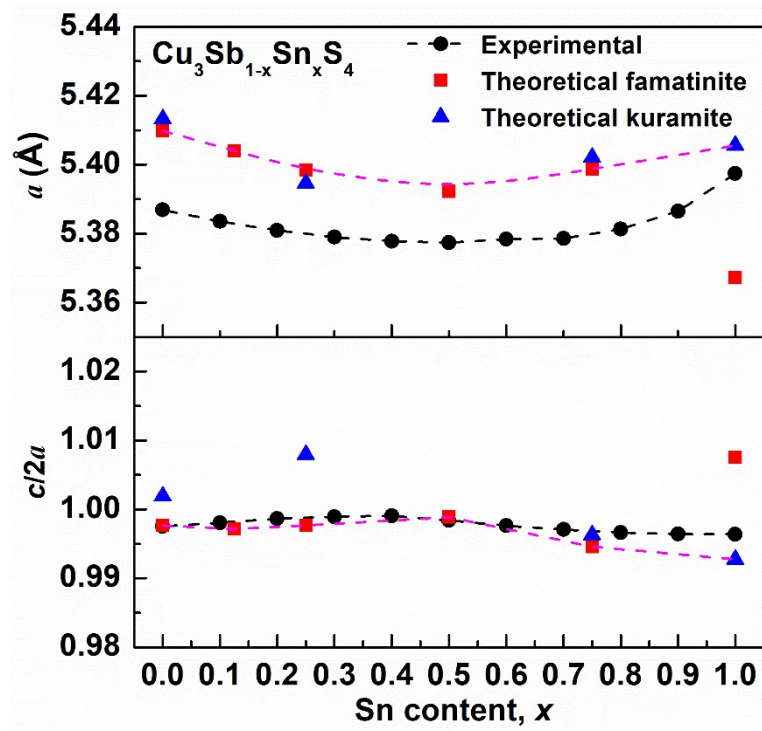


Fig. S5. Compositional variation of lattice parameter a (upper) and lattice parameter ratio, $c/2a$ (lower).

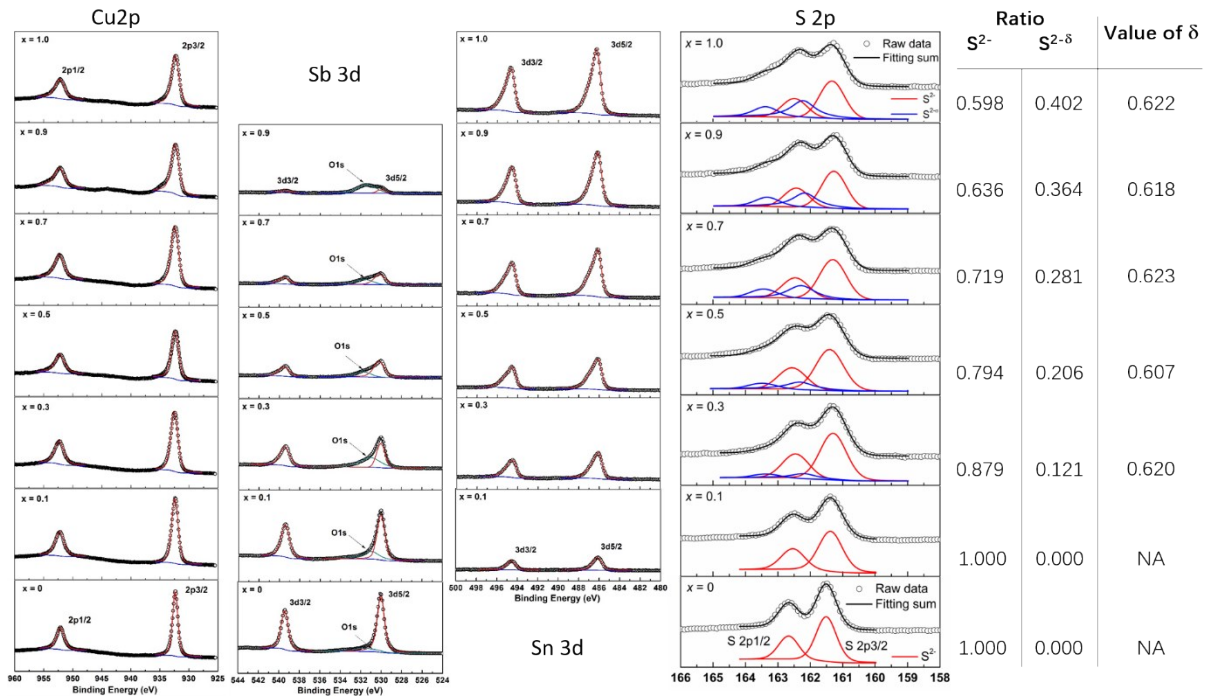


Fig. S6. Fitted high resolution XPS spectra for compositions in the $Cu_3Sb_{1-x}Sn_xS_4$ system. All spectra were calibrated using C1s with a binding energy of 284.8 eV. For $x = 0.3 \sim 1.0$ sample, S2p peaks were fitted into two different S species of S^{2-} and $S^{2-\delta}$. The ratio of S^{2-} and $S^{2-\delta}$ and values of δ were listed.