Electronic Supplementary Information

Structural and Electronic Evolution in the Cu$_3$SbS$_4$ - Cu$_3$SnS$_4$ Solid Solution

Kan Chen, Cono Di Paola, Savio Laricchia, Mike Reece, Cedric Weber, Emma McCabe, Isaac Abrahams and Nicola Bonini.

Table S1. Compositional analysis of representative samples Cu$_3$SbS$_4$(BM), Cu$_3$SbS$_4$, Cu$_3$Sb$_{0.3}$Sn$_{0.7}$S$_4$ and Cu$_3$SnS$_4$. 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).
Table S2. Comparison of R-factors in ordered and disordered models for Cu$_3$Sb$_{1-x}$Sn$_x$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 |
|                  | $\chi^2$   | 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 |
|                  | $\chi^2$   | 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$_3$SnS$_4$ (bs = back scattering bank and la = low angle bank).

Atomic positions: 2a = 0, 0, 0; 2b = 0, 0, ½; 4d = 0, ½, ¼

(a)

| Model                    | Rwp neut bs | Rwp neut la | Rwp X-ray | $\chi^2$ |
|--------------------------|-------------|-------------|-----------|----------|
| 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    |
Table S4. XPS Cu 2p, Sb 3d, Sn 3d and S 2p binding energies (eV) for compositions in the Cu₃Sb₁₋ₓSnₓS₄ system.

|      | x = 0.0 | x = 0.1 | x = 0.3 | x = 0.5 | x = 0.7 | x = 0.9 | x = 1.0 |
|------|---------|---------|---------|---------|---------|---------|---------|
| Cu 2p 1/2 | 952.3   | 952.2   | 952.2   | 952.1   | 952.2   | 952.1   | 952.1   |
| Cu 2p 3/2 | 932.5   | 932.4   | 932.4   | 932.3   | 932.4   | 932.3   | 932.3   |
| S 2p 1/2  | 163.1   | 163.0   | 162.9   | 162.9   | 162.8   | 162.7   | 162.8   |
| S 2p 3/2  | 162.0   | 161.8   | 161.7   | 161.7   | 161.6   | 161.5   | 161.6   |
| S' 2p 1/2 | NA      | NA      | 163.7   | 163.8   | 163.7   | 163.6   | 163.7   |
| S' 2p 3/2 | NA      | NA      | 162.5   | 162.6   | 162.5   | 162.4   | 162.5   |
| Sb 3d 3/2 | 539.6   | 539.5   | 539.5   | 539.4   | 539.5   | 539.4   | NA      |
| Sb 3d 5/2 | 530.2   | 530.1   | 530.1   | 530.0   | 530.1   | 530.0   | NA      |
| Sn 3d 3/2 | 494.5   | 494.4   | 494.5   | 494.5   | 494.5   | 494.5   | 494.7   |
| Sn 3d 5/2 | NA      | 486.1   | 486.1   | 486.1   | 486.1   | 486.1   | 486.3   |
Fig. S1. Fitted diffraction profiles for Cu$_3$SbS$_4$: (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.
Fig. S2. Fitted diffraction profiles for Cu$_3$Sb$_{0.6}$Sn$_{0.4}$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.
Fig. S3. Fitted diffraction profiles for Cu$_3$Sb$_{0.3}$Sn$_{0.7}$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.
Fig. S4. Fitted diffraction profiles for Cu$_3$SnS$_4$: (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$_3$SnS$_4$ (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 \( \text{Cu}_3\text{Sb}_{1-x}\text{Sn}_x\text{S}_4 \) 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 \( \text{S}^{2-} \) and \( \text{S}^{2-\delta} \). The ratio of \( \text{S}^{2-} \) and \( \text{S}^{2-\delta} \) and values of \( \delta \) were listed.