Electronic Supplementary Information

Crystal Structure, Electronic Band Structure and High-Temperature Thermoelectric Properties of Te-Substituted Tetrahedrites Cu$_{12}$Sb$_{4-x}$Te$_x$S$_{13}$ ($0.5 \leq x \leq 2.0$)

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1. **Table S1.** Single-crystal data collection and structure refinement at 300 K.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical formula</td>
<td>Cu$_{12}$Sb$_2$Te$<em>2$S$</em>{13}$ (series S1)</td>
</tr>
<tr>
<td>Molar mass (g.mol$^{-1}$)</td>
<td>1678.02</td>
</tr>
<tr>
<td>Symmetry</td>
<td>Cubic</td>
</tr>
<tr>
<td>Space group</td>
<td>$I-43m$</td>
</tr>
<tr>
<td>$a$ (Å)</td>
<td>10.3520(1)</td>
</tr>
<tr>
<td>$V$ (Å$^3$)</td>
<td>1108.91(1)</td>
</tr>
<tr>
<td>$Z$</td>
<td>2</td>
</tr>
<tr>
<td>$\rho$ (g.cm$^{-3}$)</td>
<td>5.025</td>
</tr>
<tr>
<td>Radiation</td>
<td>Mo Kα</td>
</tr>
<tr>
<td>$\theta$ range</td>
<td>3 – 79.39°</td>
</tr>
<tr>
<td>Linear Abs. coeff. $\mu$ (mm$^{-1}$)</td>
<td>17.24</td>
</tr>
<tr>
<td>Reflection collected</td>
<td>3465</td>
</tr>
<tr>
<td>Reflection unique</td>
<td>666</td>
</tr>
<tr>
<td>Number of parameters</td>
<td>18</td>
</tr>
<tr>
<td>Final $R$ value (%)</td>
<td>2.79</td>
</tr>
<tr>
<td>$S$ (Goodness of fit)</td>
<td>0.942</td>
</tr>
</tbody>
</table>
2. SEM images and X-ray mapping of the $x = 0.61$, 1.40 and 1.79 samples (series S1)

**Figure S1.** BSE images and X-ray mapping performed on the $x = 0.61$ sample.
Figure S2. BSE images and X-ray mapping performed on the $x = 1.40$ sample.
Figure S3. BSE images and X-ray mapping performed on the $x = 1.79$ sample.
2. **Table S2.** Atomic coordinates, site occupancies and equivalent atomic thermal displacement parameters (Å²).

<table>
<thead>
<tr>
<th>Site</th>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>s.o.f</th>
<th>U₁₁</th>
<th>U₂₂</th>
<th>U₃₃</th>
<th>U₁₂</th>
<th>U₁₃</th>
<th>U₂₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>12d</td>
<td>Cu₁</td>
<td>0.5</td>
<td>0</td>
<td>0.25</td>
<td>0.25</td>
<td>0.0192(3)</td>
<td>0.0192(3)</td>
<td>0.0256(5)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>12e</td>
<td>Cu₂</td>
<td>0</td>
<td>0</td>
<td>0.2168(3)</td>
<td>0.25</td>
<td>0.0737(1)</td>
<td>0.0737(1)</td>
<td>0.0185(1)</td>
<td>0</td>
<td>0</td>
<td>-0.052(1)</td>
</tr>
<tr>
<td>8c</td>
<td>Sb</td>
<td>0.26391(4)</td>
<td>0.26391(4)</td>
<td>0.26391(4)</td>
<td>0.1667</td>
<td>0.0124(2)</td>
<td>0.0124(2)</td>
<td>0.0124(2)</td>
<td>-0.0008(1)</td>
<td>-0.0008(1)</td>
<td></td>
</tr>
<tr>
<td>24g</td>
<td>S₁</td>
<td>0.8855(1)</td>
<td>0.8855(1)</td>
<td>0.3622(2)</td>
<td>0.5</td>
<td>0.0141(4)</td>
<td>0.0141(4)</td>
<td>0.0110(6)</td>
<td>0.001(4)</td>
<td>0.001(4)</td>
<td>-0.011(5)</td>
</tr>
<tr>
<td>2a</td>
<td>S₂</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.04167</td>
<td>0.0174(1)</td>
<td>0.0174(1)</td>
<td>0.0174(1)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

3. **Table S3.** Refined bond distances and bond angles from single-crystal XRD data at room temperature. Data obtained by Pfitzner et al. and Makovicky and Skinner on single-crystals of the ternary compound have been added for comparison.

<table>
<thead>
<tr>
<th>Composition</th>
<th>( \text{Cu}_{12}\text{Sb}_2\text{Te}<em>2\text{S}</em>{13} )</th>
<th>( \text{Cu}_{12}\text{Sb}<em>4\text{S}</em>{13} )</th>
<th>( \text{Cu}_{12.3}\text{Sb}<em>4\text{S}</em>{13} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu₁ – S₁ (×4)</td>
<td>2.33508</td>
<td>2.3133(8)</td>
<td>2.311(4)</td>
</tr>
<tr>
<td>Cu₂ – S₁ (×2)</td>
<td>2.25911</td>
<td>2.264(2)</td>
<td>2.246(7)</td>
</tr>
<tr>
<td>Cu₂ – S₂</td>
<td>2.16048</td>
<td>2.249(2)</td>
<td>2.250(6)</td>
</tr>
<tr>
<td>Cu₂ – Cu₂ (×4)</td>
<td>3.05538</td>
<td>3.180(3)</td>
<td>3.186(8)</td>
</tr>
<tr>
<td>Cu₂ – Sb/Te (×2)</td>
<td>3.47533</td>
<td>3.4090(4)</td>
<td>3.386</td>
</tr>
<tr>
<td>Sb/Te – S₁ (×3)</td>
<td>2.45991</td>
<td>2.438(1)</td>
<td>2.452(4)</td>
</tr>
<tr>
<td>S₁ – Cu₁ – S₁ (×2)</td>
<td>112.55</td>
<td>106.37(4)</td>
<td>105.45(15)</td>
</tr>
<tr>
<td>S₁ – Cu₂ – S₁</td>
<td>91.24</td>
<td>96.6(1)</td>
<td>96.04(25)</td>
</tr>
<tr>
<td>S₂ – Cu₂ – S₁ (×2)</td>
<td>134.38</td>
<td>131.70(7)</td>
<td>131.98(10)</td>
</tr>
<tr>
<td>Sb/Te – Cu₂ – Sb/Te</td>
<td>170.48</td>
<td>174.6(1)</td>
<td>175.2</td>
</tr>
<tr>
<td>S₁ – Sb/Te – S₁ (×3)</td>
<td>96.67</td>
<td>95.87(4)</td>
<td>95.70(10)</td>
</tr>
</tbody>
</table>
5. High-temperature PXRD patterns of the $x = 0.61$ (a) and 1.79 (b) samples (series S1)

![High-temperature PXRD patterns](image)

**Figure S4.** High-temperature PXRD spectra of the $x = 0.61$ sample.
Figure S5. High-temperature PXRD spectra of the $x = 1.79$ sample.

6. Temperature dependence of the specific heat of the $x = 0.80$ sample (series S1)

Figure S6. Temperature dependence of the specific heat $C_p$ of the $x = 0.80$ sample.