Role of Annealing Atmosphere on the Crystal Structure and Composition of Tetrahedrite-Tennantite Alloy Nanoparticles

Scott A. McClary*, Robert B. Balow**, Rakesh Agrawal*

*Davidson School of Chemical Engineering, Purdue University, 480 Stadium Mall Drive, West Lafayette, IN 47907.

**Department of Chemistry, Purdue University, 560 Oval Drive, West Lafayette, IN 47907.

†Denotes equal contribution to the manuscript.

RBB Current Address: National Research Council Research Associateship Program at U.S. Naval Research Laboratory, 4555 Overlook Avenue, SW, Washington, DC 20375, United States

Supporting Information
Figure S1. Calculated lattice parameter for as-synthesized TET-TEN NPs using Rietveld refinement. A linear shift in lattice parameter is observed with increasing Sb content, consistent with Vegard’s law for alloy materials.
Figure S2. SEM micrographs of (A) Cu$_{12}$Sb$_4$S$_{13}$, (B) Cu$_{12}$(As$_{0.25}$Sb$_{0.75}$)$_4$S$_{13}$ (C) Cu$_{12}$(As$_{0.50}$Sb$_{0.50}$)$_4$S$_{13}$, (D) Cu$_{12}$(As$_{0.75}$Sb$_{0.25}$)$_4$S$_{13}$, and (E) Cu$_{12}$As$_4$S$_{13}$ nanoparticles. Scale bars are 300 nm.

**Supplemental Characterization for Heat Treated Cu$_{12}$(As$_{1-x}$Sb$_x$)$_4$S$_{13}$ Nanoparticles**

Table S1. Rietveld refinement-determined weight percent of resulting phases after Cu$_{12}$(As$_{1-x}$Sb$_x$)$_4$S$_{13}$ NPs were annealed in sulfur for 1 h at 450 °C. The more As-rich phases partially formed a mixture of the orthorhombic enargite and tetragonal famatinite/luzonite crystal structures. The tendency to form the orthorhombic phase was suppressed with increasing Sb concentration.

<table>
<thead>
<tr>
<th>Resultant Phases</th>
<th>x = 0</th>
<th>x = 0.25</th>
<th>x = 0.50</th>
<th>x = 0.75</th>
<th>x = 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Famatinite/Luzonite</td>
<td>28.0</td>
<td>38.8</td>
<td>55.3</td>
<td>100.0</td>
<td>100.0</td>
</tr>
<tr>
<td>Enargite</td>
<td>72.0</td>
<td>61.2</td>
<td>44.7</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>
Figure S3. GIXRD and Raman spectra of nanoparticles treated in a sulfur atmosphere at 350 °C for 1 h. (A) Cu$_{12}$Sb$_4$S$_{13}$, (B) Cu$_{12}$(As$_{0.25}$Sb$_{0.75}$)$_4$S$_{13}$, (C) Cu$_{12}$(As$_{0.50}$Sb$_{0.50}$)$_4$S$_{13}$, (D) Cu$_{12}$(As$_{0.75}$Sb$_{0.25}$)$_4$S$_{13}$, and (E) Cu$_{12}$As$_4$S$_{13}$. Peaks marked with a * correspond to the (210) plane in enargite Cu$_3$As$_4$S$_4$ (JCPDS 01-082-1464). In the GIXRD and Raman spectra, slight deviations of the purely arsenic endmember from the reference spectra are attributed to Sb impurities in the reference spectra themselves. The Raman peaks near 490 cm$^{-1}$ are likely due to surface condensed elemental sulfur.$^{1-3}$

Table S2. Rietveld refinement-determined weight percent of resulting phases after Cu$_{12}$(As$_{1-x}$Sb$_x$)$_4$S$_{13}$ NPs were annealed in H$_2$S for 1 h at 450 °C. Significant decomposition is observed in the purely Sb- and As-samples, while the mixed alloy compositions displayed significantly higher resistance to decomposition into crystalline secondary phases.

<table>
<thead>
<tr>
<th>Resultant Phases</th>
<th>Starting Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$<em>{12}$(As$</em>{1-x}$Sb$_x$)$<em>4$S$</em>{13}$</td>
<td>25.4 x = 0</td>
</tr>
<tr>
<td>Digenite Cu$_{1.8}$S</td>
<td>74.6</td>
</tr>
<tr>
<td>Skinnerite Cu$<em>{3}$SbS$</em>{3}$</td>
<td>0.0</td>
</tr>
</tbody>
</table>
Figure S4. GIXRD and Raman spectra of nanoparticles treated in H₂S at 350 °C for 1 h. (A) Cu₁₂Sb₁₃, (B) Cu₁₂(As₀.₂₅Sb₀.₇₅)₄S₁₃, (C) Cu₁₂(As₀.₅₀Sb₀.₅₀)₄S₁₃, (D) Cu₁₂(As₀.₇₅Sb₀.₂₅)₄S₁₃, and (E) Cu₁₂As₄S₁₃. In the Raman spectrum, deviations of the antimony endmember from the reference spectrum are attributed to Zn impurities in the reference spectrum itself.

Figure S5. GIXRD and Raman spectra of Cu₁₂As₄S₁₃ nanoparticles treated in an H₂S atmosphere for 1 h at 350 °C with H₂S flow maintained during the cool down procedure. The Cu₁₂As₄S₁₃ phase is maintained both here and in the case where H₂S flow is stopped during the cool down procedure (Figure S4, spectrum E). This result eliminates the possibility of a phase change during the cool down procedure, further confirming that H₂S promotes the formation of the cubic Cu₁₂As₄S₁₃ phase.
Figure S6. Raman spectra of two different spots on the Cu$_{12}$Sb$_4$S$_{13}$ NC film treated in H$_2$S for 1 h at 450 °C. Peaks corresponding to tetrahedrite Cu$_{12}$Sb$_4$S$_{13}$, chalcostibite CuSbS$_2$, and skinnerite Cu$_3$SbS$_3$ (denoted with *) are observed, suggesting an inhomogeneous film after heat treatment.

Table S3. Rietveld refinement-determined weight percent of resulting phases after Cu$_{12}$(As$_{1-x}$Sb$_x$)$_4$S$_{13}$ NPs were annealed in nitrogen for 1 h at 450 °C. Significant decomposition is observed in the purely Sb- and As-samples, while the mixed alloy compositions displayed significantly higher resistance to decomposition into crystalline secondary phases.

<table>
<thead>
<tr>
<th>Starting Composition</th>
<th>x = 0</th>
<th>x = 0.25</th>
<th>x = 0.50</th>
<th>x = 0.75</th>
<th>x = 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$<em>{12}$(As$</em>{1-x}$Sb$_x$)$<em>4$S$</em>{13}$</td>
<td>46.1</td>
<td>93.2</td>
<td>99.6</td>
<td>100.0</td>
<td>94.4</td>
</tr>
<tr>
<td>Digenite Cu$_{13}$S</td>
<td>53.9</td>
<td>6.8</td>
<td>0.4</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Skinnerite Cu$_3$SbS$_3$</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>5.6</td>
</tr>
</tbody>
</table>
Figure S7. GIXRD and Raman spectra of nanoparticles treated in a nitrogen atmosphere at 350 °C for 1 h. (A) Cu$_{12}$Sb$_4$S$_{13}$, (B) Cu$_{12}$(As$_{0.25}$Sb$_{0.75}$)$_4$S$_{13}$, (C) Cu$_{12}$(As$_{0.50}$Sb$_{0.50}$)$_4$S$_{13}$, (D) Cu$_{12}$(As$_{0.75}$Sb$_{0.25}$)$_4$S$_{13}$, and (E) Cu$_{12}$As$_4$S$_{13}$. In the Raman spectrum, slight deviations of the purely antimony endmember from the reference spectrum are attributed to Zn impurities in the reference spectrum itself.

Figure S8. SEM micrographs of (A) Cu$_{12}$Sb$_4$S$_{13}$, (B) Cu$_{12}$(As$_{0.25}$Sb$_{0.75}$)$_4$S$_{13}$ (C) Cu$_{12}$(As$_{0.50}$Sb$_{0.50}$)$_4$S$_{13}$, (D) Cu$_{12}$(As$_{0.75}$Sb$_{0.25}$)$_4$S$_{13}$, and (E) Cu$_{12}$As$_4$S$_{13}$ nanoparticles heat treated in a flowing 1% H$_2$S (balance argon) atmosphere at 450 °C for 1 h. Scale bars are 5 µm.
Figure S9. SEM micrographs of (A) $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$, (B) $\text{Cu}_{12}(\text{As}_{0.25}\text{Sb}_{0.75})_4\text{S}_{13}$, (C) $\text{Cu}_{12}(\text{As}_{0.50}\text{Sb}_{0.50})_4\text{S}_{13}$, (D) $\text{Cu}_{12}(\text{As}_{0.75}\text{Sb}_{0.25})_4\text{S}_{13}$, and (E) $\text{Cu}_{12}\text{As}_4\text{S}_{13}$ nanoparticles heat treated in a flowing nitrogen atmosphere at 450 °C for 1 h. Scale bars are 5 µm.

Figure S10. SEM micrographs of (A) $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$, (B) $\text{Cu}_{12}(\text{As}_{0.25}\text{Sb}_{0.75})_4\text{S}_{13}$, (C) $\text{Cu}_{12}(\text{As}_{0.50}\text{Sb}_{0.50})_4\text{S}_{13}$, (D) $\text{Cu}_{12}(\text{As}_{0.75}\text{Sb}_{0.25})_4\text{S}_{13}$, and (E) $\text{Cu}_{12}\text{As}_4\text{S}_{13}$ nanoparticles heat treated in a flowing sulfur/argon atmosphere at 450 °C for 1 h. Scale bars are 5 µm.
Figure S11. Calculated lattice parameters of Cu$_{12}$(As$_{1-x}$Sb$_x$)$_4$S$_{13}$ NP films after heat treatment at 450 °C for 1 h in the indicated atmospheres. A nearly linear trend is observed as expected from Vegard’s law, implying that the crystalline portion of the material retained its original Sb/(Sb+As) ratio.
Supplemental Characterization for Heat Treated Cu$_{3}$As$_{1-x}$Sb$_{x}$S$_{4}$ Nanoparticles

Cu$_{3}$As$_{1-x}$Sb$_{x}$S$_{4}$ nanoparticles were synthesized according to the methods of Balow et al. They were then heat treated in sulfur, H$_2$S, and nitrogen atmospheres at 450 °C for 1 h as detailed in the main body of the paper.

Figure S12. GIXRD and Raman spectra of nanoparticles treated in an elemental sulfur atmosphere at 450 °C for 1 h. (A) Cu$_3$SbS$_4$, (B) Cu$_3$As$_{0.25}$Sb$_{0.75}$S$_4$, (C) Cu$_3$As$_{0.50}$Sb$_{0.50}$S$_4$, (D) Cu$_3$As$_{0.75}$Sb$_{0.25}$S$_4$, and (E) Cu$_3$As$_4$. Peaks marked with a * correspond to orthorhombic enargite Cu$_3$AsS$_4$ (JCPDS 01-082-1464). In the GIXRD and Raman spectra, slight deviations of the purely arsenic endmember from the reference spectra are attributed to Sb impurities in the reference spectra themselves. The Raman peaks around 490 cm$^{-1}$ are attributed to excess sulfur on the surface.$^{1-3}$
Figure S13. GIXRD and Raman spectra of nanoparticles treated in an H$_2$S atmosphere at 450 °C for 1 h. (A) Cu$_3$SbS$_4$, (B) Cu$_3$As$_{0.25}$Sb$_{0.75}$S$_4$, (C) Cu$_3$As$_{0.50}$Sb$_{0.50}$S$_4$, (D) Cu$_3$As$_{0.75}$Sb$_{0.25}$S$_4$, and (E) Cu$_3$AsS$_4$. In the GIXRD spectra, the peak marked with (*) in A is attributable to the (222) stretch of tetrahedrite Cu$_{12}$Sb$_4$S$_{13}$ (JCPDS #42-560), and the peaks marked with (+) in spectra C-E are attributable to digenite Cu$_{1.8}$S (JCPDS 01-088-2045). In the Raman spectra, slight deviations of the purely antimony endmember from the reference spectrum are attributed to Zn impurities in the reference spectrum itself. Severe reductions in the Cu$_{12}$As$_4$S$_{13}$ $\nu_1$ stretch relative to the Cu$_{12}$Sb$_4$S$_{13}$ $\nu_1$ stretch imply more significant decomposition in the arsenic-rich compositions relative to the antimony-rich compositions. Cu$_3$SbS$_3$ was not detected by Raman in these films; the reader is referred elsewhere for a reference spectrum.
Figure S14. GIXRD and Raman spectra of nanoparticles treated in a nitrogen atmosphere at 450 °C for 1 h. (A) Cu$_3$SbS$_4$, (B) Cu$_3$As$_{0.25}$Sb$_{0.75}$S$_4$, (C) Cu$_3$As$_{0.50}$Sb$_{0.50}$S$_4$, (D) Cu$_3$As$_{0.75}$Sb$_{0.25}$S$_4$, and (E) Cu$_3$AsS$_4$. In GIXRD spectra D and E, the (*) correspond to a digenite Cu$_{1.8}$S impurity phase (JCPDS 01-088-2045). In the Raman spectrum, slight deviations of the purely antimony endmember from the reference spectrum are attributed to Zn impurities in the reference spectrum itself. Additionally, severe reductions in the Cu$_{12}$As$_4$S$_{13}$ $\nu_1$ stretch relative to the Cu$_{12}$Sb$_4$S$_{13}$ $\nu_1$ stretch imply more significant decomposition in the arsenic-rich compositions relative to the antimony-rich compositions.

REFERENCES