Electronic Supplementary Information (ESI)

Electronic and Thermoelectric Properties of Zn and Se Double Substituted Tetrahedrite

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Figure S1: Refined XRD pattern for Cu\textsubscript{11}Zn\textsubscript{1}Sb\textsubscript{4}S\textsubscript{12.75}Se\textsubscript{0.25} done using Rietveld analysis.
Figure S2: Refined XRD pattern for Cu$_{11}$Zn$_{1}$Sb$_{4}$S$_{12.5}$Se$_{0.5}$ done using Rietveld analysis.

Figure S3: Refined XRD pattern for Cu$_{11}$Zn$_{1}$Sb$_{4}$S$_{12.25}$Se$_{0.75}$ done using Rietveld analysis.
Figure S4: Refined XRD pattern for Cu$_{11}$Zn$_1$Sb$_4$S$_{12}$Se$_1$ done using Rietveld analysis.

Figure S5: Refined XRD pattern for Cu$_{11}$Zn$_1$Sb$_4$S$_{11}$Se$_2$ done using Rietveld analysis.
Figure S6: X-ray photoelectron spectroscopy (XPS) spectrum of Cu in Cu$_{11}$Zn$_1$Sb$_4$S$_{12.5}$Se$_{0.5}$

Figure S7: X-ray photoelectron spectroscopy (XPS) spectrum of Sb in Cu$_{11}$Zn$_1$Sb$_4$S$_{12.5}$Se$_{0.5}$
Figure S8: X-ray photoelectron spectroscopy (XPS) spectrum of S in Cu$_{11}$Zn$_4$Sb$_4$S$_{12.5}$Se$_{0.5}$
Figure S9: Bandstructure of pristine compound Cu$_{12}$Sb$_4$S$_{13}$

Figure S10: Projected density of states (PDOS) of the pristine compound Cu$_{12}$Sb$_4$S$_{13}$
Figure S11: Bandstructure of Zn only substituted compound Cu_{11}Zn_{1}Sb_{4}S_{13}

Figure S12: Projected density of states (PDOS) of the Zn only substituted compound

Cu_{11}Zn_{1}Sb_{4}S_{13}
Table S1: XPS peak assignment corresponding to the oxidation states of individual elements.

<table>
<thead>
<tr>
<th>Element</th>
<th>Peak</th>
<th>B.E(eV)(^a)</th>
<th>Oxidation state</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>2p(_{3/2})</td>
<td>931.6 eV</td>
<td>+1</td>
</tr>
<tr>
<td></td>
<td>2p(_{3/2})</td>
<td>941.7 eV</td>
<td>+2</td>
</tr>
<tr>
<td></td>
<td>2p(_{1/2})</td>
<td>951.8 eV</td>
<td>+1</td>
</tr>
<tr>
<td></td>
<td>2p(_{1/2})</td>
<td>962.3 eV</td>
<td>+2</td>
</tr>
<tr>
<td>Sb</td>
<td>3d(_{5/2})</td>
<td>529.3 eV</td>
<td>+3</td>
</tr>
<tr>
<td></td>
<td>3d(_{3/2})</td>
<td>538.9 eV</td>
<td>+3</td>
</tr>
<tr>
<td>S</td>
<td>2p(_{3/2})</td>
<td>160.2 eV</td>
<td>-2</td>
</tr>
<tr>
<td></td>
<td>2p(_{3/2})</td>
<td>161.6 eV</td>
<td>-2</td>
</tr>
</tbody>
</table>

\(^a\) The binding energy of the XPS peaks are indexed from the NIST database.
For comparison of the Zn (only) and Se (only) substituted samples, Figures S14 – S18 show the transport properties of Cu$_{11}$Zn$_1$Sb$_4$S$_{13}$ (ref: Tippireddy et al., J. Phys. Chem. C., 122, 8735 - 8749) and Cu$_{12}$Sb$_4$S$_{12}$Se$_1$ (The data reprinted with permission from Lu et al., Chem. Mater, 2016, 28, 1781-1786. Copyright (2016) American Chemical Society).
Figure S16

Figure S17
Figure S18