Supporting Information


The Effects of Te\(^{2−}\) and I\(^{−}\) Substitutions on the Electronic Structures, Thermoelectric Performance, and Hardness in Melt-Quenched Highly Dense Cu\(_{2−x}\)Se

Lanling Zhao, Xiaolin Wang, * Frank F. Yun, Jiyang Wang, Zhenxiang Cheng, Shixue Dou, Jun Wang, and G. Jeffrey Snyder
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The effects of $\text{Te}^{2-}$ and $\Gamma$ Substitutions on Electronic structures, Thermoelectric Performance, and hardness in Melt-quenching Formed Highly Dense $\text{Cu}_2\text{xSe}$

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Figure S1. First Brillouin zone of the primitive cell for high temperature $\beta$-phase $\text{Cu}_2\text{Se}$. The blue lines indicate the Brillouin zone path used for the electronic band structure calculations.
Table S1. Atomic positions for the as-prepared un-doped, and I-doped Cu$_2$Se samples deduced from Rietveld refinements of XRD patterns.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Cu$_2$Se</th>
<th>Cu$<em>2$I$</em>{0.06}$Se$_{0.94}$</th>
<th>Cu$<em>2$I$</em>{0.10}$Se$_{0.92}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$x/a$</td>
<td>$y/b$</td>
<td>$z/c$</td>
</tr>
<tr>
<td>Cu1</td>
<td>0.3817(1)</td>
<td>0.0806(1)</td>
<td>0.3208(6)</td>
</tr>
<tr>
<td>Cu2</td>
<td>0.8910(1)</td>
<td>0.9160(0)</td>
<td>0.4405(1)</td>
</tr>
<tr>
<td>Cu3</td>
<td>0.8552(8)</td>
<td>0.2484(6)</td>
<td>0.3231(6)</td>
</tr>
<tr>
<td>Cu4</td>
<td>0.4343(0)</td>
<td>0.0708(9)</td>
<td>0.4510(8)</td>
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<tr>
<td>Cu5</td>
<td>0.1915(7)</td>
<td>0.1844(8)</td>
<td>0.3888(5)</td>
</tr>
<tr>
<td>Cu6</td>
<td>0.8995(0)</td>
<td>0.2488(2)</td>
<td>0.4353(7)</td>
</tr>
<tr>
<td>Cu7</td>
<td>0.6401(8)</td>
<td>0.9003(2)</td>
<td>0.3658(9)</td>
</tr>
<tr>
<td>Cu8</td>
<td>0.8215(6)</td>
<td>0.8998(6)</td>
<td>0.2931(9)</td>
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<tr>
<td>Cu9</td>
<td>0.4958(5)</td>
<td>0.2639(5)</td>
<td>0.3488(2)</td>
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<tr>
<td>Cu10</td>
<td>0.6836(2)</td>
<td>0.0858(8)</td>
<td>0.3915(5)</td>
</tr>
<tr>
<td>Cu11</td>
<td>0.9684(8)</td>
<td>0.0201(5)</td>
<td>0.3490(5)</td>
</tr>
<tr>
<td>Cu12</td>
<td>0.2703(5)</td>
<td>0.9276(9)</td>
<td>0.3977(7)</td>
</tr>
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<td>Se1</td>
<td>0.0677(9)</td>
<td>0.0700(6)</td>
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<tr>
<td>Se2</td>
<td>0.6782(6)</td>
<td>0.0867(6)</td>
<td>0.2995(7)</td>
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<tr>
<td>Se3</td>
<td>0.2013(4)</td>
<td>0.2442(1)</td>
<td>0.3140(3)</td>
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<tr>
<td>Se4</td>
<td>0.0720(9)</td>
<td>0.7441(4)</td>
<td>0.4425(1)</td>
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<tr>
<td>Se5</td>
<td>0.5669(2)</td>
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<tr>
<td>Se6</td>
<td>0.1927(0)</td>
<td>0.9177(8)</td>
<td>0.3103(2)</td>
</tr>
<tr>
<td>I</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Te</td>
<td>-</td>
<td>-</td>
<td>-</td>
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</table>
Table S2. Atomic positions for the as-prepared Te-doped Cu$_{2-x}$Se samples deduced from Rietveld refinements of XRD patterns.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Cu$<em>{2-x}$Te$</em>{0.06}$Se</th>
<th>Cu$<em>{2-x}$Te$</em>{0.16}$Se$_{0.94}$</th>
<th>Cu$<em>{2-x}$Te$</em>{0.16}$Se$_{0.84}$</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>x/a</td>
<td>y/b</td>
<td>z/c</td>
</tr>
<tr>
<td>Cu1</td>
<td>0.4116(4)</td>
<td>0.0832(9)</td>
<td>0.3272(0)</td>
</tr>
<tr>
<td>Cu2</td>
<td>0.8912(2)</td>
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<td>0.4293(3)</td>
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<tr>
<td>Cu3</td>
<td>0.8714(6)</td>
<td>0.2481(1)</td>
<td>0.3035(5)</td>
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<tr>
<td>Cu4</td>
<td>0.4283(5)</td>
<td>0.0747(7)</td>
<td>0.4454(4)</td>
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<tr>
<td>Cu5</td>
<td>0.2264(0)</td>
<td>0.2055(2)</td>
<td>0.3962(5)</td>
</tr>
<tr>
<td>Cu6</td>
<td>0.9075(9)</td>
<td>0.2423(0)</td>
<td>0.4389(5)</td>
</tr>
<tr>
<td>Cu7</td>
<td>0.6125(4)</td>
<td>0.9103(1)</td>
<td>0.3686(0)</td>
</tr>
<tr>
<td>Cu8</td>
<td>0.8702(6)</td>
<td>0.9091(9)</td>
<td>0.2877(9)</td>
</tr>
<tr>
<td>Cu9</td>
<td>0.5734(4)</td>
<td>0.3094(9)</td>
<td>0.3915(1)</td>
</tr>
<tr>
<td>Cu10</td>
<td>0.6609(8)</td>
<td>0.0921(1)</td>
<td>0.3930(8)</td>
</tr>
<tr>
<td>Cu11</td>
<td>0.9354(5)</td>
<td>0.0590(5)</td>
<td>0.3566(1)</td>
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<tr>
<td>Cu12</td>
<td>0.2634(3)</td>
<td>0.9343(7)</td>
<td>0.3971(3)</td>
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<tr>
<td>Se1</td>
<td>0.0569(5)</td>
<td>0.0758(7)</td>
<td>0.4456(7)</td>
</tr>
<tr>
<td>Se2</td>
<td>0.6930(0)</td>
<td>0.0876(5)</td>
<td>0.3063(0)</td>
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<tr>
<td>Se3</td>
<td>0.2062(4)</td>
<td>0.2166(8)</td>
<td>0.3068(5)</td>
</tr>
<tr>
<td>Se4</td>
<td>0.0814(7)</td>
<td>0.7500(1)</td>
<td>0.4444(6)</td>
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<td>Se5</td>
<td>0.5724(9)</td>
<td>0.8987(5)</td>
<td>0.4479(9)</td>
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<td>0.2214(9)</td>
<td>0.9078(7)</td>
<td>0.3134(5)</td>
</tr>
<tr>
<td>I</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Te</td>
<td>0.1660(8)</td>
<td>0.9510(7)</td>
<td>0.3156(1)</td>
</tr>
</tbody>
</table>
Table S3. Lattice parameters, R-factors for the as-prepared Te-doped Cu$_{2-x}$Se samples deduced from Rietveld refinements of XRD patterns.

<table>
<thead>
<tr>
<th>Sample</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>β</th>
<th>V (Å$^3$)</th>
<th>Rp</th>
<th>Rwp</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$_2$Se</td>
<td>7.117(7)</td>
<td>12.358(6)</td>
<td>27.278(2)</td>
<td>94.112(6)</td>
<td>2392.0(1)</td>
<td>1.820</td>
<td>2.793</td>
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<tr>
<td>Cu$<em>{2-0.02}$Se$</em>{0.98}$</td>
<td>7.159(4)</td>
<td>12.249(1)</td>
<td>27.366(8)</td>
<td>94.556(2)</td>
<td>2392.2(1)</td>
<td>2.126</td>
<td>3.225</td>
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<tr>
<td>Cu$<em>{2-0.01}$Se$</em>{0.99}$</td>
<td>7.136(5)</td>
<td>12.361(6)</td>
<td>27.310(6)</td>
<td>94.572(7)</td>
<td>2401.6(3)</td>
<td>1.989</td>
<td>2.971</td>
</tr>
<tr>
<td>Cu$<em>{2-0.15}$Se$</em>{0.85}$</td>
<td>7.214(7)</td>
<td>12.345(2)</td>
<td>27.608(6)</td>
<td>94.789(3)</td>
<td>2450.4(3)</td>
<td>2.383</td>
<td>3.401</td>
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<tr>
<td>Cu$<em>{2-0.08}$Se$</em>{0.92}$</td>
<td>7.115(1)</td>
<td>12.350(3)</td>
<td>27.306(5)</td>
<td>94.155(2)</td>
<td>2393.2(1)</td>
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<tr>
<td>Cu$<em>{2-0.08}$Se$</em>{0.92}$</td>
<td>7.117(2)</td>
<td>12.368(1)</td>
<td>27.274(4)</td>
<td>94.033(4)</td>
<td>2394.9(2)</td>
<td>2.586</td>
<td>3.505</td>
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</table>
**Figure S2.** Typical cross-section FE-SEM images for the fabricated un-doped, Te-doped and I-doped Cu$_{2-x}$Se bulks