Supporting Information

Rattling-Induced Ultralow Thermal Conductivity Leading to Exceptional Thermoelectric Performance in AgIn₅S₈

Rinkle Juneja and Abhishek K. Singh*

Materials Research Centre, Indian Institute of Science, Bangalore 560012, India

E-mail: abhishek@iisc.ac.in
**Electron localization function for CuIn₅S₈**

Figure S1 shows the ELF for CuIn₅S₈ along (110) plane. There is very weak bonding of Cu with the neighboring S atoms, whereas In and neighboring S atoms have stronger bonding.

![Electron localization function for CuIn₅S₈](image)

Figure S1: Electron localization function along (110) plane for CuIn₅S₈.

**Phonon dispersion and phonon density of states**

Figure S2 a and d show the phonon dispersion for AgIn₅S₈ and CuIn₅S₈, respectively. There are no imaginary frequencies, hence both the systems are dynamically stable. Figure S2 b and e show the phonon density of states for AgIn₅S₈ and CuIn₅S₈, respectively. The heavier atoms Ag and In for AgIn₅S₈ (Cu and In for CuIn₅S₈) lie in low frequency regime, whereas lighter S atoms span across high frequencies. Due to lighter mass of Cu, it spans slightly high frequency regime as compared to Ag. These differences result in different $\kappa_l$ in AgIn₅S₈ and CuIn₅S₈, as shown in table S1. Figure S2 c and f show the phonon density of states for the deformed lattice under 5 % hydrostatic pressure. Under this deformation, the rattler states are getting affected. In AgIn₅S₈, the Ag atoms shift more prominently towards higher frequency side than Cu atoms in CuIn₅S₈.
Figure S2: (a) and (d) Phonon dispersion, (b) and (e) Phonon density of states, (c) and (f) Phonon density of states for the deformed lattice, for AgIn$_5$S$_8$ and CuIn$_5$S$_8$, respectively.

Table S1: Parameters deciding the differences in $\kappa_l$ in AgIn$_5$S$_8$ and CuIn$_5$S$_8$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mass of rattler atom</th>
<th>Frequency span</th>
<th>$\kappa_l$ at 1000 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgIn$_5$S$_8$</td>
<td>107.668</td>
<td>2.0 - 2.3</td>
<td>0.29 W/mK</td>
</tr>
<tr>
<td>CuIn$_5$S$_8$</td>
<td>63.546</td>
<td>2.5 - 3.0</td>
<td>0.54 W/mK</td>
</tr>
</tbody>
</table>
Electronic band structure, electronic density of states, and charge density

Figure S3 a and c show the electronic band structure and density of states for AgIn$_5$S$_8$ and CuIn$_5$S$_8$, respectively. Both the systems are semiconductors with similar dispersion. The valence band states near the Fermi level has major contribution from Cu in CuIn$_5$S$_8$, as compared to Ag in AgIn$_5$S$_8$. This implies that Cu will have more significant effect on the $p$-type electronic transport in CuIn$_5$S$_8$. This is further evident from the charge density contribution of the top most valence band as shown in Figure S3 b and d for AgIn$_5$S$_8$ and CuIn$_5$S$_8$, respectively. In case of AgIn$_5$S$_8$, it is contributed by 3 S and 1 Ag atoms, whereas it is only contributed by Cu atoms in CuIn$_5$S$_8$.

Figure S3: (a) and (c) Electronic band structure and density of states for AgIn$_5$S$_8$ and CuIn$_5$S$_8$, respectively. (b) and (d) Charge density for the top most valence band for AgIn$_5$S$_8$ and CuIn$_5$S$_8$, respectively.
Electronic transport properties of CuIn$_5$S$_8$

Figure S4 a and b show the calculated Seebeck coefficient ($S$), and electrical conductivity divided by relaxation time ($\sigma/\tau$) for CuIn$_5$S$_8$. Due to presence of flat valence bands, $S$ is higher for $p$-doped than $n$-doped CuIn$_5$S$_8$. On the other hand, the parabolic dispersion in conduction band states result in very high $n$-type $\frac{\sigma}{\tau}$ than $p$-type. The $p$-type $\frac{\sigma}{\tau}$ in CuIn$_5$S$_8$ is even lower as compared to AgIn$_5$S$_8$. This is because the rattling Cu atom has major contribution to the valence band states near the Fermi level as compared to Cu. Assuming the major contribution to electrical conductivity is coming from these states, it gets reduced significantly in CuIn$_5$S$_8$. The scaled power factor ($S^2\sigma/\tau$) is shown in Figure S4 c. Due to very high $n$-type $\frac{\sigma}{\tau}$, the power factor for $n$-doped CuIn$_5$S$_8$ is higher than $p$-doped. However, this $n$-type scaled power factor for CuIn$_5$S$_8$ is lower as compared to $p$-type in AgIn$_5$S$_8$.

Figure S4: Calculated (a) Seebeck coefficient, (b) electrical conductivity divided by relaxation time, (c) power factor divided by relaxation time as a function of carrier concentration for CuIn$_5$S$_8$. The solid and dotted curves correspond to $p$-type and $n$-type doping, respectively.