Realizing a Stable High Thermoelectric $zT \sim 2$ over a Broad Temperature Range in Ge$_{1-x-y}$Ga$_x$Sb$_y$Te – via Band Engineering and Hybrid Flash-SPS Processing

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10. $zT$ for Ge$_{0.90}$Sb$_{0.10}$Te
1. SPS vs Hybrid Flash-SPS

The schematics of the experimental set-up and the current flow paths for SPS (graphite punches and die), Flash-SPS (graphite punches and no die) and Hybrid Flash-SPS (graphite punches and a thin walled stainless steel die) configurations are shown in Figure S1.

**Figure S1.** Flow of current in SPS (a, b); Flash-SPS (c); and Hybrid Flash-SPS (d) configurations. Information pertaining to each configuration are tabulated below in **Table S1**.

<table>
<thead>
<tr>
<th>Configurations</th>
<th>Figure (a)</th>
<th>Figure (b)</th>
<th>Figure (c)</th>
<th>Figure (d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Description / Notation</td>
<td>SPS, graphite punches and die</td>
<td>SPS, graphite punches and die</td>
<td>Flash-SPS, graphite punches and no die</td>
<td>‘Hybrid’ Flash-SPS, graphite punches and a <em>thin walled stainless steel die</em></td>
</tr>
<tr>
<td>Sample Resistivity</td>
<td>&gt; 100 µΩm</td>
<td>&lt; 10 µΩm</td>
<td>&lt; 10 µΩm</td>
<td>&lt; 10 µΩm</td>
</tr>
<tr>
<td>Sample Current Density</td>
<td>&lt; 10 A/cm²</td>
<td>10 – 400 A/cm²</td>
<td>&gt; 400 A/cm²</td>
<td>&gt; 400 A/cm²</td>
</tr>
<tr>
<td>Typical Heating Rate</td>
<td>~ 100 °C/min</td>
<td>~ 10,000 °C/min</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
2. DSC Curves

Figure S2. DSC curves for Ge$_{1-x}$Ga$_x$Te ($x = 0.02$) and Ge$_{1-x-y}$Ga$_x$Sb$_y$Te ($x = 0.02$; $y = 0.10$) samples. For pristine GeTe, the transition temperature was around 700 K, which reduced to 630 K for Ga-doped GeTe and further to 580 K for Ga-Sb codoped GeTe.
3. Thermal Diffusivity D

![Figure S3](image)

**Figure S3.** Temperature-dependent thermal diffusivity, D for Ge$_{1-x}$Ga$_x$Te ($x = 0.00 – 0.07$) and Ge$_{1-x}$Ga$_x$Sb$_y$Te ($x = 0.02; y = 0.08, 0.10$) samples.
4. Estimation of Lorenz number $L$

**Figure S4.** Temperature dependence of the Lorenz number ($L$) for $\text{Ge}_{1-x}\text{Ga}_x\text{Te}$ ($x = 0.00 - 0.07$) and $\text{Ge}_{1-x-y}\text{Ga}_x\text{Sb}_y\text{Te}$ ($x = 0.02; y = 0.08, 0.10$) samples, calculated by fitting the respective Seebeck coefficient values.
5. Electronic ($\kappa_e$) and lattice ($\kappa_{\text{latt}}$) thermal conductivities

Figure S5. Temperature-dependent (a) electronic ($\kappa_e$) thermal conductivity and (b) lattice ($\kappa_{\text{latt}}$) thermal conductivity, for Ge$_{1-x}$Ga$_x$Te ($x = 0.00$ – $0.07$) and Ge$_{1-x-y}$Ga$_x$Sb$_y$Te ($x = 0.02$; $y = 0.08$, $0.10$) samples.
6. $zT$ for $\text{Ge}_{0.90}\text{Ga}_{0.10}\text{Te}$

*Figure S6. Temperature-dependent figure of merit, $zT$ for $\text{Ge}_{1-x}\text{Ga}_x\text{Te}$ ($x = 0.10$) sample.*
7. $zT$ for Ge$_{0.96}$Ga$_{0.02}$Sb$_{0.02}$Te and Ge$_{0.96}$Ga$_{0.02}$Sb$_{0.04}$Te

![Graph showing temperature-dependent $zT$ for Ge$_{0.96}$Ga$_{0.02}$Sb$_{0.02}$Te and Ge$_{0.94}$Ga$_{0.02}$Sb$_{0.04}$Te samples.]

*Figure S7. Temperature-dependent $zT$ for Ge$_{0.96}$Ga$_{0.02}$Sb$_{0.02}$Te and Ge$_{0.94}$Ga$_{0.02}$Sb$_{0.04}$Te samples.*
8. Transport properties for $\text{Ge}_{0.90}\text{Ga}_{0.02}\text{Sb}_{0.08}\text{Te}$ – Hybrid Flash-SPS Vs SPS

Figure S8. Temperature-dependent electrical and thermal transport properties for $\text{Ge}_{0.90}\text{Ga}_{0.02}\text{Sb}_{0.08}\text{Te}$ sample prepared by SPS and Hybrid Flash-SPS.
9. Band folding in GeTe super-cell

**Figure S9.** Brillouin zone of the irreducible cell (black) and several Brillouin zone of the 4 x 4 x 4 c-GeTe super-cell (red, green, blue). The orange point indicate the approximate position of the second valence band maximum.

For the 4 x 4 x 4 c-GeTe super-cell, the reciprocal vectors (and the Brillouin zone) are four times smaller. To understand where the \( \Sigma \) direction is folded, one can draw the adjacent Brillouin zones. The \( \Sigma \) direction correspond to a path \( \Gamma K X' K'' \) (where prime and double prime indicate nearest and next nearest Brillouin zone special points). What can be confusing is that the K point for the first zone (red) correspond to the U' point of the adjacent zone (green).

To study the band structure of a super-cell in the \( \Sigma \) direction, one needs to represent the path \( \Gamma K X' \) (or equivalently the two paths \( \Gamma K \) and UX). However, for the 4 x 4 x 4 super-cell, the maximum is located on the \( \Gamma K \) path, which is the one that is actually considered in our computations. But the case of 3 x 3 x 3 super-cell is quite different, where the maximum is located on the UX path.
Figure S10. Band structure of the 4 x 4 x 4 c-GeTe super-cell along the $\Sigma$ direction. The L maximum is folded on the $\Gamma$ point. The second maximum is located just after the $K''$ point and is thus folded just before the $K$ point.
10. $zT$ for $\text{Ge}_{0.90}\text{Sb}_{0.10}\text{Te}$

![Graph showing temperature-dependent figure of merit, $zT$, for Hybrid Flash-SPSed $\text{Ge}_{1-x}\text{Sb}_x\text{Te}$ ($x = 0.10$) sample.](image)

*Figure S11. Temperature-dependent figure of merit, $zT$ for Hybrid Flash-SPSed $\text{Ge}_{1-x}\text{Sb}_x\text{Te}$ ($x = 0.10$) sample.*