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Realizing a Stable High Thermoelectric *zT* ~ 2 over a Broad Temperature Range in $Ge_{1-x-y}Ga_xSb_yTe$ – via Band Engineering and Hybrid Flash-SPS Processing

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Synopsis – Supporting Information

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.

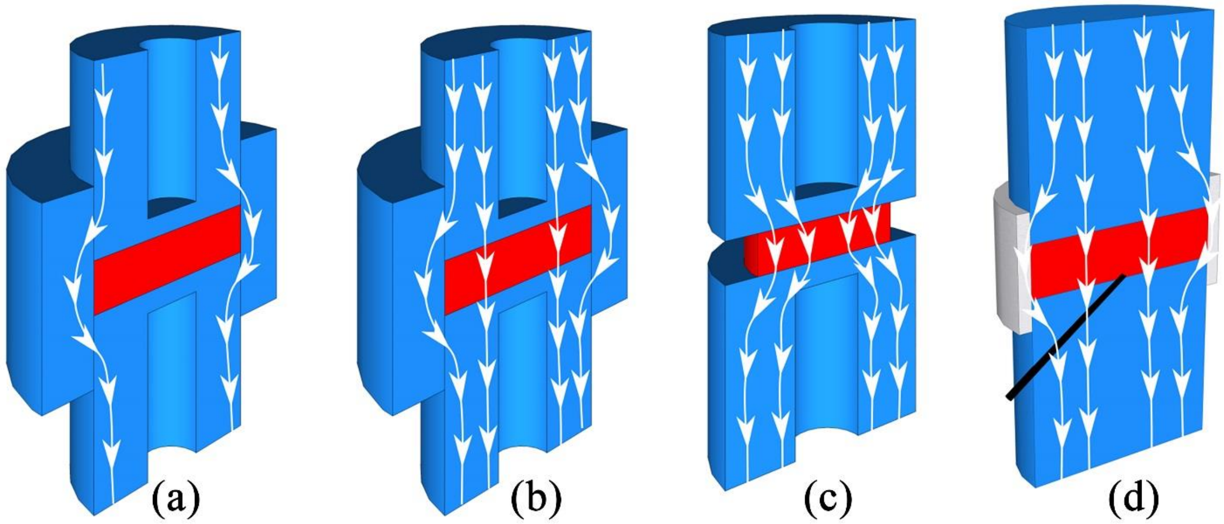

Figure S1. *Flow of current in SPS (a, b); Flash-SPS (c); and Hybrid Flash-SPS (d) configurations. Information pertaining to each configuration are tabulated below in* ***Table S1****.*

Configurations	Figure (a)	Figure (b)	Figure (c)	Figure (d)
Description / Notation	**SPS**, graphite punches and die	**SPS**, graphite punches and die	**Flash-SPS**, graphite punches and no die	**'Hybrid' Flash-SPS**, graphite punches and a ***<u>thin walled stainless steel die</u>***
Sample Resistivity	> 100 μΩm	< 10 μΩm	< 10 μΩm	< 10 μΩm
Sample Current Density	< 10 A/cm^2	10 – 400 A/cm^2	> 400 A/cm^2	> 400 A/cm^2
Typical Heating Rate	~ 100 ^{o}C/min		~ 10,000 ^{o}C/min	

2. DSC Curves

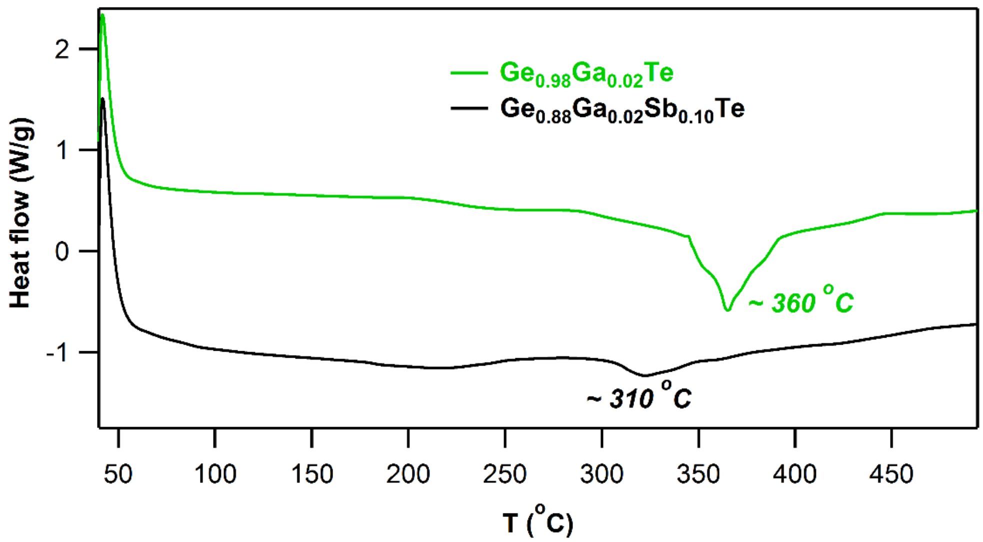

***Figure S2**. DSC curves for $Ge_{1-x}Ga_xTe$ (x = 0.02) and $Ge_{1-x-y}Ga_xSb_yTe$ (x = 0.02; y = 0.10) samples. For pristine GeTe, the transition temperature was around 700 K, which reduced to 630 K for Ga-doped GeTe and further to 580 K for Ga-Sb codoped GeTe.*

3. Thermal Diffusivity D

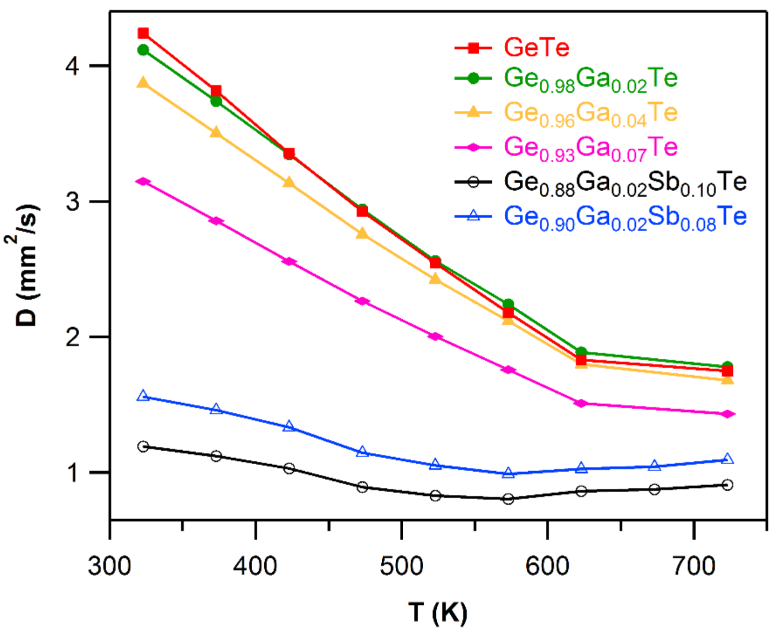

***Figure S3**. Temperature-dependent thermal diffusivity, D for $Ge_{1-x}Ga_xTe$ (x = 0.00 – 0.07) and $Ge_{1-x-y}Ga_xSb_yTe$ (x = 0.02; y = 0.08, 0.10) samples.*

4. Estimation of Lorenz number L

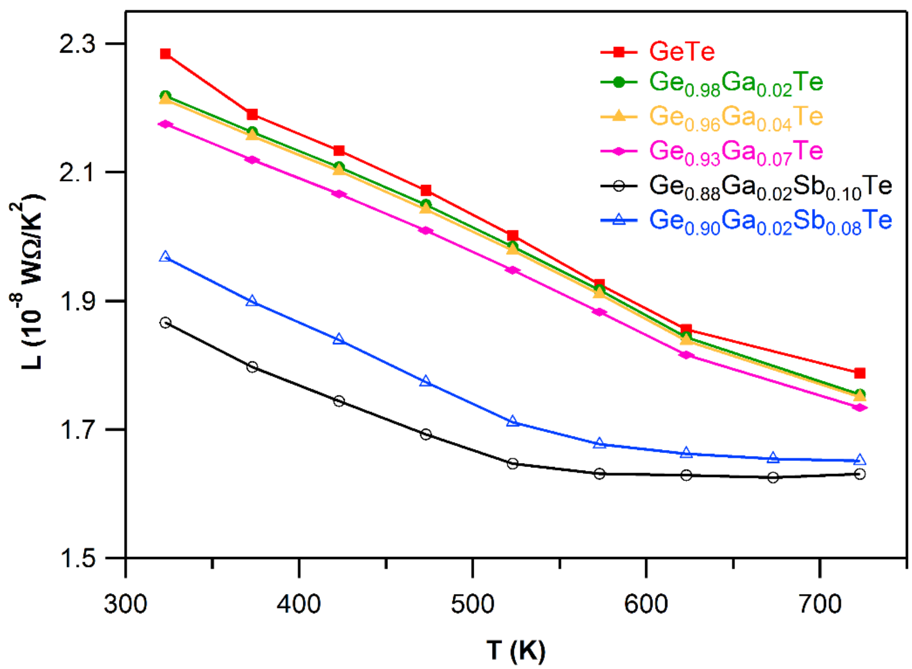

Figure S4. *Temperature dependence of the Lorenz number (L) for $Ge_{1-x}Ga_xTe$ (x = 0.00 – 0.07) and $Ge_{1-x-y}Ga_xSb_yTe$ (x = 0.02; y = 0.08, 0.10) samples, calculated by fitting the respective Seebeck coefficient values.*

5. Electronic (κ_e) and lattice (κ_{latt}) thermal conductivities

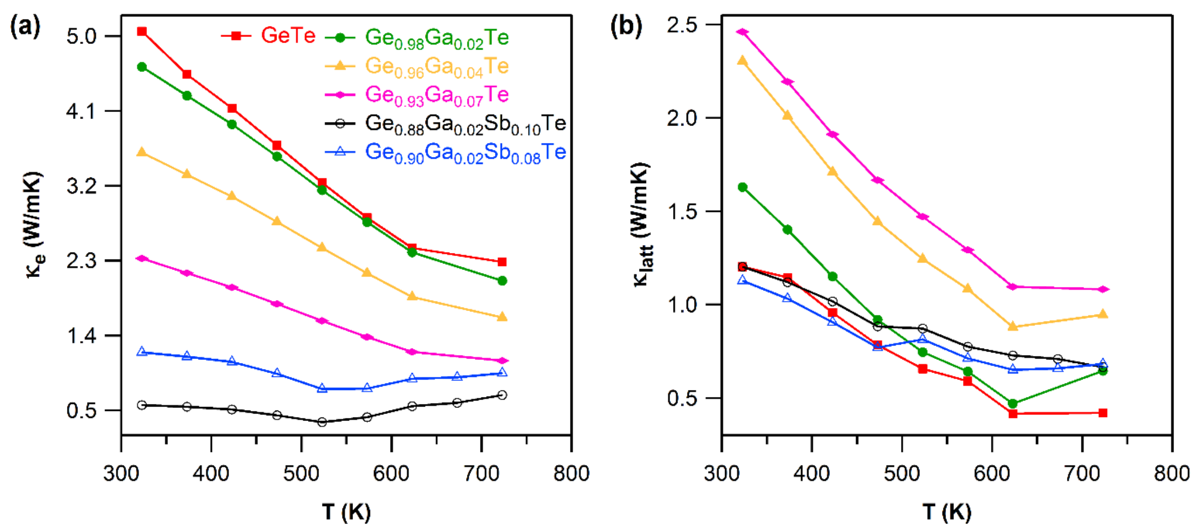

***Figure S5**. Temperature-dependent (a) electronic (κ_e) thermal conductivity and (b) lattice (κ_{latt}) thermal conductivity, for $Ge_{1-x}Ga_xTe$ (x = 0.00 – 0.07) and $Ge_{1-x-y}Ga_xSb_yTe$ (x = 0.02; y = 0.08, 0.10) samples.*

6. *zT* for $Ge_{0.90}Ga_{0.10}Te$

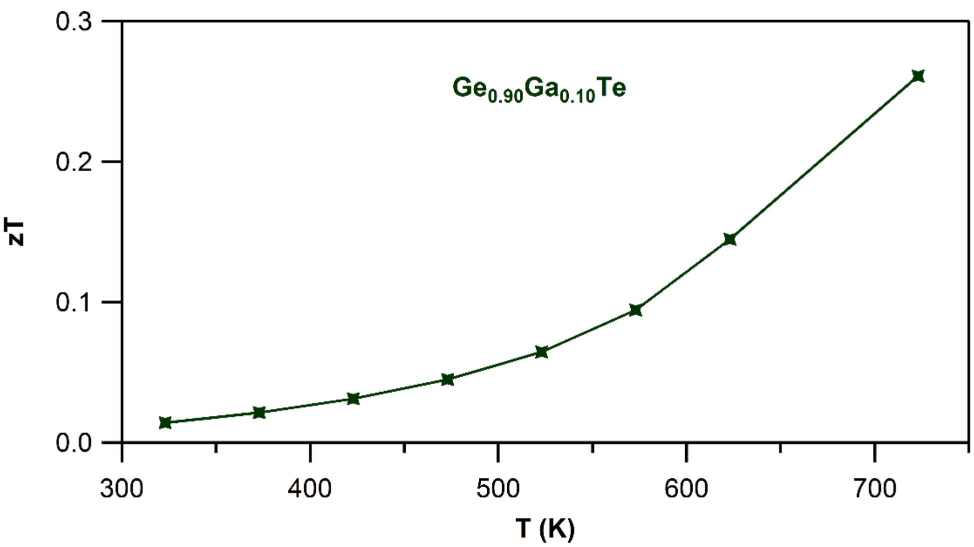

***Figure S6**. Temperature-dependent figure of merit, zT for $Ge_{1-x}Ga_xTe$ (x = 0.10) sample.*

7. *zT* for $Ge_{0.96}Ga_{0.02}Sb_{0.02}Te$ and $Ge_{0.96}Ga_{0.02}Sb_{0.04}Te$

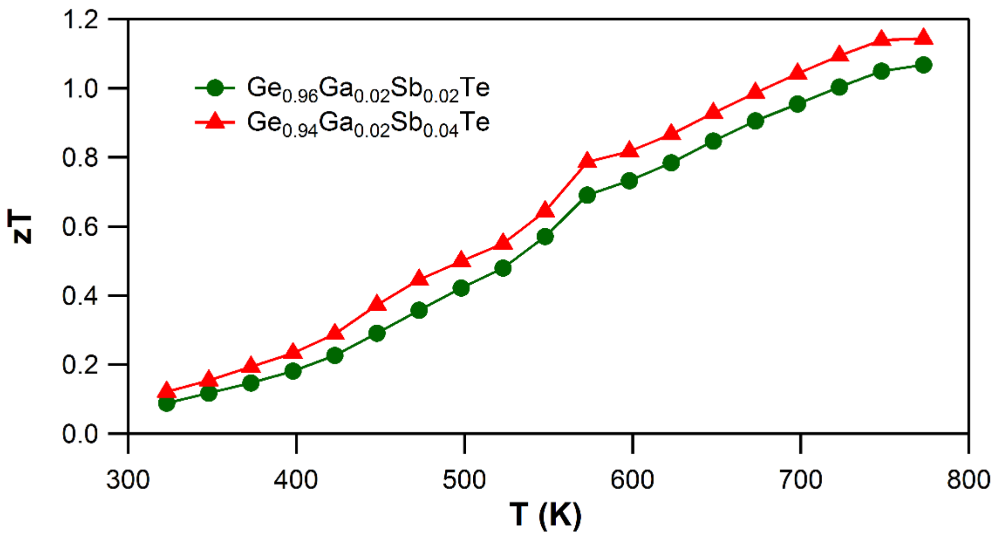

Figure S7. *Temperature-dependent zT for $Ge_{0.96}Ga_{0.02}Sb_{0.02}Te$ and $Ge_{0.94}Ga_{0.02}Sb_{0.04}Te$ samples.*

8. Transport properties for $Ge_{0.90}Ga_{0.02}Sb_{0.08}Te$ – Hybrid Flash-SPS Vs SPS

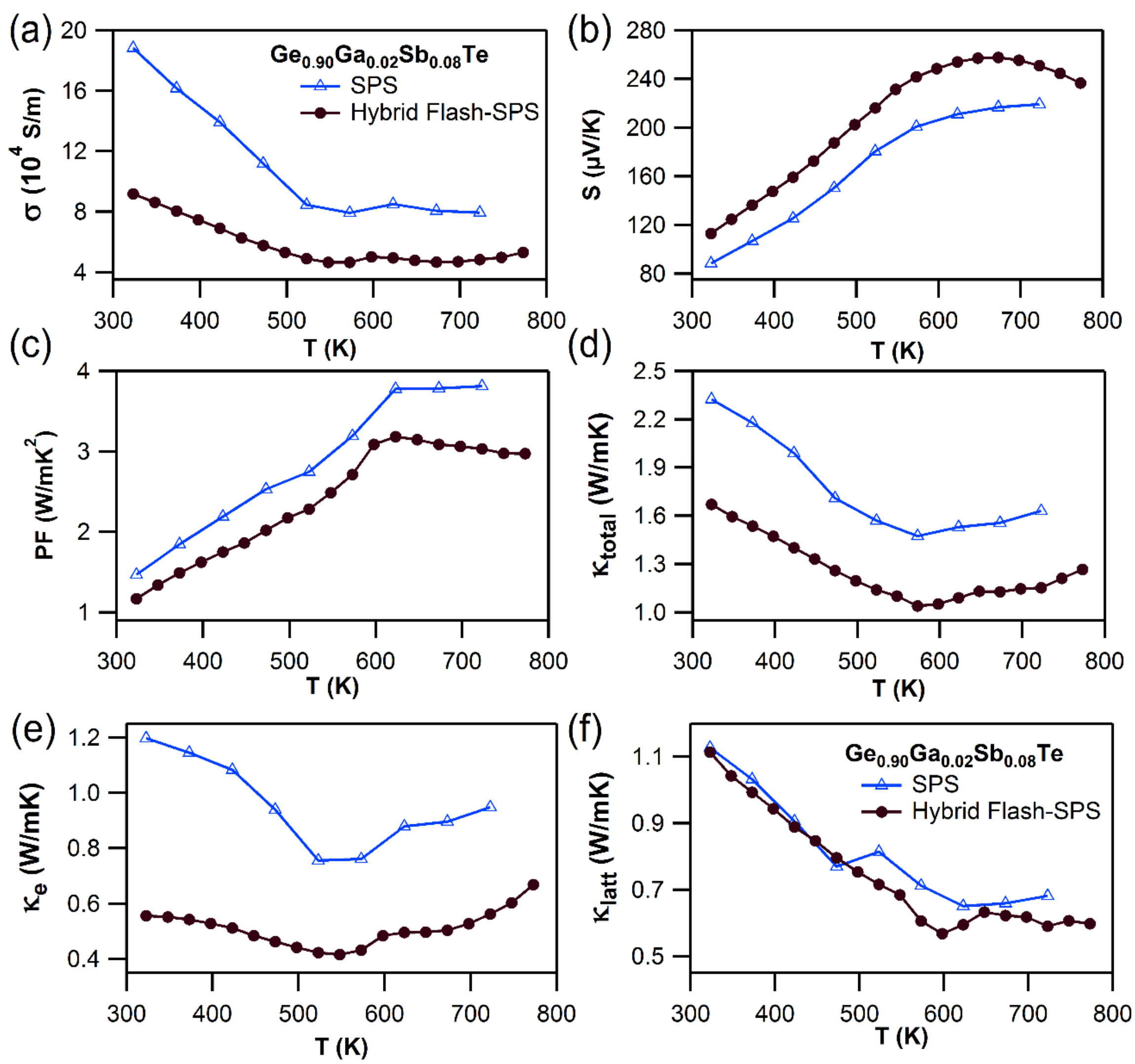

***Figure S8**. Temperature-dependent electrical and thermal transport properties for $Ge_{0.90}Ga_{0.02}Sb_{0.08}Te$ sample prepared by SPS and Hybrid Flash-SPS.*

9. Band folding in GeTe super-cell

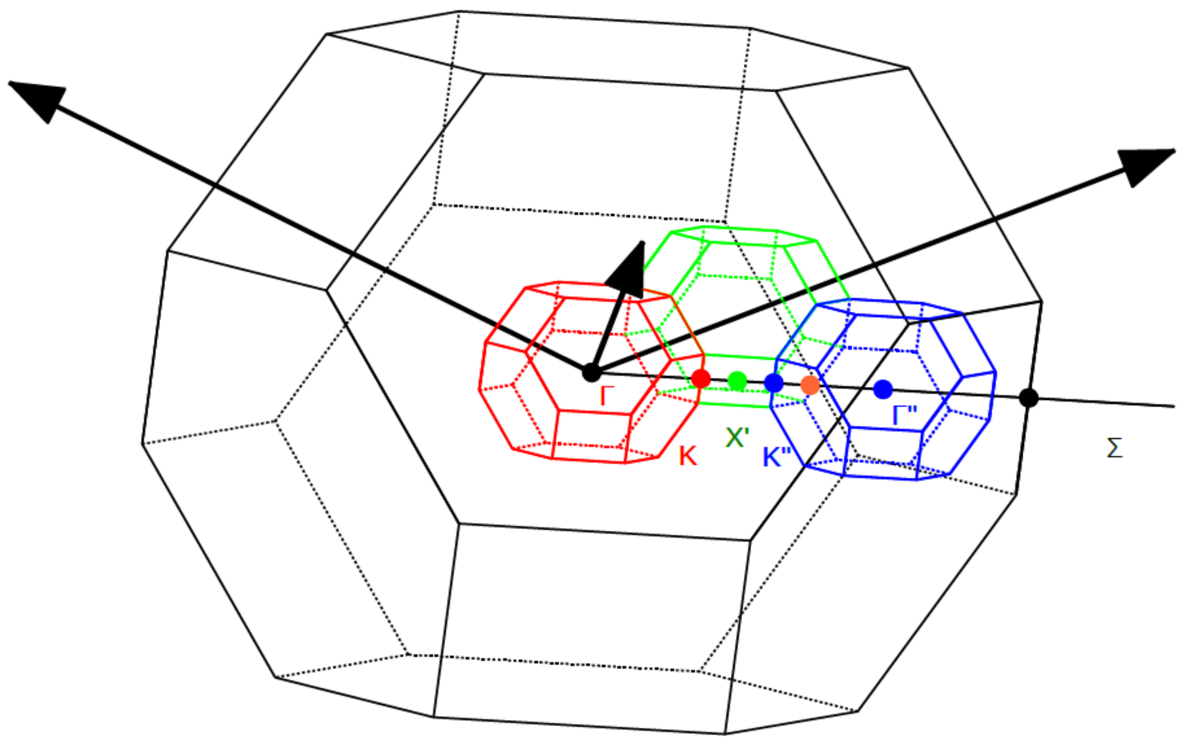

Figure S9. *Brillouin zone of the irreducible cell (black) and several Brillouin zone of the 4 x 4 x 4 c-GeTe super-cell (red, green, blue). The orange point indicate the approximate position of the second valence band maximum.*

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 Σ direction is folded, one can draw the adjacent Brillouin zones. The Σ direction correspond to a path ΓKX'K''Γ'' (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 Σ direction, one needs to represent the path ΓKX' (or equivalently the two paths ΓK and UX). However, for the 4 x 4 x 4 super-cell, the maximum is located on the ΓK 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.

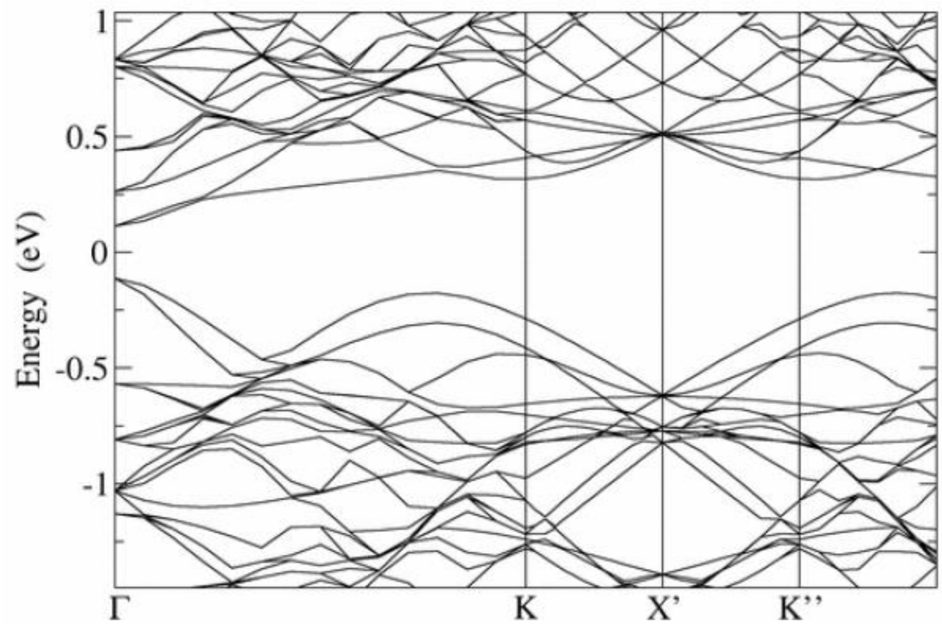

Figure S10. *Band structure of the 4 x 4 x 4 c-GeTe super-cell along the Σ direction. The L maximum is folded on the Γ point. The second maximum is located just after the K'' point and is thus folded just before the K point.*

10. *zT* for $Ge_{0.90}Sb_{0.10}Te$

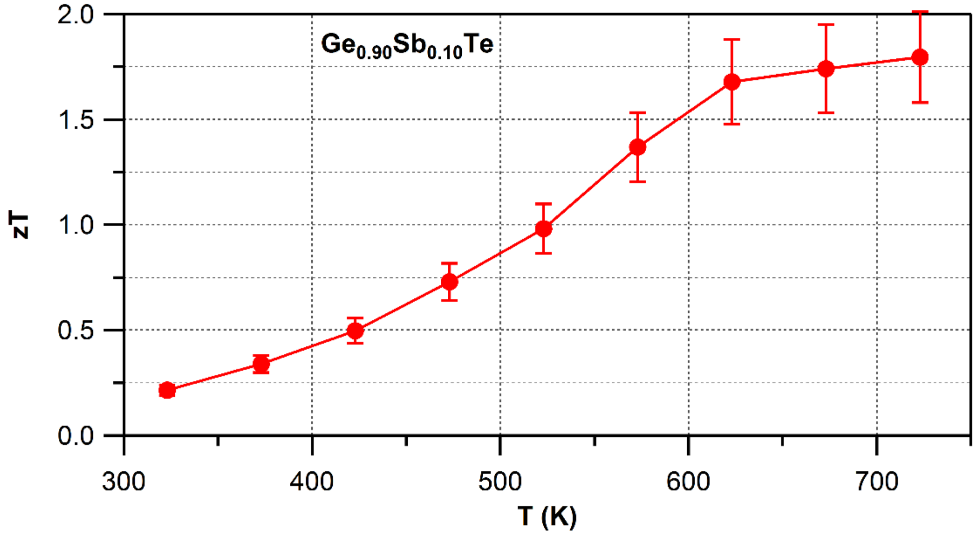

Figure S11. *Temperature-dependent figure of merit, zT for Hybrid Flash-SPSed $Ge_{1-x}Sb_xTe$ (x = 0.10) sample.*