## Supporting Information

## Suppressing Ge-vacancies to Achieve High Single-Leg Efficiency in GeTe with Ultra-High Room Temperature Power Factor

Ning Jia<sup>a,c#</sup>, Jing Cao<sup>b#</sup>, Xian Yi Tan<sup>b,c#</sup>, Jie Zheng<sup>b#</sup>, Sheau Wei Chien<sup>b</sup>, Le Yang<sup>b,d</sup>, Kewei Chen<sup>e</sup>, Hong Kuan Ng<sup>b</sup>, Solco Samantha Faye Duran<sup>b</sup>, Hongfei Liu<sup>b</sup>, Chee Kiang Ivan Tan<sup>b</sup>, Zibiao Li<sup>b,d</sup>, Jianwei Xu<sup>b\*</sup>, Jing Wu<sup>b\*</sup>, Qingyu Yan<sup>c\*</sup>, Ady Suwardi<sup>b,d\*</sup>

<sup>a</sup> State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, China.

<sup>b</sup> Institute of Materials Research and Engineering, #08-03, 2 Fusionopolis Way, Agency for Science, Technology and Research, Singapore 138634.

<sup>c</sup> School of Materials Science and Engineering, Nanyang Technological University, Singapore 639798.

<sup>d</sup> Department of Materials Science and Engineering, National University of Singapore, Singapore 117575.

<sup>e</sup> School of Mechanical and Aerospace Engineering, Nanyang Technological University, Singapore 639798.

<sup>#</sup>Equal contribution: N.J, J.C, X.Y.T, and J.Z. contributed equally to this work.

\*Corresponding authors: jw-xu@imre.a-star.edu.sg; wujing@imre.a-star.edu.sg;

alexyan@ntu.edu.sg; ady\_suwardi@imre.a-star.edu.sg

#### **Materials and Methods**

Bulk polycrystalline GeTe-based samples were prepared by mixing a stoichiometric amount of high-purity element (99.99%) at a high vacuum of 10<sup>-5</sup> mbar in quartz ampoules. Samples were subsequently melted at 1223 K and were kept at this temperature for 12 hours, followed by quenching in ice water. Annealing was performed at 900 K for 72 hours. The final ingots were then hand ground into fine powder before being consolidated using plasma activated sintering (PAS) at 823 K for 10 minutes under a pressure of 50 MPa. The size of the graphite die was 12.7 mm in diameter. The sintering was done under 1 Pa vacuum. Extra caution was taken during the cooling down by slow cooling at 15 K/min and slowly releasing the pressure to the die to avoid cracking the sample. The final density of the pellets was tested using Archimedes method (~98% theoretical density). Pellets were then cut and polished into rectangular bars for electrical testing as well as square bars for thermal measurements.

The phase purity of all samples was characterized by X-ray diffraction (XRD) equipment (D8 Advance, Bricker, Germany) with Cu Ka radiation. The high temperature Seebeck coefficient and electrical resistivity were measured using ZEM-3 from ULVAC. High temperature thermal conductivity was measured from LFA 457 Netzsch. The heat capacity used for thermal conductivity calculation was estimated using Dulong-Petit approximation. Microscopy analysis was done in field emission scanning electron microscopy FESEM (JEOL JSM 7600F). TEM was collected using JEOL 2010. Charge carrier concentrations and mobilities of the GeTe samples were determined from the Hall coefficient measurement using the Van der Pauw method (Bio-Rad Microscience, Hall measurement system HL5500, United States). Sound velocity measurement was conducted in using commercial pulsed ultrasonic generator and receiver (ithera Medical GmbH). The mechanical properties (Young's Modulus) were investigated using a nanoindentation system (Agilent G200 Nanoindenter XP) with a diamond Berkovich tip.

# Hall Concentration and Mobility

Composition	$n_H$ (cm <sup>-3</sup> )	$\mu_H(\mathrm{cm}^2/\mathrm{Vs})$
GeTe	7.5 x 10 <sup>20</sup>	59
$(GeTe)_{0.985}(Cu_2Te)_{0.015}$	2.5 x 10 <sup>20</sup>	127
$(GeTe)_{0.975}(Cu_2Te)_{0.015}In_{0.01}$	$2.05 \ge 10^{20}$	106
$(GeTe)_{0.955}(Cu_2Te)_{0.015}In_{0.01}Bi_{0.02}$	$1.15 \ge 10^{20}$	85
$(GeTe)_{0.935}(Cu_2Te)_{0.015}In_{0.01}Bi_{0.04}$	7.9 x 10 <sup>19</sup>	83
$(GeTe)_{0.915}(Cu_2Te)_{0.015}In_{0.01}Bi_{0.06}$	5.7 x 10 <sup>19</sup>	66

Table S1. Hall concentration and Hall mobility of all samples.

**Table S2.** Physical properties used to model  $\kappa_L$  in GeTe based on various phonon scattering processes.

Parameters	Values
vL, m/s	3410
vT, m/s	1995
vm, m/s	2210
Atomic mass, kg	$1.66 \ge 10^{25}$
Sample density, g/cm3	6.14
Debye T, K	122
γ	1.45
Poisson's ratio	0.24
Bulk modulus, GPa	39.9
Young's Modulus, GPa	62.2
Shear Modulus, GPa	25.5
Grain size, um	5.2



Figure S1. Room temperature Jonker analysis of the transport properties of all samples, showing



highest electronic transport quality for  $(GeTe)_{0.985}(Cu_2Te)_{0.015}$  and  $(GeTe)_{0.975}(Cu_2Te)_{0.015}In_{0.01.5}$ 

Figure S2. Transport coefficient  $\sigma_{E0}$  as a function of temperature for all samples.



Figure S3. Grain size analysis of the electron backscatter diffraction.



Figure S4. (a) Backscattered Electron Image (BEI) and (b) elemental mapping of the optimized  $(GeTe)_{0.935}(Cu_2Te)_{0.015}In_{0.01}Bi_{0.04}$  sample (scale bar: 10 µm). (c) Close-up view from the green-bordered area in (a), with the magenta-bordered inset showing the quantification results from the Energy Dispersive Spectroscopy (EDS) analysis.





Figure S5. Electronic thermal conductivity of all samples.





Figure S7. Quality factor analysis at 723 K showing potential for higher zT with doping optimization.

### **Single-leg Efficiency Measurements**

For single leg thermoelectric device characterization, sample with the size of 2.2 mm x 1.9 mm x 9.5 mm with Ag capping on both sides was used. Sample was loaded in between the hot side with embedded heater on top and the cold side connected to heat sink on the bottom, as shown in Figure S8 left figure. The heater used is Omega cartridge heater brand with 150 W power. In order to maintain a reservoir of latent energy, the heat sink is immersed under ice water while the heater is on to keep the cold side at constant temperature of 323 K. The temperature stability can be

maintained up to 2 hours with temperature fluctutation of  $\pm 1$  K. To ensure low contact resistance and low circuit resistance, the cold side is soldered to Cu plates while the hot side is attached using silver paste brand Ag Paste MDot S262 (Sliver contents- 88.0 wt%) from Mitshuboshi. Finally, to accurately characterize the amount of heat flow through the single leg device, heat flux sensor from gSKIN xm-296c with a size of 4.4 mm x 4.4 mm was installed on the cold side directly.

Figure S8 (right side) shows the schematic of the setup used to measure the single leg efficiency. The cold sides of single-leg devices were soldered to Cu plates using a Pb/Sn solder. The hot sides were attached to the copper using silver paste. K-type thermocouples were embed onto the respective Cu plates on the hot and cold sides and connected to the heater with PID feedback loop. In order to maintain a reservoir of latent energy, the heat sink is immersed under ice water while the heater is on to keep the cold side at constant temperature of 280 K. The thermoelectric efficiency is measured by comparing the power output to the heat flux input based on the following equation:

$$\eta = \frac{P}{P + Q_h} \tag{1}$$

Where P is the power output of the single leg,  $Q_h$  is the heat flux from hot side to cold side, and  $\eta$  is efficiency. The heat flux  $Q_h$  can be defined as :

$$Q_h = \frac{\kappa A \Delta T}{L} \tag{2}$$

Where  $\kappa$  is the effective thermal conductivity through the single leg, A is the single leg cross sectional area, and L is the length of the single leg,  $\Delta T$  is the temperature difference. In order to accurately measure the heat flux through the single leg, a heat flux sensor from gSKIN is placed at the cold side with thermal grease to both the samples and the copper block.



Figure S8. Single leg thermoelectric device in-house measurement setup.



Figure S9. Phase diagram of GeTe-Cu<sub>2</sub>Te from literature.<sup>1</sup>

### **XRD** characterization

The room temperature XRD patterns of GeTe-based samples are given in Figure S10, showing that rhombohedral GeTe phase has been successfully obtained with detectable weak peaks of Ge as indicated by two red rectangles.



Figure S10. Powder XRD patterns for GeTe-based samples with indicating of the secondary phase Ge.



Figure S11. Cyclic test for Seebeck and resistivity showing negligible deterioration in properties for the optimal sample  $Ge_{0.935}(Cu_2)_{0.015}In_{0.01}Bi_{0.04}Te$ .



Figure S12. DSC heat capacity and the comparison of thermal conductivity and zT between DSC and Dulong-Petit heat capacity for  $Ge_{0.935}(Cu_2)_{0.015}In_{0.01}Bi_{0.04}Te$ .

### **Electronic Transport Analysis**

The reduced Fermi level,  $\eta$  can be extracted from Seebeck value:

$$S = \pm \frac{k_B}{e} \left[ \eta - \frac{\left(r + \frac{5}{2}\right) F_{r+1.5}(\eta)}{\left(r + \frac{3}{2}\right) F_{r+0.5}(\eta)} \right]$$
(3)

For every Seebeck value,  $\eta$  corresponding to acoustic phonon scattering (r = -0.5) and ionized impurity scattering (r = 1.5) can be calculated. Subsequently, the corresponding  $\eta$  values can be used to obtain electrical conductivities  $\sigma$  for particular transport coefficient value,  $\sigma_{E_0}$ :

$$\sigma = \sigma_{E_0} \ln \left( 1 + e'' \right) \tag{4}$$

The results were then plotted as  ${}^{\sigma_E}{}_0$ , which can then be estimated by looking at the position and trend of the experimental data from each sample. Essentially,  ${}^{\sigma_E}{}_0$  is a convenient expression of electrical conductivity that is independent of carrier concentration. This is especially useful in our case since the carrier concentration values obtained via Hall measurements may not be accurate due to the non-linearity of the Hall voltage versus magnetic field. (i.e. the Hall carrier concentration is typically taken as the linear slope of Hall voltage versus magnetic field, non-linearity in Hall voltage versus magnetic field makes data interpretation inaccurate). Large  ${}^{\sigma_E}{}_0$  can be associated with good crystalline quality and vice versa. Furthermore, the carrier mobility-equivalent for  ${}^{\sigma_E}{}_0$  can be expressed as weighted-mobility  ${}^{\mu}{}_W$ . The relation between  ${}^{\sigma_E}{}_0$  and  ${}^{\mu}{}_W$  can be expressed as:

$$\sigma_{E_0} = \frac{e(2m_e k_B T)^{3/2}}{3\pi^2 \hbar^3} \mu_W$$
(5)  
$$\mu_W = \mu_0 \left(\frac{m_{DOS}}{m_e}\right)^{3/2}$$
(6)

The main advantage of using weighted-mobility over inaccurately determined Hall mobility lies in the fact that weighted-mobility takes into account the  $m_{DOS}^*$  (density of states effective mass). Since the density of states effective mass provides a direct correlation to the Seebeck coefficient, the inverse correlation between electrical conductivity and Seebeck coefficient can be clearly accounted for by looking at the weighted mobility. Hence, it can be used as a robust indication of the thermoelectric power factor. It is important to note that while weighted mobility share some similarities with Hall mobility, their magnitude generally differs, especially for compounds with high band-degeneracy (high  $m_{DOS}^*$ ). This comes from the fact that weighted mobility has a  $m_{DOS}^{*}$ 

dependence whereas Hall mobility only depends on  $\mu_0$ (intrinsic mobility) as well as the reduced Fermi level and scattering mechanism.

Lastly, the quality factor B can be evaluated from  $\sigma_{E_0}$  based on the following:

$$B = \left(\frac{k_B}{e}\right)^2 \frac{T}{k_L} \sigma_{E_0} \tag{7}$$

It is evident from equation 7 that in order to enhance the quality factor,  ${}^{\sigma_{E_0}}$  must be enhanced, either via band convergence, resonant doping, energy filtering, or deformation potential engineering to increase  $m_{DOS}^*$ . Alternatively,  $k_L$  can be reduced via point defects, strain, dislocation, or stacking faults.

#### Simplified Debye-Callaway model for lattice thermal conductivity

In order to model the lattice thermal conductivity, Debye frequency was first determined from:

$$\omega_{max} = \omega_D = \left(\frac{6\pi^2}{V}\right)^{1/3} v_m \tag{8}$$

Where V is the atomic volume and  $v_m$  was obtained from equation (4). The acoustic branch maximum frequency can be expressed as:

$$\omega_a = \frac{\omega_D}{N^{1/3}} \tag{9}$$

Where N is the number of atoms per unit cell.

The Debye temperature  $\theta_D$  can then be expressed as:

$$\hbar\omega_D = k_B \theta_D \tag{10}$$

Subsequently, the phonon relaxation time  $\tau(\omega)$  can be calculated by accounting for contribution from Umklapp, grain boundaries, and point defects as following:

$$\tau_{U}^{-1} = \frac{2}{(6\pi^{2})^{1/3}} \frac{k_{B} V^{1/3} \gamma^{2} \omega^{2} T}{M v^{3}}$$
(11)  
$$\tau_{B}^{-1} = \frac{v}{d}$$
(12)

$$\tau_{PD}^{-1} = \frac{V\omega^4}{4\pi\nu^3} \left( \sum_{i} f_i \left( 1 - \frac{m_i}{\bar{m}} \right)^2 + \sum_{i} f_i \left( 1 - \frac{r_i}{\bar{r}} \right)^2 \right)$$
(13)

In our case, the spectral heat capacity  $C_s(\omega)$  can be expressed as:  $C_s(\omega) = \frac{3k_B\omega^2}{2\pi^2 v^3}$ (14)

By assuming constant group velocity (sound velocity), we can express the spectral thermal conductivity  $\kappa_s(\omega)$  as:

$$\kappa_s(\omega) = C_s(\omega)v^2\tau(\omega) \tag{15}$$

Finally, the lattice thermal conductivity can be obtained by integrating the spectral thermal conductivity over the entire frequency range up to  $\omega_a$ :

$$\kappa_L = \frac{1}{3} \int_0^{\omega_{max}} C_s(\omega) v^2 \tau(\omega) d\omega$$
(16)

In our experiments, we obtained both elastic constant (*E*) from nanoindentation as well as longitudinal sound velocity ( $v_L$ ) from ultrasonic measurements. In order to obtain other elastic properties, we made use of the following equations:

$$B = \frac{E}{3(1 - 2v_p)} \tag{17}$$

where B = Bulk modulus;  $v_p =$  Poisson ratio

Both sides of the above equation can be expressed in terms of  $v_L$  and  $v_T$  (longitudinal and transverse sound velocity, respectively) as follows:

$$B = \rho \left( v_L^2 - \frac{4}{3} v_T^2 \right)$$
(18)  
$$v_p = \frac{1 - 2(\frac{v_T}{v_L})^2}{2 - 2(\frac{v_T}{v_L})^2}$$
(19)

where  $\rho = \text{density}$ 

The transverse sound velocity  $v_T$  can then be calculated by substituting equation (18) and (19) into equation (17) and solving for  $v_T$ . Subsequently, the average sound velocity,  $v_m$  can be determined via:

$$v_m = \left(\frac{1}{3} \left[\frac{1}{v_L^3} + \frac{2}{v_T^3}\right]\right)^{-\frac{1}{3}}$$
(20)

Shear modulus  $\mu$  can be obtained from:

$$\mu = \rho v_T^2 \tag{21}$$

In addition, after obtaining the poisson ratio  $v_p$  from equation (3), the Gruneisen parameter  $\gamma$  can be determined by:

$$\gamma = \frac{3}{2} \left( \frac{1 + v_p}{2 - 3v_p} \right) \tag{22}$$

#### References

1. O. S. Gogishvili, V. Kononykhin, I. Lavrinenko and S. Lalykin, *Izv. Akad. Nauk SSSR, Neorg. Mater*, 1982, **18**, 372-375.