Supplementary Information:

Realizing high thermoelectric performance in GeTe through decreasing phase transition temperature *via* entropy engineering

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EXPERIMENTAL:

Structural characterization: For all samples, the phase purity and crystal structure were examined by the powder x-ray diffraction (XRD) with Cu Kα (λ =1.5418 Å) radiation. The morphology and homogeneity of samples were performed with scanning electron microscope (SEM, Zeiss Supra 55), which is equipped with an electron diffraction x-ray spectrometry (EDXS) for local chemical analysis (Inca, Oxford Instrument). Samples for scanning transmission electron microscopy (STEM) analysis were prepared using gentle ion milling (PIPS 691, Gatan) after mechanical thinning and precision polishing. Plasma cleaning (EC-52000IC, JEOL) was carried out to remove any residual surface contaminations before STEM analysis. High-angle annular dark-field (HAADF) imaging were carried out in an aberration-corrected microscope (ARM200F, JEOL) operated at 200 kV, using an inner detector angle of 72 mrad and a convergence semi-angle for the electron probe of 30 mrad.

Hall measurements: Hall coefficient (R_H) was measured with the Van der Pauw method in Lake Shore 8400. Carrier concentration (n_H) and carrier mobility (μ_H) were estimated by $n_H = 1/(eR_H)$ and $\mu_H = \sigma \cdot R_H$, respectively.

Electrical transport properties: The Seebeck coefficient and electrical conductivity were measured by Cryoall CTA instrument under a helium atmosphere from room temperature to 800 K. The uncertainty of the Seebeck coefficient and electrical conductivity measurement is 5%.

Thermal conductivity: The thermal conductivity was calculated through $\kappa = D \cdot C_P \cdot \rho$, where D, C_P, ρ are thermal diffusivity, heat capacity and sample density, respectively. The thermal diffusivity (D) was measured by the laser flash diffusivity method with Netzsch LFA 457, the heat capacity (C_P) was estimated with the Dulong-Petit law, the sample density (ρ) was calculated using the measured dimensions and weight. The combined uncertainty for all measurements involved in the calculation of ZT is around 20%.

Differential scanning calorimeter (DSC) measurements: The differential scanning calorimeter (DSC) measurements were performed on Netzsch STA 449 F3 simultaneous thermal analyzer in crucible under a N_2 flow, in the proper temperature range.

Lorenz number calculations: A single parabolic band (SPB) model with acoustic

phonon scattering was used to estimate Lorenz number (L). Generally, Lorenz number can estimate the lattice thermal conductivity, which will not change the total thermal conductivity and final ZT values. The Lorenz number is given by the formula[1] :

$$L = \left(\frac{k_B}{e}\right)^2 \left(\frac{(r+7/2)F_{r+5/2}(\eta)}{(r+3/2)F_{r+1/2}(\eta)} - \left[\frac{(r+5/2)F_{r+3/2}(\eta)}{(r+3/2)F_{r+1/2}(\eta)}\right]^2 \right) \quad (1)$$

where k_B is the Boltzmann constant and η is the reduced Fermi energy, which can be derived from the measured Seebeck coefficients *via* the following equations:

$$S = \pm \frac{k_B}{e}\left(\frac{(r+5/2)F_{r+3/2}(\eta)}{(r+3/2)F_{r+1/2}(\eta)} \right) \quad (2)$$

where $F_n(\eta)$ is the nth order Fermi integral:

$$F_n(\eta) = \int_0^\infty \frac{\chi^n}{1+e^{\chi-\eta}} d\chi \quad (3)$$

$$\eta = \frac{E_f}{k_B T} \quad (4)$$

Acoustic phonon scattering is the main carrier scattering mechanism, resulting in r value of -1/2.

Cahill model calculations: The theoretical minimum lattice thermal conductivity κ_{min} of a normal solid is calculated by Cahill's formula[2]:

$$\kappa_{min} = \left(\frac{\pi}{6}\right)^{\frac{1}{3}} \kappa_B n^{\frac{2}{3}} \sum_i \nu_i \left(\frac{T}{\theta_i}\right)^2 \int_0^{\frac{\theta_i}{T}} \frac{x^3 e^x}{(e^x-1)^2} dx \quad (5)$$

where k_B is the Boltzmann constant, n is the number density of atoms, ν_i is the speed sound, and Θ_i ($=\nu_i \left(\mathrm{h}/k_B\right)\left(6\pi^2 n\right)^{1/3}$) is the cut-off frequency for each polarization. This model is taken over three sound modes including one longitudinal ν_l and two transverse ν_t branches. The longitudinal ν_l and transverse speed sound ν_t for each sample are measured, respectively. The obtained κ_{min} ~ 0.42 W m^{-1} K^{-1} of GeTe sample is shown in **Figure 6b** by a dashed line. Clearly, the measured κ_L of solid solution is close to κ_{min} especially in the high temperature range.

Callaway model calculations: Above Debye temperature, the ratio between the lattice thermal conductivity of multiple component samples ($Ge_{0.88}In_{0.02}Pb_{0.1}Te$, $Ge_{0.89}In_{0.010}P_{b0.1}Te_{0.997}I_{0.003}$, $Ge_{0.84}In_{0.010}Pb_{0.1}Sb_{0.05}Te_{0.997}I_{0.003}$) and parent sample (

GeTe) can be expressed as follows[3, 4]:

$$\frac{\kappa_{lat}}{\kappa_{lat,p}} = \frac{\tan^{-1} u}{u} \tag{6}$$

where κ_{lat} and $\kappa_{lat,p}$ are lattice thermal conductivities of multiple component samples and parent sample, respectively. The parameter u is defined as follows[5, 6]:

$$u = \left(\frac{\pi^2 \theta_D \Omega}{h v_a^2} \kappa_{lat,p} \Gamma \right)^{\frac{1}{2}} \tag{7}$$

where h is the Planck constant, Ω is the volume per atom, v_a is the average lattice sound velocity (v_a = 2055 m/s). Γ is the imperfection-scaling parameter included mass fluctuation Γ_M and strain field fluctuation Γ_S. The relation between Γ_M and Γ_S can be written as $\Gamma = \Gamma_M + \varepsilon\Gamma_S$, where Γ_M is calculated by averaging sublattice mass, Γ_S is calculated by averaging sublattice ionic radius, ε is an adjustable parameter. $\varepsilon = 2(W+6.4\gamma)^2$ is determined by the Grüneisen parameter γ=1.45 and W=4[7]. Finally, we can obtain the theoretical predication κ_{lat} with Callaway model. The results are presented in **Figure 6c**.

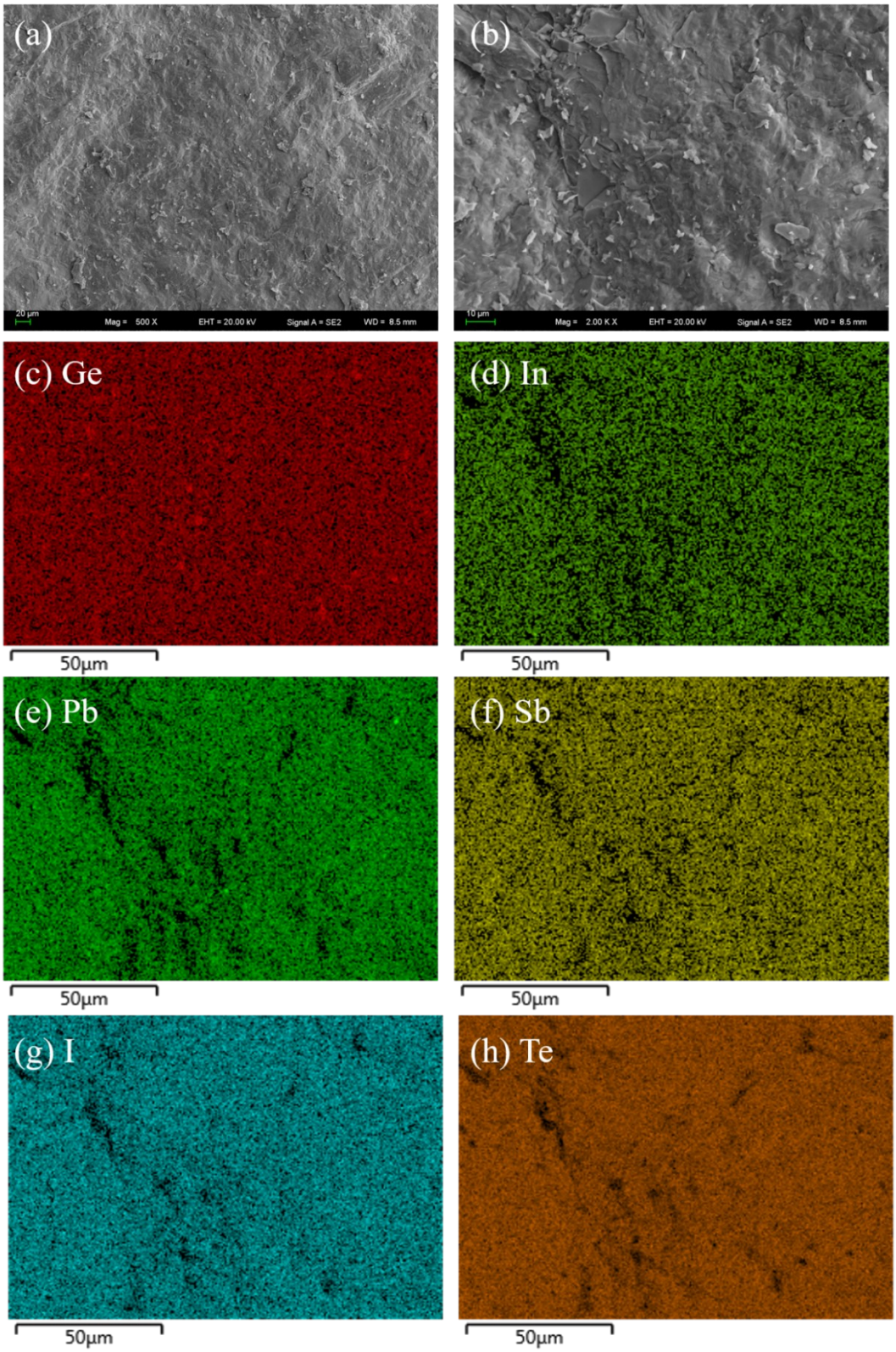

Figure S1. Secondary electron images for $Ge_{0.84}In_{0.010}Pb_{0.1}Sb_{0.05}Te_{0.997}I_{0.003}$ (a) at low magnification and (b) at high magnification, respectively; Secondary X-ray maps in the selected area for (c) Ge element; (d) In element; (e) Pb element; (f) Sb element; (g) I element and (h) Te element.

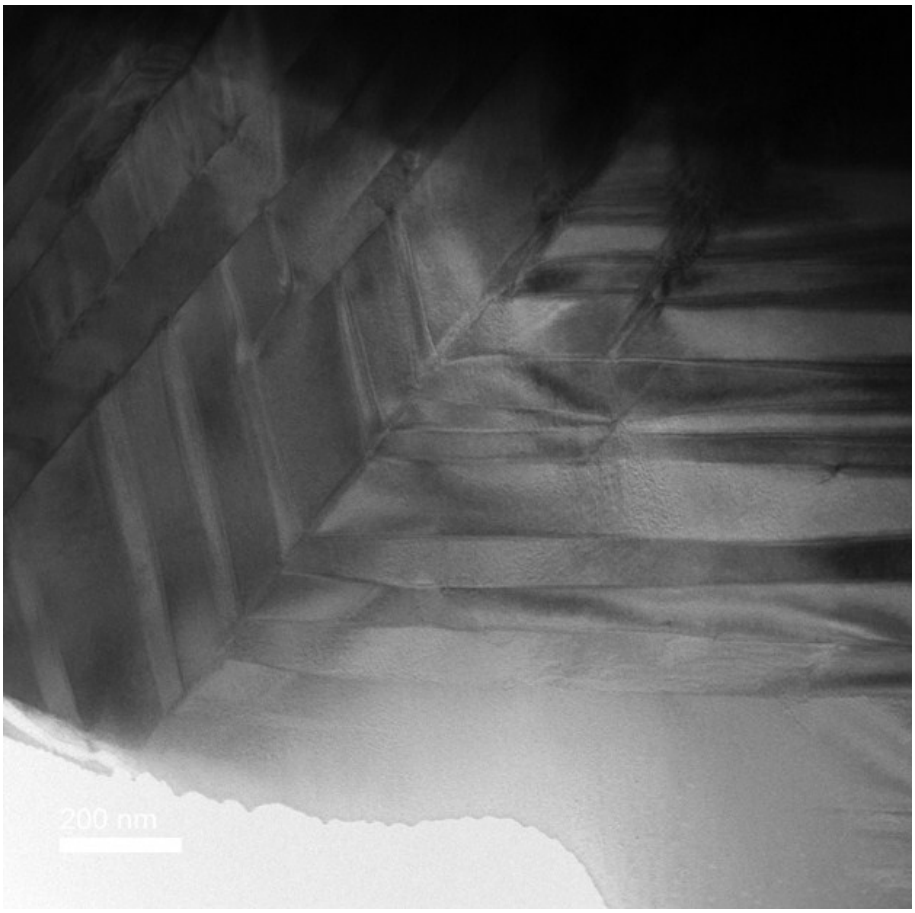

Figure S2. Low-magnification TEM images for $Ge_{0.84}In_{0.010}Pb_{0.1}Sb_{0.05}Te_{0.997}I_{0.003}$.

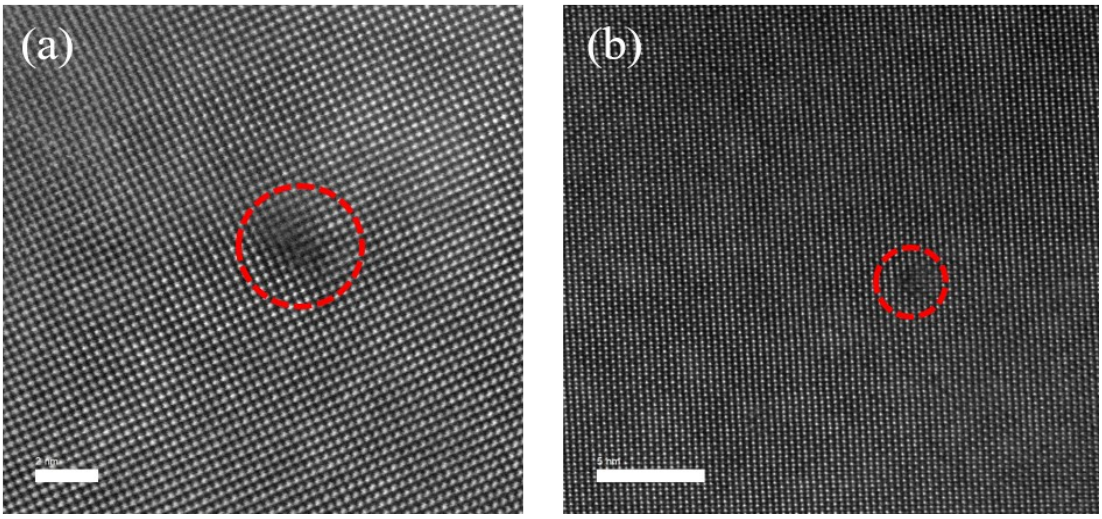

Figure S3. High-magnification STEM images taken along (a) [100] and (b) [001] zone axes of $Ge_{0.84}In_{0.010}Pb_{0.1}Sb_{0.05}Te_{0.997}I_{0.003}$.

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