Supporting Information

The role of electronegativity on the thermoelectric performance of GeTe - I-V-VI_2 solid solutions

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1. Single parabolic band (SPB) model

The following equations are used to estimate the effective mass[1]:

$$s = -\frac{k_B}{e}\left(\frac{\left(\frac{5}{2}+\lambda\right)F_{\frac{3}{2}+\lambda}(\eta)}{\left(\frac{3}{2}+\lambda\right)F_{\frac{1}{2}+\lambda}(\eta)} - \eta\right) \tag{1}$$

$$n_H = -\frac{4\pi(2m_d^* k_B T)^{\frac{3}{2}}F_{\frac{1}{2}}(\eta)}{h^3 r_H} \tag{2}$$

$$r_H = \frac{3}{2}F_{\frac{1}{2}}(\eta)\frac{\left(\frac{3}{2}+2\lambda\right)F_{\frac{1}{2}+2\lambda}(\eta)}{\left(\frac{3}{2}+\lambda\right)^2 F_{\frac{1}{2}+\lambda}(\eta)^2} \tag{3}$$

$$F_i(\eta) = \int_0^\infty \frac{x^i}{1+exp(x-\eta)}dx \tag{4}$$

where $\eta = E_F/k_BT$ is the reduced Fermi level, x is the reduced carrier energy, $F_i(\eta)$ is the Fermi-Dirac integral, r_H is the Hall factor, m_d^* is the density of states (DOS) effective mass, h is the Planck constant, and λ is the scattering factor which depends on the energy dependence of the carrier relaxation time τ via $\tau = \tau_0\xi^\lambda$. When the acoustic phonon scattering or alloy scattering is dominant, $\lambda = -1/2$.

2. B factor & zT

β is defined by the relation[2]:

$$\beta = \left(\frac{\kappa}{e}\right)^2 \frac{\sigma_{E0}T}{\lambda_L} \tag{5}$$

where κ is the Boltzmann constant, λ_L is the lattice thermal conductivity, σ_0 is a quantity termed as transport coefficient that depends on the carrier mobility and the effective mass according to:

$$\sigma_{E0} = 2e\mu\left(\frac{2\pi m_d^*}{h^2}\right)^{3/2} \tag{6}$$

where μ is the carrier mobility, m_d^* is the density of states (DOS) effective mass, h is the Planck constant.

To see how the definition of β is justified, we can now separate the η-dependent terms from zT[3]:

$$zT = \frac{S^2\sigma T}{\lambda_L + \lambda_e} = \frac{S^2}{\lambda_L/\sigma T + L}$$

$$= \frac{S^2(\eta)}{\frac{\lambda_L}{T\sigma_{E0} \cdot ln(1 + e^\eta)} + L(\eta)}$$

$$= \frac{S^2(\eta)}{\frac{(\kappa_B/e)^2}{\beta \cdot \ln(1+e^{\eta})} + L(\eta)}$$

where β combines all the η-independent material parameters, giving the definition of the dimensionless material quality factor in Eq.5. The natural unit of the Lorenz number $(\kappa_B/e)^2$ was multiplied in the term containing $1/\beta$ to make β dimensionless for convenience.

References

1. X. Liu, T. Zhu, H. Wang, L. Hu, H. Xie, G. Jiang, G. J. Snyder and X. Zhao, Advanced Energy Materials, **2013**, 3, 1238-1244.

2. Goldsmid, H. J. Thermoelectric Refrigeration (Plenum, **1964**).

3. S. D. Kang and G. J. Snyder, Nature Materials, **2017**, 16, 252-257.

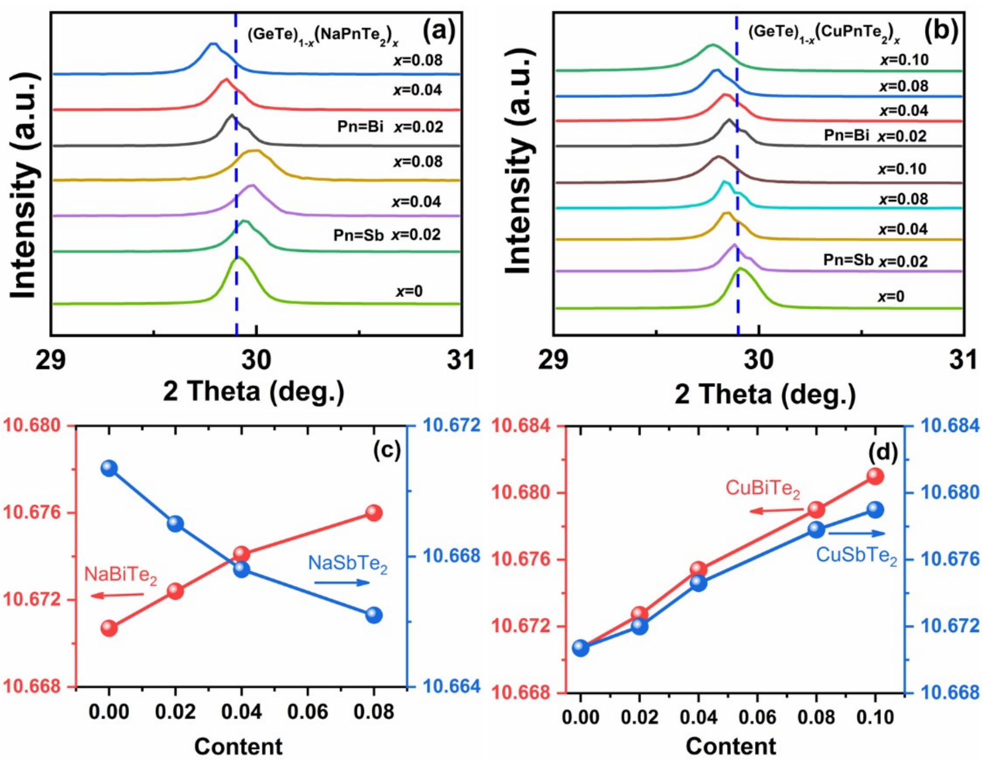

Figure S1. (a-b) The magnified area of the powder X-ray diffraction pattern of $(GeTe)_{1-x}(NaPnTe_2)_x$ and $(GeTe)_{1-x}(CuPnTe_2)_x$ in the angles(2θ) from 29° to 31°. (c-d) The lattice constants (c-axis) of $(GeTe)_{1-x}(NaPnTe_2)_x$ and $(GeTe)_{1-x}(CuPnTe_2)_x$.

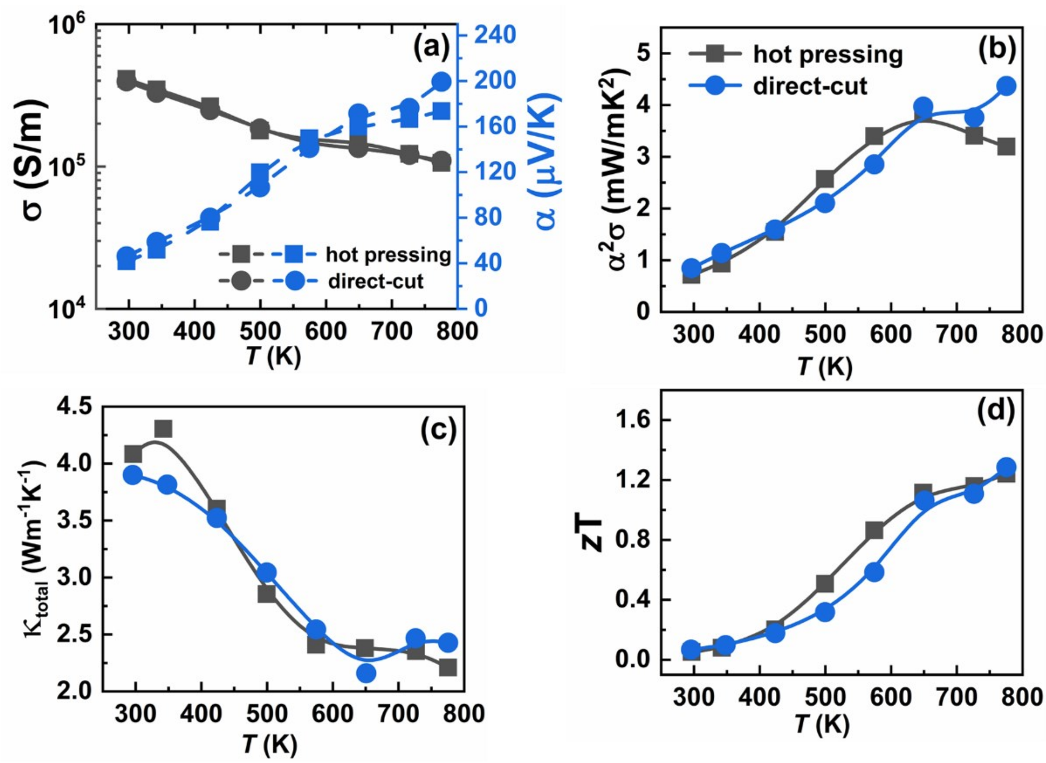

Figure S2. The comparison of the thermal and electrical performance data of $(GeTe)_{0.98}(NaBiTe_2)_{0.02}$ after hot pressing (powder was consolidated to a disk by a direct-current-induced hot pressing at about 873 K for 40 min and under the pressure of ~50 MPa) and direct cutting.

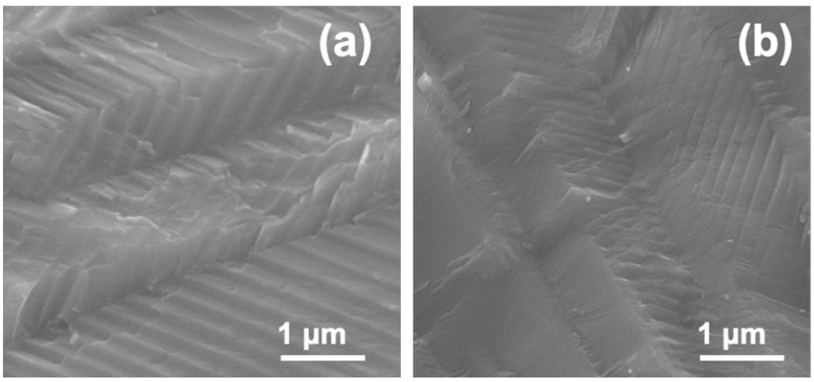

Figure S3. SEM image of fresh fracture surface morphology of $(GeTe)_{0.98}(NaBiTe_2)_{0.02}$ after (a) direct cutting and (b) hot pressing.