Supporting Information

Demonstration of Low-symmetry Rhombohedral GeTe Single Crystals with Anisotropic Thermoelectric Properties

Siqi Lin[1,#], Hao Chen[1,#], Zhenyu Lai[1], Xiaofei Yue[1], Yongxian Mu[1], Xinyue Zhang[2,*], Jiye Zhang[2,*], Min Jin[1,2,3*]

[1] College of Materials, Shanghai Dianji University, Shanghai 201306, China

[2] School of Materials Science and Engineering, Shanghai University, 99 Shangda Road, Shanghai 200444, China

[3] State Key Laboratory of Functional Crystals and Devices, Shanghai Institute of Ceramics, Chinese Academy of Sciences, 200050, China

[*] Email: xinyuezhang@shu.edu.cn (XZ), jychang@shu.edu.cn (JZ), jmaish@aliyun.com (MJ)

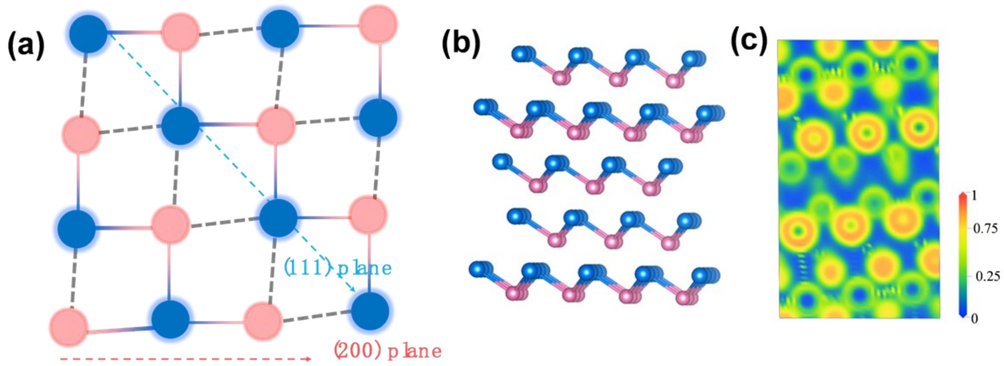

Figure S1. (a) Crystal structure of rhombohedral GeTe with distorted Ge-Te bonds, leading to a (b) layered structure. (c) The ELF indicating the weaker chemical bonds between the layers.

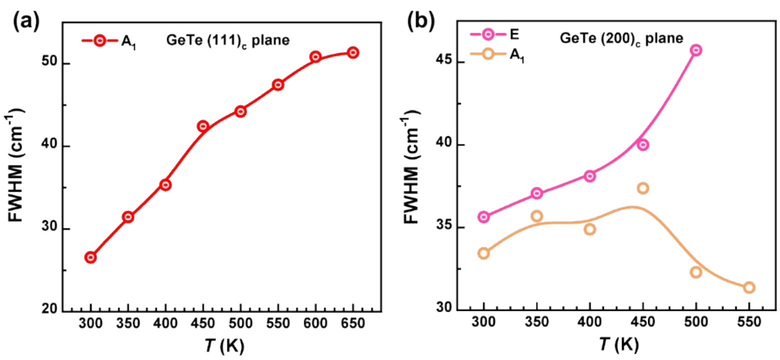

Figure S2. Temperature-dependent FWHM of the Raman peaks for GeTe single crystals (a) along $(111)_c$ plane and (b) along $(200)_c$ plane.

Methods for prediction model:

For a single parabolic band semiconductor with electron scattering by acoustic phonons (SPB-APS), the electrical quality factor B_E can be expressed using Fermi integrals (F_j) as:

$$B_E = S^2\sigma \Big/ [(\frac{2F_1}{F_0} - \eta)^2 F_0] \text{ with } F_j = \int_0^\infty \frac{\xi^j}{1+\exp(\xi-\eta)} d\xi \text{ ,} \quad \text{(S1)}$$

where F_j can be determined from the reduced Fermi energy η that can be solved with the measured Seebeck coefficient (S) via:

$$S = \frac{k_B}{e}(\frac{2F_1}{F_0} - \eta) \text{ .} \quad \text{(S2)}$$

In addition, conductivity can be written as:

$$\sigma = B_E(\frac{e}{k_B})^2 F_0 \text{ ,} \quad \text{(S3)}$$

and electronic thermal conductivity as:

$$\kappa_E = L\sigma T = B_E\left[\frac{3F_2}{F_0} - \left(\frac{2F_1}{F_0}\right)^2\right]F_0 T \text{ ,} \quad \text{(S4)}$$

as well as the thermoelectric figure of merit as:

$$zT = \frac{S^2\sigma T}{\kappa_L + \kappa_E} = \frac{B_E T}{\kappa_L}\frac{(\frac{2F_1}{F_0} - \eta)^2 F_0}{1 + \frac{B_E T}{\kappa_L}F_0[\frac{3F_2}{F_0} - (\frac{2F_1}{F_0})^2]} \text{, meaning the quality factor } B = \frac{B_E T}{\kappa_L}. \quad \text{(S5)}$$

In the above equations, k_B is Boltzmann constant, e is electric charge, L is Lorenz factor and κ_L is lattice thermal conductivity respectively.

An approximate analytical solution of B_E:[1]

$$B_E = S^2 \Big/ \rho[\frac{S_r^2\exp(2 - S_r)}{1 + \exp[-5(S_r - 1)]} + \frac{S_r\pi^2/3}{1 + \exp[5(S_r - 1)]}] \quad \text{(S6)}$$

Here, $S_r = \frac{|S|}{k_B/e} = \frac{2F_1}{F_0} - \eta$. This enables a simple estimation of B_E using Seebeck coefficient (S) and electrical resistivity (ρ) at any temperature.

References:

1. X. Zhang, Z. Bu, X. Shi, Z. Chen, S. Lin, B. Shan, M. Wood, A. H. Snyder, L. Chen, G. J. Snyder and Y. Pei, Electronic quality factor for thermoelectrics, *Sci. Adv.*, 2020, **6**, eabc0726.