Supplementary Material: Stable Atomic Stackings and Thermoelectric Properties of Layered $Ge_1Sb_6Te_{10}$

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Estimation of elastic moduli

Using elastic stiffness constant c_{ij} combined with Voigt approximation, bulk modulus (B_V) and shear modulus (G_V) are expressed as:[1]

$$B_V = \frac{2(c_{11}+c_{12}) + c_{33} + 4c_{13}}{9}, \tag{1}$$

$$G_V = \frac{c_{11} + c_{12} + 2c_{33} + 12(c_{44}+c_{66}) - 4c_{13}}{30}, \tag{2}$$

Within the Reuss model, they are given by[1]

$$B_R = \frac{c_{33}(c_{11} + c_{12}) - 2c_{13}^2}{2c_{33} + c_{11} + c_{12} - 4c_{13}}, \tag{3}$$

$$G_R = \frac{5\left[c_{33}(c_{11} + c_{12}) - 2c_{13}^2\right](c_{44}c_{66} - c_{14}^2)}{6B_V(\ )(c_{44}c_{66} - c_{14}^2) + 2\left[c_{33}(c_{11} + c_{12}) - 2c_{13}^2\right](c_{44} + c_{66})}. \tag{4}$$

In this work, the bulk modulus (B_H) and shear modulus (G_H) are obtained using Voigt-Reuss-Hill approximation[2]

$$B_H = \frac{B_V + B_R}{2}, \tag{5}$$

$$G_H = \frac{G_V + G_R}{2}. \tag{6}$$

The calculated results are summarized in Supplementary Table 1 and Supplementary Table 2.

Theory-experiment comparison

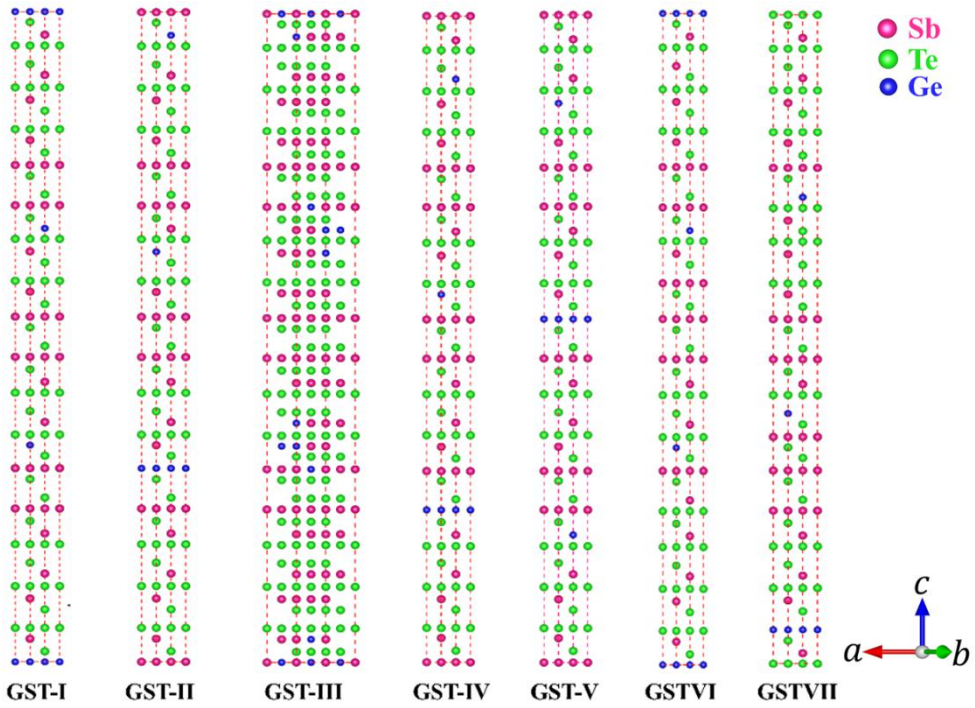
Supplementary Figure 6a shows the theoretically predicted Seebeck coefficient with respect to temperature under the constant carrier concentration of 7.3×10^{20} cm^{-3}. Obviously, the calculation results reproduce the same trend as experiment measures,[3] that is, the Seebeck coefficient increases with increasing temperature. More importantly, the estimated Seebeck coefficients are in excellent agreement with the experimental data above 600 K, though the theoretical values marginally deviate from the measured results in the lower temperature region (below 600 K), suggesting good reliability of our theoretical simulation. The small discrepancies between theory and experiment could be understood as the carrier concentration in experiments may vary slightly with temperature but we assume it to be a constant in our calculations. Within the constant relaxation-time approximation (CRTA), electrical conductivity (σ) can be estimated only if electronic relaxation time is given. Here, τ is determined by comparing the calculated σ/τ value with the measured σ.[3] Supplementary Figure 6b shows the calculated temperature dependence of the σ/τ at 7.3×10^{20} cm^{-3}, in comparison with the experiment results. The resulting τ values of stacking GST-I at different temperatures are shown in Supplementary Figure 6c, in which τ decreases with temperature (e.g., 20.1 fs at 310 K, 11.8 fs at 520 K, and 7.0 fs at 710 K). Owing to the minor differences in crystal and electronic structures between GST-I and GST-II, we thus assume that the relaxation time to be the same for both configurations.

Supplementary Table 1. Elastic constant cij (GPa) for different atomic arrangements of $Ge_1Sb_6Te_{10}$.

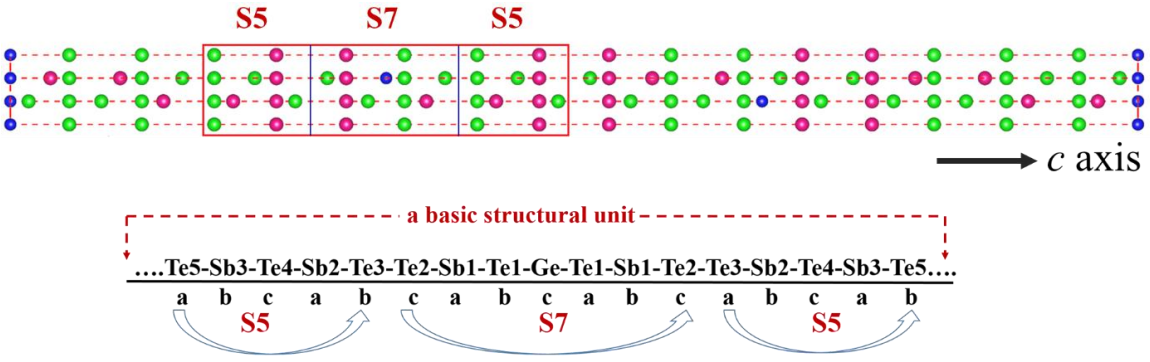
Atomic arrangement	c_{11}	c_{12}	c_{13}	c_{14}	c_{33}	c_{44}
GST-I	84.33	19.81	26.47	-16.96	51.70	33.03
GST-II	80.81	20.32	25.40	-16.65	49.48	31.75
GST-IV	71.47	27.73	30.30	-15.51	56.03	38.48
GST-V	14.20	-17.82	58.73	-19.61	21.16	36.33
GST-VI	-72.52	-94.13	123.15	-20.62	-62.13	39.46
GST-VII	44.35	0.15	70.95	-19.63	-40.53	40.36

Supplementary Table 2. Bulk modulus B (GPa) and shear modulus G (GPa) of stackings GST-I and GST-II.

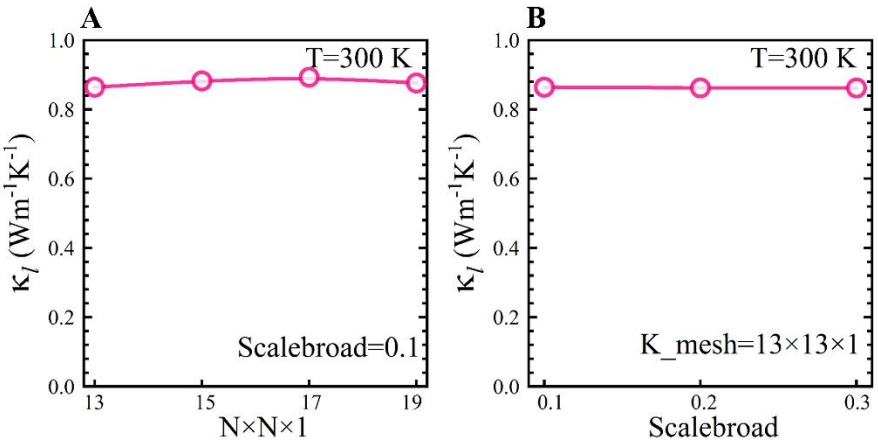
Stacking	B_V	G_V	B_R	G_R	B_H	G_H
GST-I	40.65	29.50	39.18	21.82	39.91	25.66
GST-II	39.26	28.08	37.71	20.41	38.48	24.25



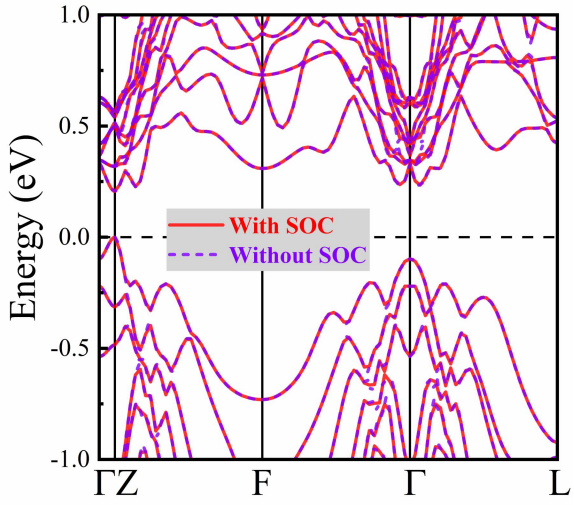
Supplementary Figure 1. Hexagonal lattice for seven kinds of atomic stacking configurations of layered $Ge_1Sb_6Te_{10}$.



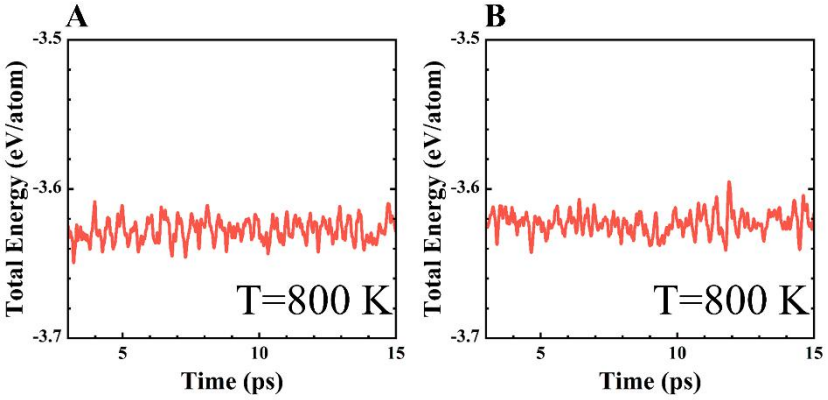
Supplementary Figure 2. Crystal structure of atomic stacking GST-I.



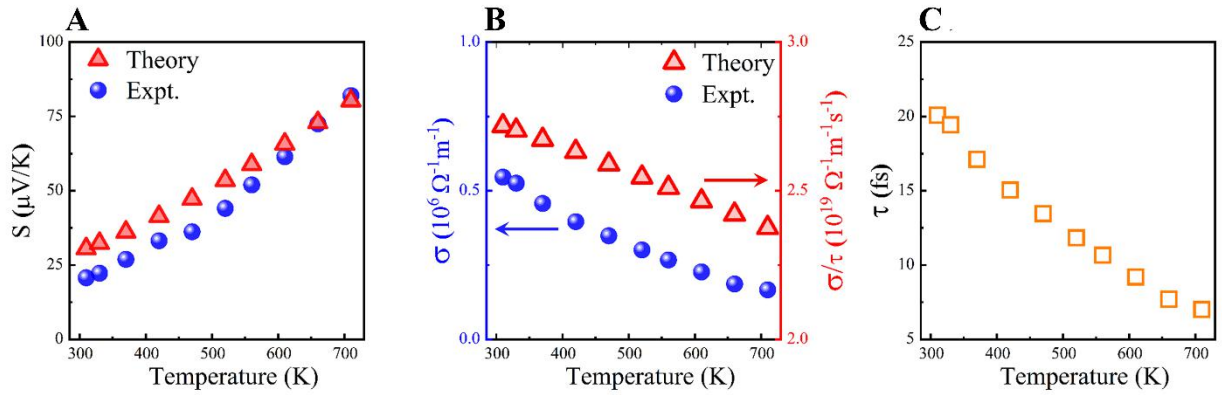
Supplementary Figure 3. Convergence tests of lattice thermal conductivity as a function of (A) *k*-point grid and (B) scalebroad for stacking GST-I at 300 K.



Supplementary Figure 4. Electronic band structures of stacking GST-I with and without spin-orbital coupling (SOC).



Supplementary Figure 5. Evolution of total energy of (A) GST-I and (B) GST-II with respect to time in AIMD simulations at 800 K.



Supplementary Figure 6. A: Calculated Seebeck coefficient S (red triangles) of stacking GST-I at hole concentration of 7.3×10^{20} cm^{-3} and available experimental results (blue dots).[3] B: Electrical conductivity with respect to relaxation time σ/τ (red triangles) for stacking GST-I and experimental data of σ (blue dots).[3] C: Estimated relaxation time of GST-I at different temperatures.

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