

Supporting Information for :

Largely enhanced thermoelectric performance in p-type Bi₂Te₃-based materials through entropy engineering

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Section S1. Finite element simulations for the TE module

The geometry-dependent analysis of power output and energy conversion efficiency for BiSbTe₂Se-based TEG was performed by the finite element method using COMSOL Multiphysics coupled with Heat Transfer (Thermoelectric Effect) and Electrical Circuits modules. The measured thermoelectric properties of BiSb_{0.95}Ag_{0.05}Te₂Se (p-type) and our previously reported Cl, W co-doped Bi₂Te_{2.7}Se_{0.3} (n-type) legs, as well as other parameters selected from the COMSOL materials library, were utilized in the simulation. For the numerical analysis, 18 pairs were series-connected in the air with a heat convection efficiency of 5 W m⁻² K⁻¹. The hot- and cold-side temperatures were fixed separately at 525 K and 300 K (ambient air). The height of p- and n-type Bi₂Te₃ legs and cross-sectional area ratios between p- and n-legs (A_p/A_n) were varied simultaneously to capture the optimum dimension of p- and n-type legs correspondingly to the maximum power output and energy conversion efficiency.

Section S2. DFT calculation methods

First-principles calculations were performed with a cutoff energy of 500 eV for the plane-wave basis set and based on density functional theory^{1, 2} using the projector-augmented wave method³, as implemented in the Vienna Ab initio Simulation Package⁴. The exchange-correlation interaction was treated with generalized gradient approximation in the form of the revised Perdew-Burke-Ernzerh⁵ and the van der Waals (vdW) interaction was treated with the DFT-D3 method of Grimme et al.⁶. The k-point sampling of 0.05 Å⁻¹ was adopted with a Monkhoust-Pack scheme including Γ point. The atomic positions were fully relaxed with the maximum residual ionic force and total energy difference converged within 0.005 eV Å⁻¹ and 10⁻⁶ eV, respectively. The experimental lattice constants are adopted. A 320-atom supercell (i.e., 4 × 4 × 4 primitive cell) is applied during calculating second-order interatomic force constant, and a 3 × 3 × 3 supercell with 9th nearest neighbors is considered for the calculation of third-order interatomic force constant for the calculations in Fig. 3(b) and (c) of the main

text. The thermal properties are obtained by solving the phonon Boltzmann transport equation implemented in ShengBTE ⁷. To mimic the random distribution of Bi and Sb atoms, special quasirandom structures (SQS) were generated with the help of the Alloy-Theoretic Automated Toolkit (ATAT) ^{8,9} and a 60-atom hexagonal structure was identified as the best one and used in our calculations that has the correct pair correlation functions identical to those of the perfect random structures up to the next nearest atomic shell with a distance of 8 Å

Section S3. Sound velocity calculation

Average sound velocity (v_a) is calculated from the sound velocity as follows¹⁰.

$$\frac{1}{v_a} = \left[\frac{1}{3} \left(\frac{1}{v_l^3} + \frac{2}{v_t^3} \right) \right]^{1/3} \quad (S1)$$

where v_l is the longitudinal sound velocity and v_t is the transverse sound velocity.

Young's modulus (E) is calculated by ¹¹

$$E = \frac{\rho v t^2 (3v_l^2 - 4v_t^2)}{v_l^2 - v_t^2}, \quad (S2)$$

where ρ is the sample density.

Poisson ratio (r) is calculated by (11)

$$r = \frac{1 - 2(v_t/v_l)^2}{2 - 2(v_t/v_l)^2}, \quad (S3)$$

Shear modulus (G) is calculated by (11)

$$G = \frac{E}{2(1 + r)}, \quad (S4)$$

The Gruneisen parameter (γ) is calculated by (11)

$$\gamma = \frac{3}{2} \left(\frac{1 + r}{2 - 3r} \right), \quad (S5)$$

Section S4. The calculations of Lattice Thermal Conductivity

According to the Debye–Callaway model ¹², k_l can be calculated by

$$k_l = \frac{k_B}{2\pi^2 v} \left(\frac{k_B T}{\hbar} \right)^3 \int_0^{\theta_D/T} \tau_{tot}(x) \frac{x^4 e^x}{(e^x - 1)^2} dx \quad (S6)$$

The integrand item in conjunction with the coefficient of Equation (S3) is the spectral lattice thermal conductivity

$$k_s(\omega) = \frac{k_B}{2\pi^2 v} \left(\frac{k_B T}{\hbar} \right)^3 \tau_{tot}(x) \frac{x^4 e^x}{(e^x - 1)^2} \quad (S7)$$

In the above equation, $x = \hbar\omega/k_B T$ is the reduced phonon frequency, k_B is the Boltzmann constant, v is the average sound velocity, which could be calculated by $v = \left[\frac{1}{3} \left(\frac{1}{v_L^3} + \frac{1}{v_T^3} \right) \right]^{-\frac{1}{3}}$ (with v_L and v_T respectively denoting the longitudinal and transverse sound velocities), $\hbar$ is reduced Plank's constant, θ_D is the Debye temperature, and ω is the frequency of phonons. τ_{tot} is the total relaxation time and calculated according to the Matthiessen's rule ¹³:

$$\tau_{tot}^{-1} = \tau_U^{-1} + \tau_{PD}^{-1} + \tau_{GB}^{-1} + \tau_{DS}^{-1} + \tau_{DC}^{-1} + \tau_P^{-1} + \tau_{SF}^{-1} \quad (S8)$$

Where τ_U , τ_{PD} , τ_{GB} , τ_{DS} , τ_{DC} , τ_P and τ_{SF} is the relaxation time for Umklapp-process scattering, point defect scattering, grain boundaries scattering, dislocation strain scattering, dislocation core scattering, precipitate scattering and stacking faults, respectively. The relevant phonon relaxation times are given by

Umklapp phonon-phonon scattering

$$\tau_U^{-1} = \frac{\hbar \gamma^2 \omega^2 T}{M v^2 \theta_D} \exp\left(-\frac{\theta_D}{3T}\right) \quad (S9)$$

Point defect phonon scattering

$$\tau_{PD}^{-1} = \frac{V \omega^4}{4\pi v^3} \Gamma \quad (S10)$$

Grain boundary phonon scattering

$$\tau_{GB}^{-1} = \frac{v}{d} \quad (S11)$$

where γ is the Grüneisen parameter, M is the average mass, m^* is the effective mass of charge carrier, ρ is the sample density, $\bar{V}$ is the average atomic volume, Γ is the point defect scattering parameter and determined by considering mass difference and d is the grain size, respectively. The Umklapp phonon–phonon scattering strength coefficient A was fit to the experimental data of the in-plane k_l of fully dense, large grained $\text{BiSb}_{0.95}\text{Ag}_{0.05}\text{Te}_2\text{Se}$.

For a material with dislocations, the scattering caused by the dislocations (D) should be considered. Relaxation time of dislocation scattering can be considered ¹⁴

$$\tau_{DS}^{-1} + \tau_{DC}^{-1} = N_D \frac{\bar{V}^3}{v^2} \omega^3 + 0.6 B_D^2 N_D (\gamma + \Delta\gamma)^2 \omega \left\{ \frac{1}{2} + \frac{1}{24} \left(\frac{1-2r}{1-r} \right)^2 \left[1 + \sqrt{2} \left(\frac{v_L}{v_T} \right) \right]^2 \right\} \quad (\text{S12})$$

N_D , B_D , γ , $\Delta\gamma$, r , v_L , v_T are dislocation density, effective Burger's vector, Grüneisen parameter, change in Grüneisen parameter due to the dislocation strain, Poisson's ratio, longitudinal phonon velocity and transverse phonon velocity, respectively. $\Delta\gamma$ can be expressed as

$$\Delta\gamma = \frac{V_{ST} C_0 K}{K_B T_a} (\gamma \alpha^2 - \alpha \beta) \quad (\text{S13})$$

$$\alpha = \frac{V_{BT} - V_{ST}}{V_{ST}} \quad (\text{S14})$$

$$\beta = \frac{M_{ST} - M_{BT}}{2M_{ST}} \quad (\text{S15})$$

where C_0 is the concentration of Bi_2Te_3 in $(\text{Bi,Sb})_2\text{Te}_3$ alloys, K is the bulk modulus of Bi_2Te_3 , T_a is the sample smelting temperature, V_{BT} and V_{ST} are the atomic volume of Bi_2Te_3 and Sb_2Te_3 , and M_{BT} and M_{ST} are the atomic mass of Bi_2Te_3 and Sb_2Te_3 .

For nanoscale precipitate, the relaxation time of nano precipitate can be expressed as¹⁵:

$$\tau_P^{-1} = \nu (\sigma_s^{-1} + \sigma_l^{-1})^{-1} V_P \quad (\text{S16})$$

$$\sigma_s = 2\pi R^2 \quad (\text{S17})$$

$$\sigma_l = \frac{4}{9} \pi R^2 \left(\frac{\Delta D}{D_{\text{matrix}}} \right)^2 \left(\frac{\omega R}{v} \right)^4 \quad (\text{S18})$$

$$\Delta D = D_{\text{matrix}} - D_{\text{precipitate}} \quad (\text{S19})$$

Where v , V_p , R , D_{matrix} and $D_{\text{precipitate}}$ are average sound speed, number density of nano precipitates, average radius of the precipitates, mass density of matrix and precipitates respectively.

Considering only the specular reflection of phonons at stacking faults Klemens found that¹⁶

$$\tau_{SF}^{-1} = 0.7 \frac{a^2}{v} \gamma^2 \omega^2 N_s \quad (\text{S20})$$

Where a , v , γ and N_s are lattice parameter, average sound speed, Grüneisen parameter and Number of stacking faults crossing a line of unit length. The detailed parameters can be found in the Table S2.

The calculations of k_b and minor electrical conductivity for *P*-type BST

In n-type Bi_2Te_3 -based materials, acoustic phonon scattering is also the dominant carrier scattering mechanism around 300 K. Thus, the hole mobility (μ_e) also obey the relationship of $\mu_e \sim T^{-3/2}$. Thus, a qualitative expression between μ_e and n_e is derived as $\mu_e \approx Bn^{-1/5}$, where B is a temperature independent constant for a fixed composition (Table S2). Then the electron partial electrical conductivity σ_e and bipolar can be calculated by the following equation:

$$k_b = \left(\frac{k_B}{e} \right)^2 T \left(5 + 2\lambda + \frac{E_g}{k_B T} \right)^2 \frac{\sigma_e}{1 + \sigma_e/\sigma_h} \quad (\text{S21})$$

Where, λ is the carrier scattering parameter, by subtracting the κ_b value from the $\kappa_l + \kappa_b$ (shown in Fig 4(E)), the experiment κ_l value can be attained (shown in Fig 4(F)).

The calculations of effective mass m^*

For a degenerate semiconductor with simple parabolic band dispersion and relaxation time approximation, m^* could be calculated by Equation (S12-14)

$$|S| = \frac{k_B [(2.5 + \lambda) F_{1.5 + \lambda}(\eta)]}{e [(1.5 + \lambda) F_{0.5 + \lambda}(\eta)] - \eta} \quad (\text{S22})$$

$$n = \frac{4\pi (2k_B T m^*)^{\frac{3}{2}}}{h^3} F_{1/2}(\eta) \quad (\text{S23})$$

$$F_n(\eta) = \int_0^\infty \frac{x^n}{1 + e^{(x - \eta)}} dx \quad (\text{S24})$$

where e and h are electron charge and Planck's constant, respectively. For acoustic scattering, λ is -0.5. The parameter η is called the reduced Fermi level, $\eta = E_F/k_B T$, where E_F is the Fermi level. By utilizing the S and n values at room temperature, the m^* is determined and plotted in fig. S8.

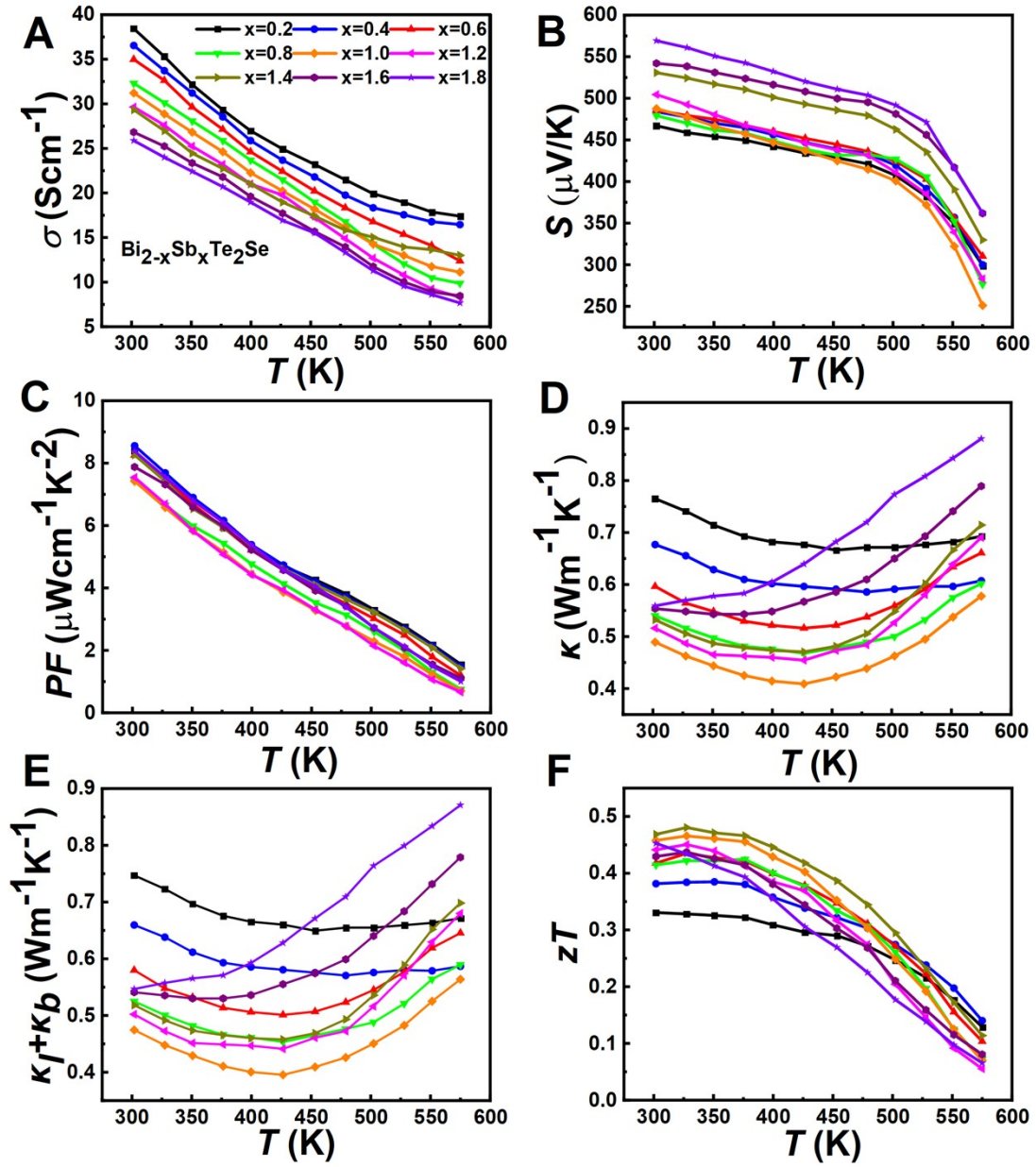
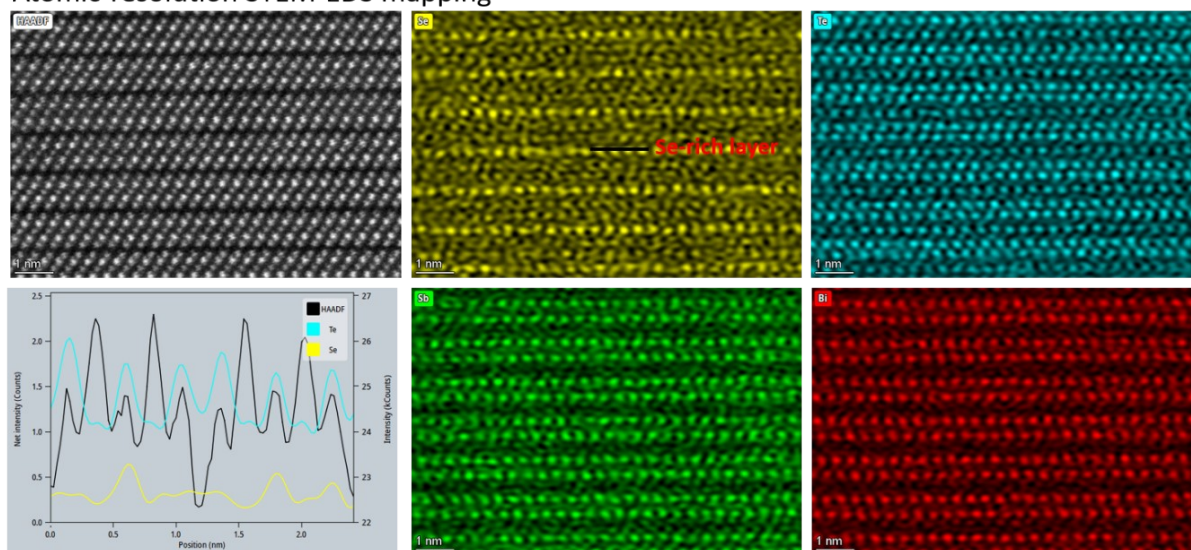


Fig S1. Thermoelectric properties of $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_2\text{Se}$ ($x=0.2$ to 1.8). (A) Electrical conductivity. (B) Seebeck coefficient (S). (C) Power Factor (D) Thermal conductivity (κ) and (E) Lattice Thermal conductivity (F) thermoelectric Fig of merit (zT) values of $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_2\text{Se}$.

A Atomic-resolution STEM-EDS mapping



B

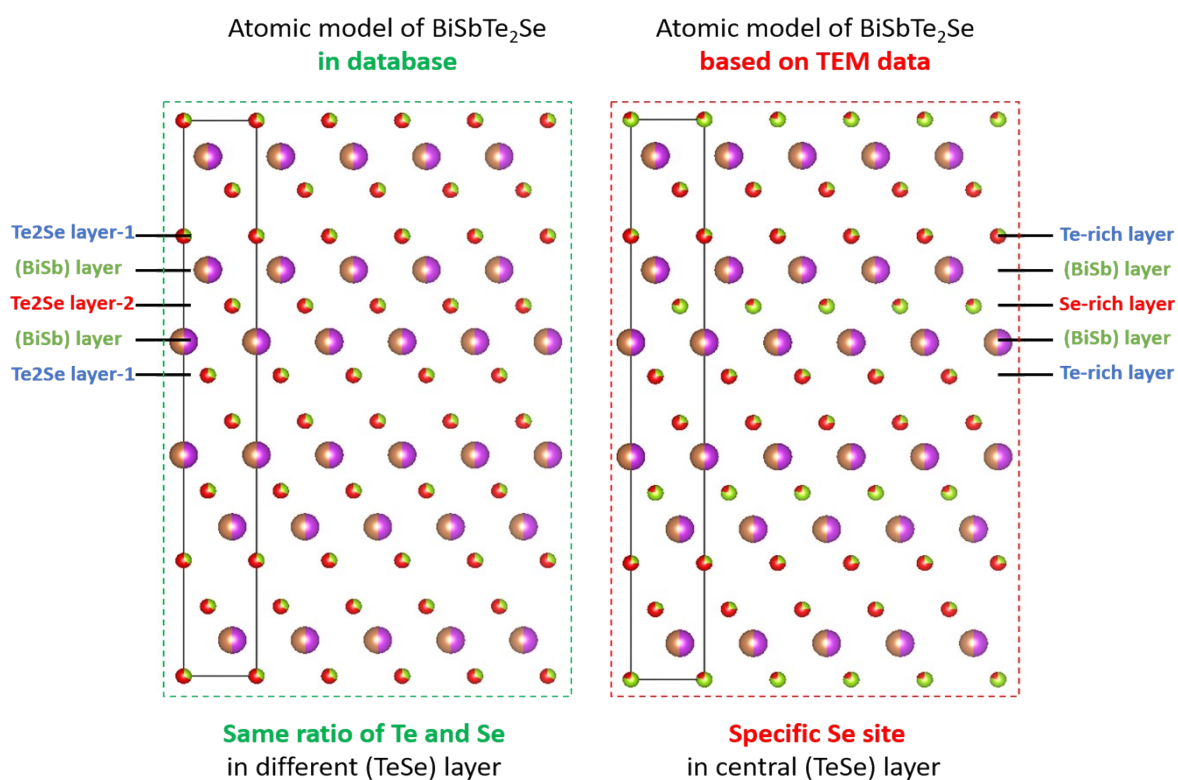


Fig S2. (A) Atomic Resolution and STEM EDS mapping and (B) Compare Atomic model of BiSbTe_2Se based on database and TEM Imaging.

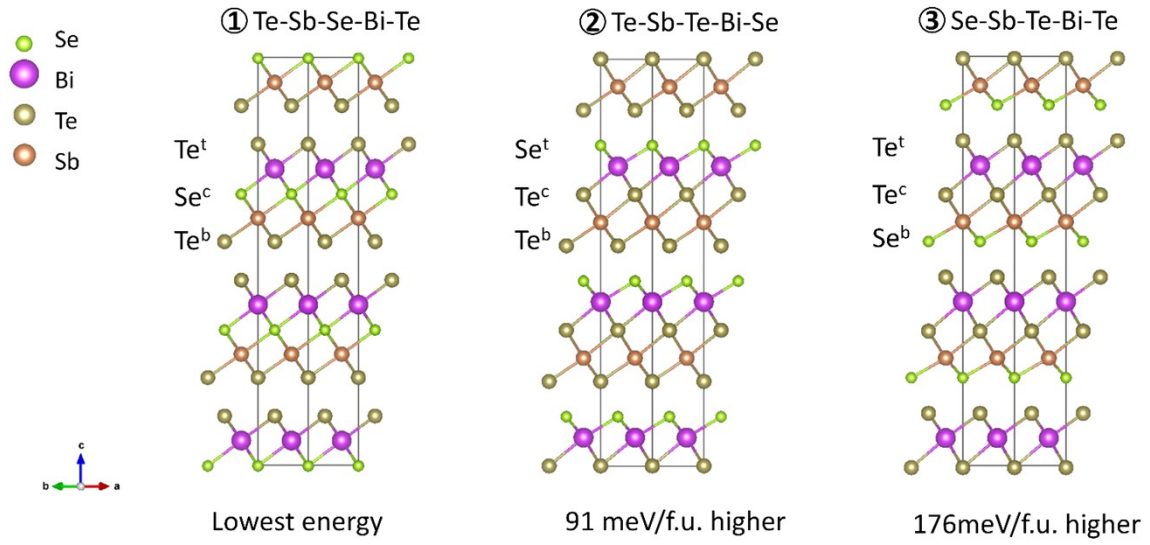


Fig S3. Crystal structures (with hexagonal lattice) for the ordered structure of BiSbTe₂Se with different Se positions.

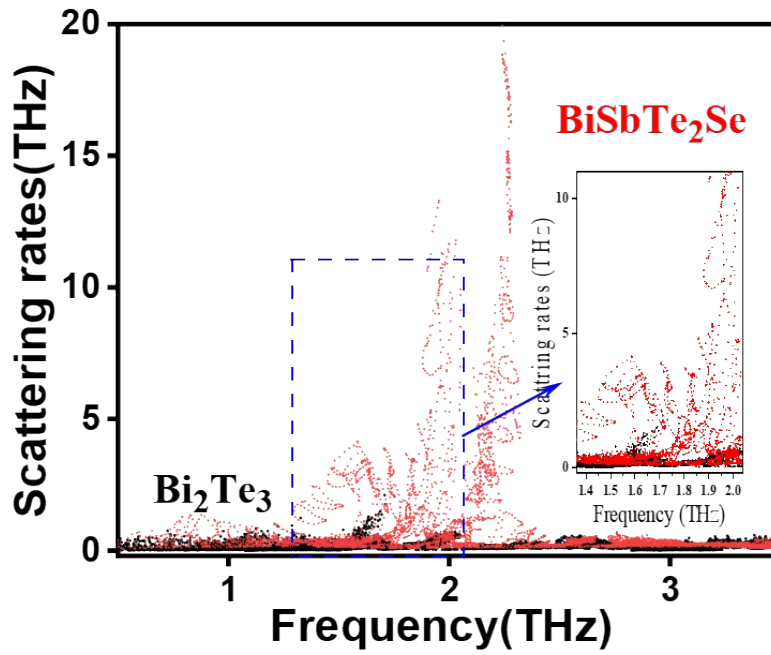


Fig S4. Phonon anharmonic scattering rate of BiSbTe₂Se and Bi₂Te₃.

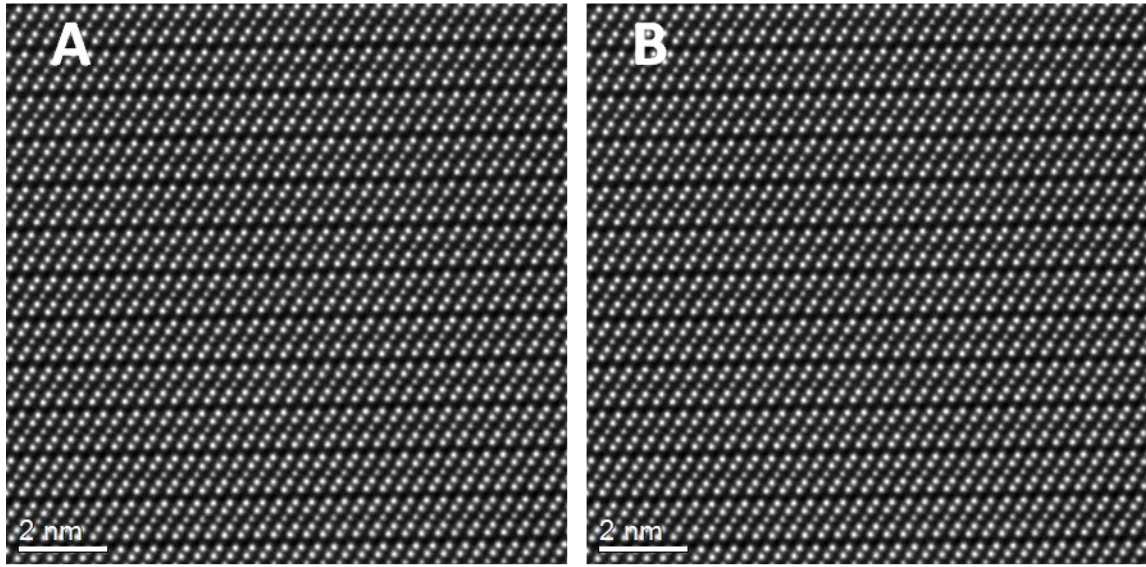


Fig S5. High-resolution STEM images along [100] orientation of (A) Bi_2Te_3 and (B) BiSbTe_2Se samples used for lattice strain analysis based on the geometric phase analysis, showing in Fig. 3C and 3D.

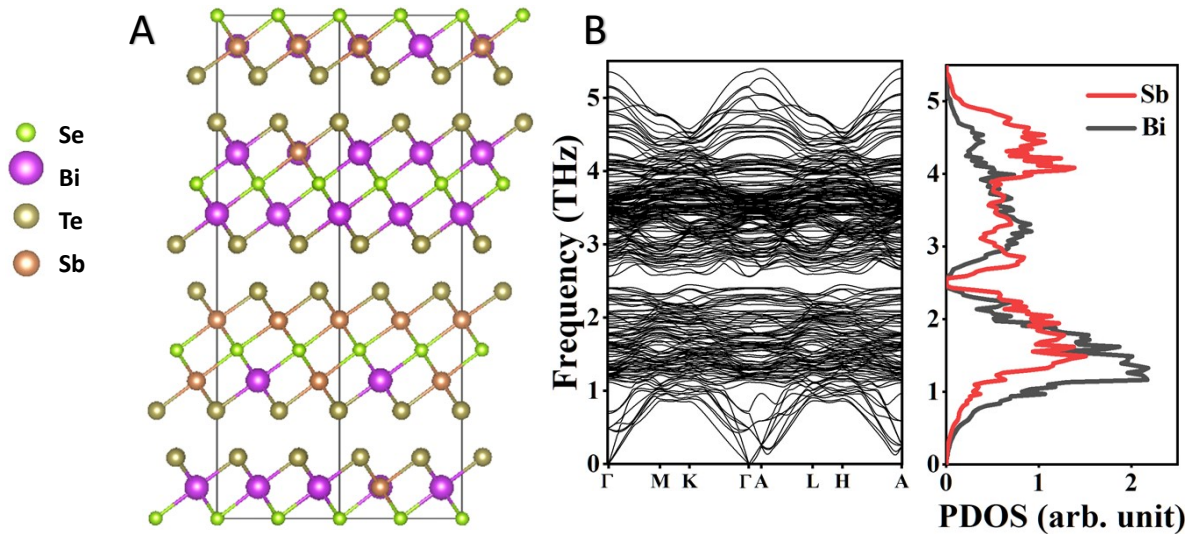


Fig S6. (A) Disordered Crystal structure of BiSbTe_2Se (B) Phonon dispersion and density of states of disordered BiSbTe_2Se .

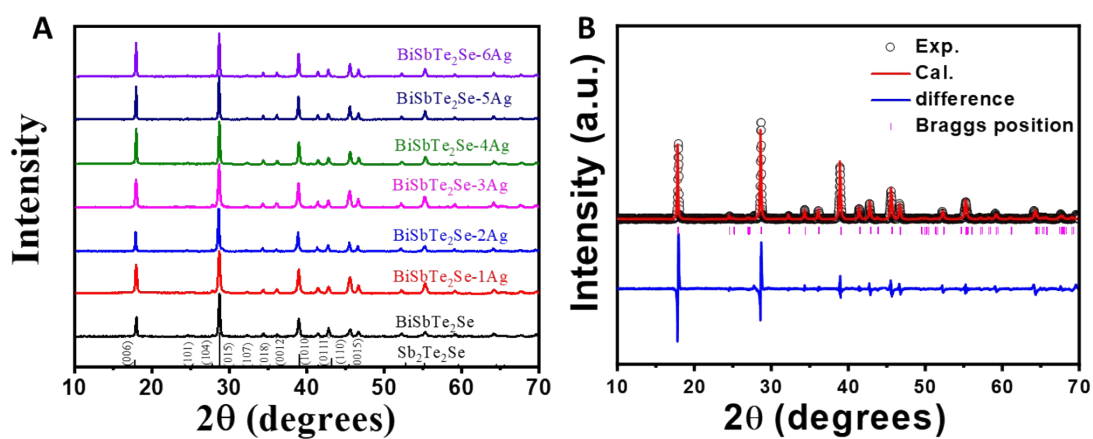


Fig S7. (A) XRD patterns of Ag-doped samples (B) Rietveld refinement plot of BiSb_{0.95}Ag_{0.05}Te₂Se.

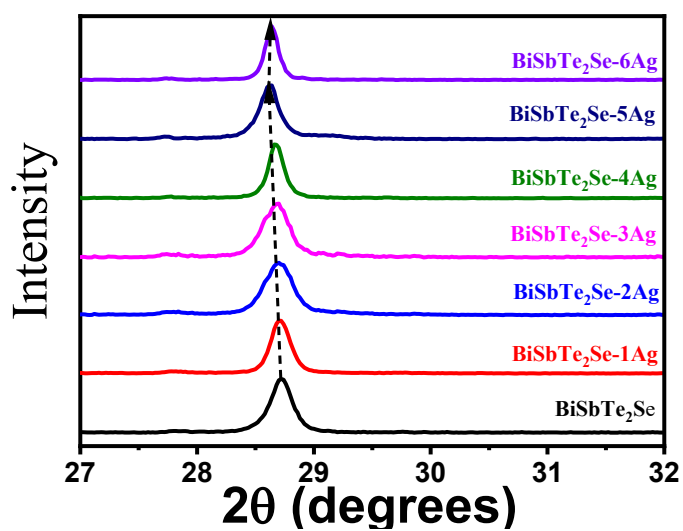


Fig S8. Diffraction peaks for BiSb_{1-x}Ag_xTe₂Se (x=0.01 to 0.06).

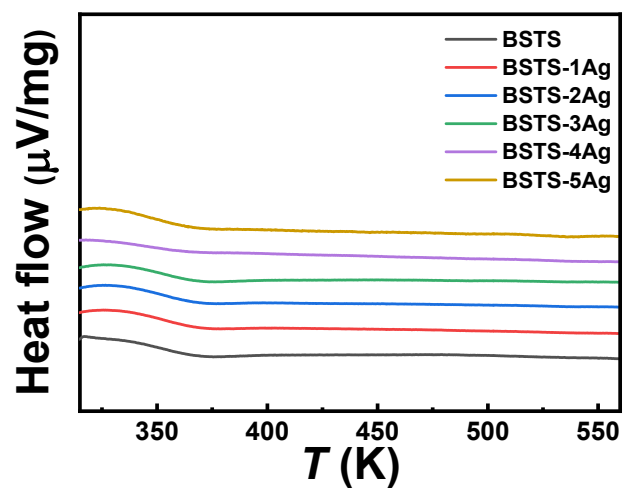


Fig S9. DSC curve of Ag doped $\text{BiSb}_{1-x}\text{Ag}_x\text{Te}_2\text{Se}$ ($x=0.01$ to 0.05).

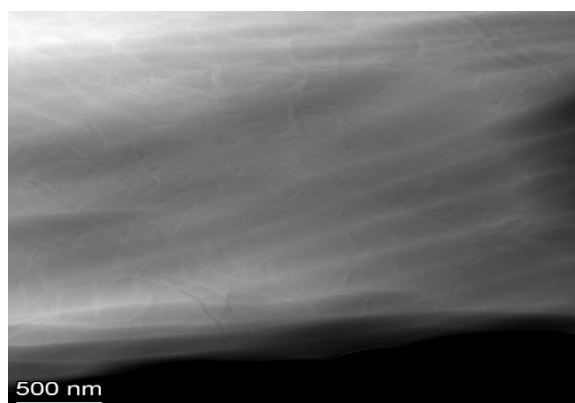


Fig S10. Low magnification TEM image for BiSbTe_2Se .

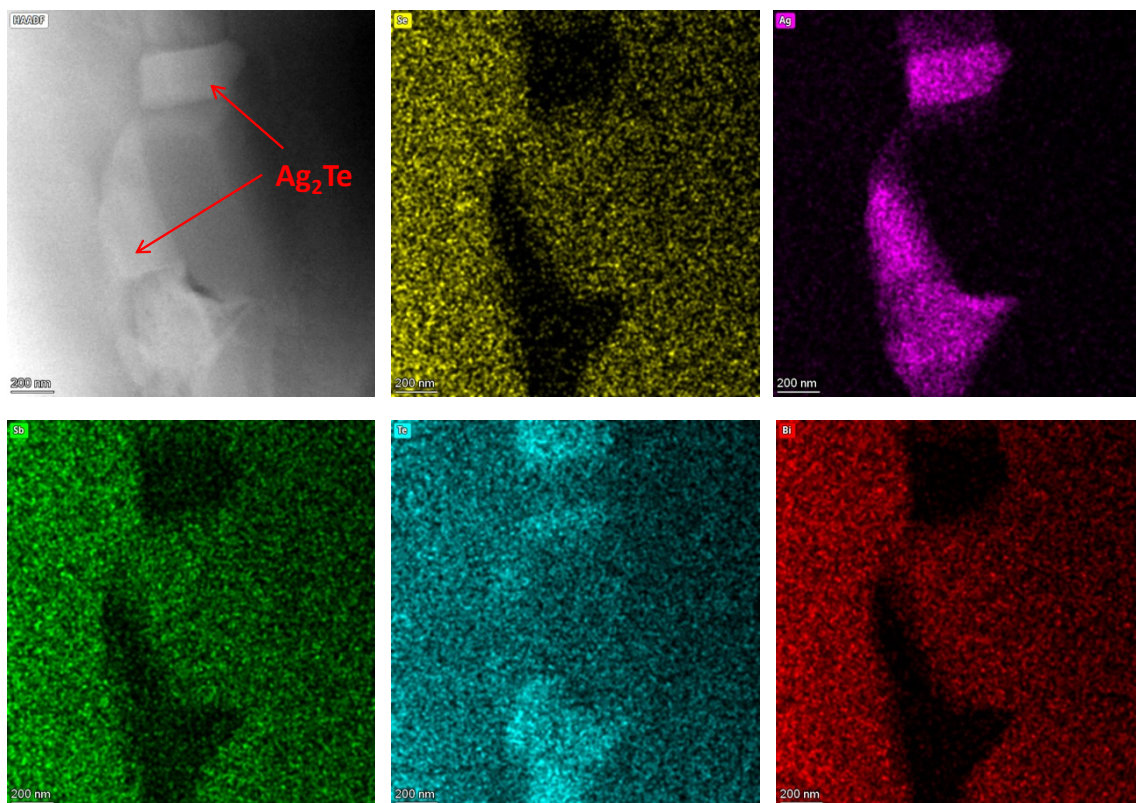


Fig S11: Low-magnification TEM image of the 0.05Ag-doped BiSbTe₂Se sample, showing the corresponding elemental distributions of Se, Ag, Te, and Bi.

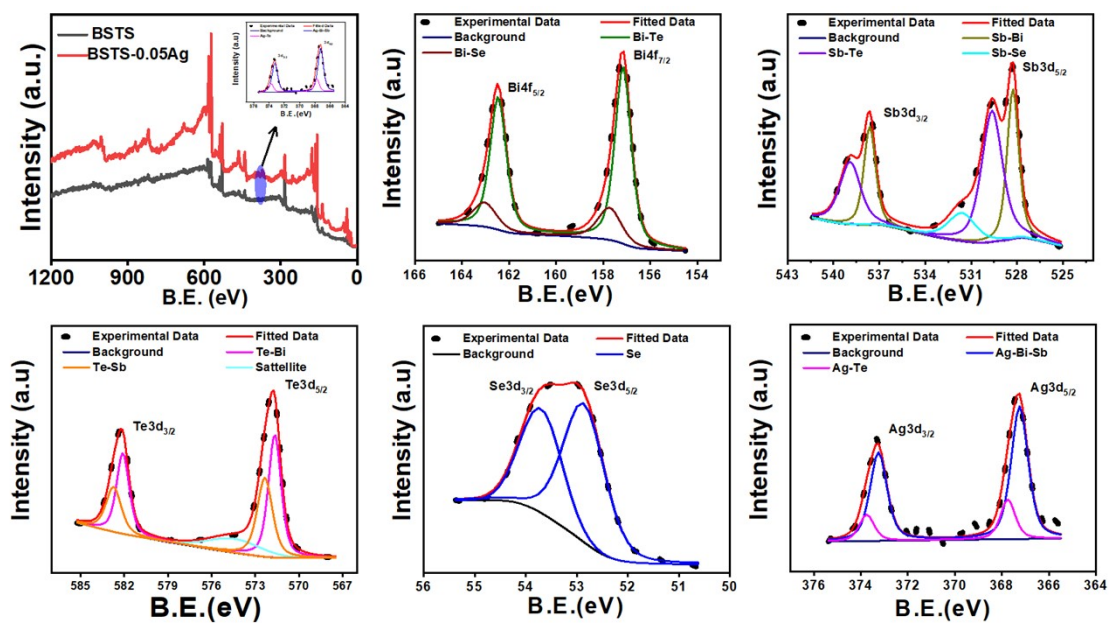


Fig S12. XPS survey spectrum of BiSbTe₂Se and Ag doped BiSbTe₂Se with their elemental states and corresponding binding energy.

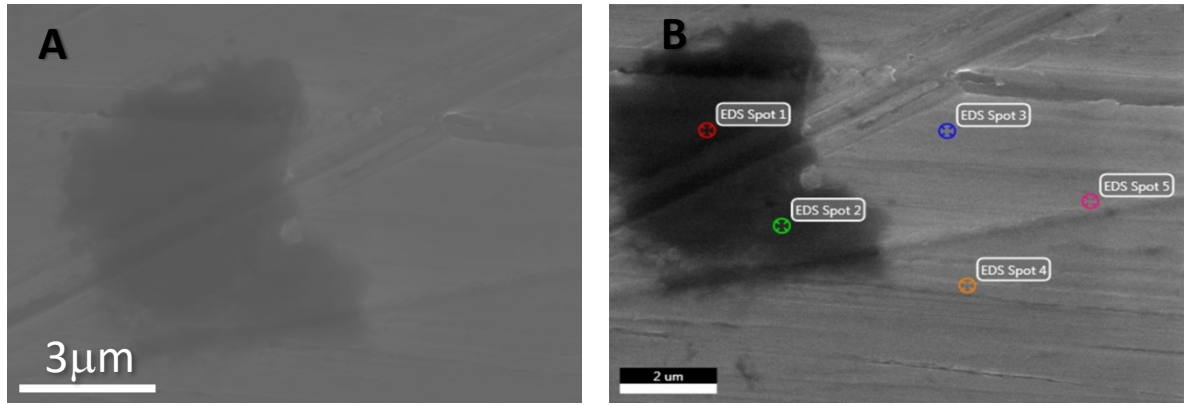


Fig S13. SEM images for (A) 0.05Ag-doped BiSbTe₂Se (B) EDS results for 0.05Ag doped BiSbTe₂Se sample data (Table S1) at different spots.

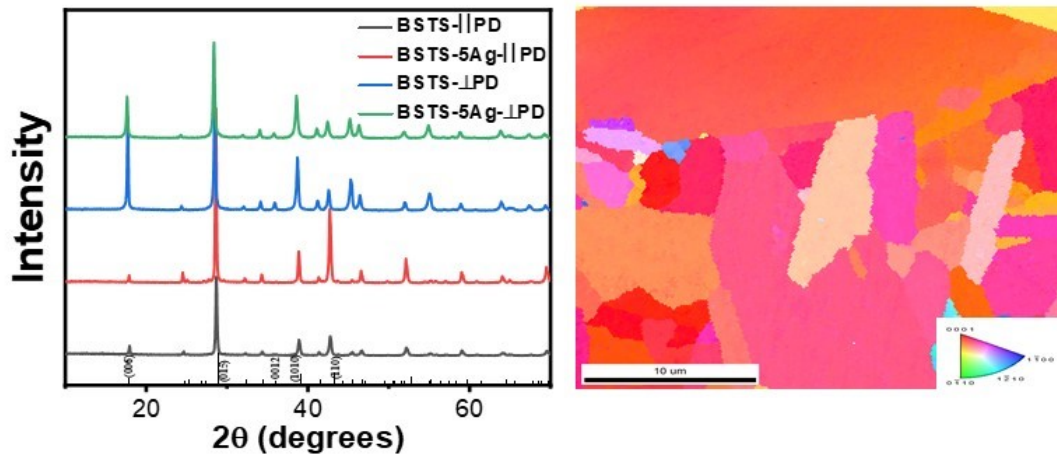


Fig 14. (A) XRD patterns parallel and perpendicular to pressing direction of BiSbTe₂Se and BiSb_{0.95}Ag_{0.05}Te₂Se samples. (B) Grain orientation distribution of the 5% Ag-doped BiSbTe₂Se sample.

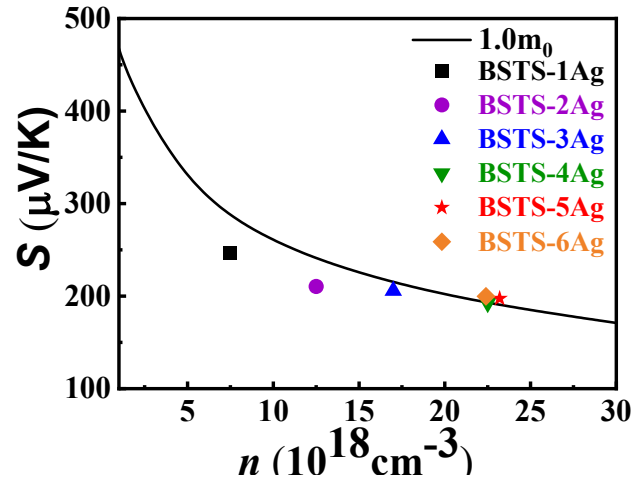


Fig S15. Pisarenko plots for Ag doped samples.

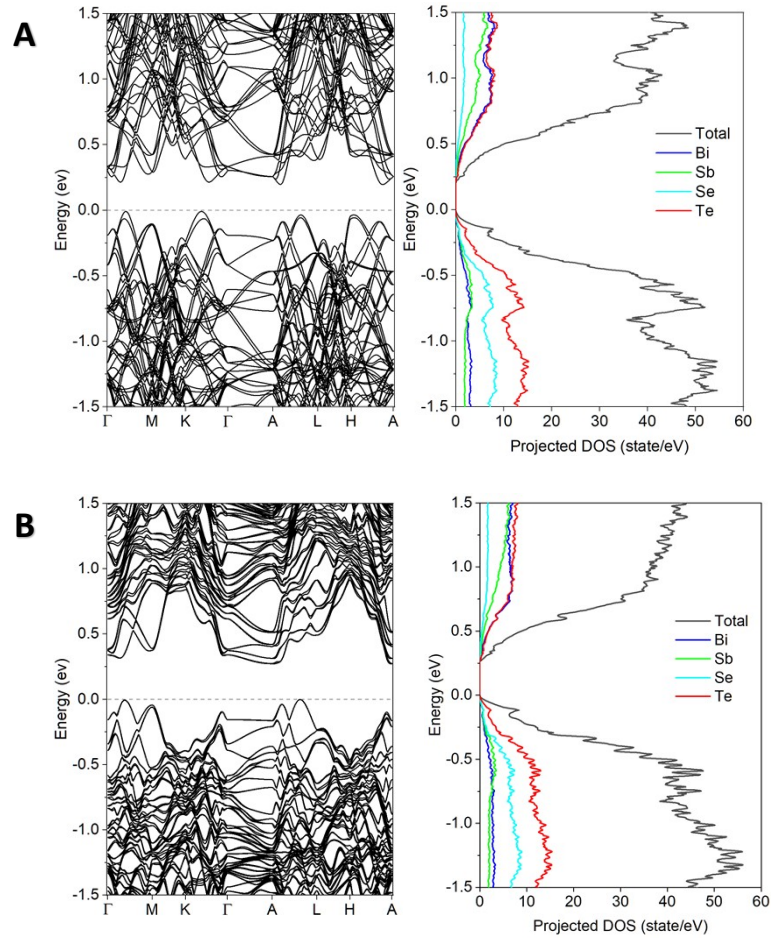


Fig S16. Electronic structure (A) BiSbTe₂Se with the ordered and (B) BiSbTe₂Se with the disordered structure.

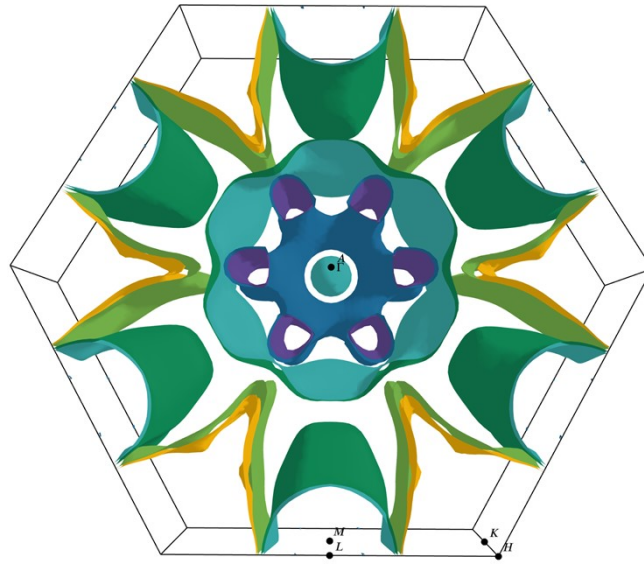


Fig S17. Fermi surface at -0.3 eV from VBM for BiSbTe₂Se with the disordered structure.

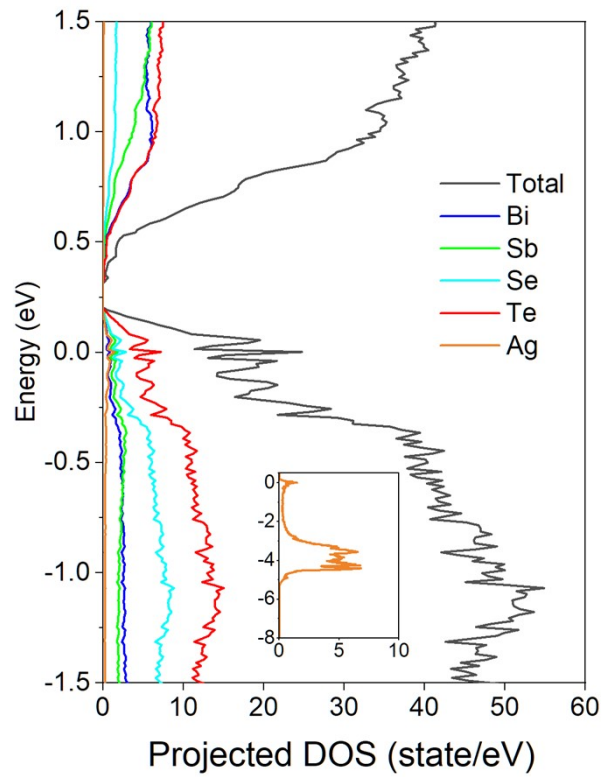


Fig S18. Density of states of Ag doped BiSbTe₂Se in disordered structure with enlarged view shown in the inset for atom-resolved density of states.

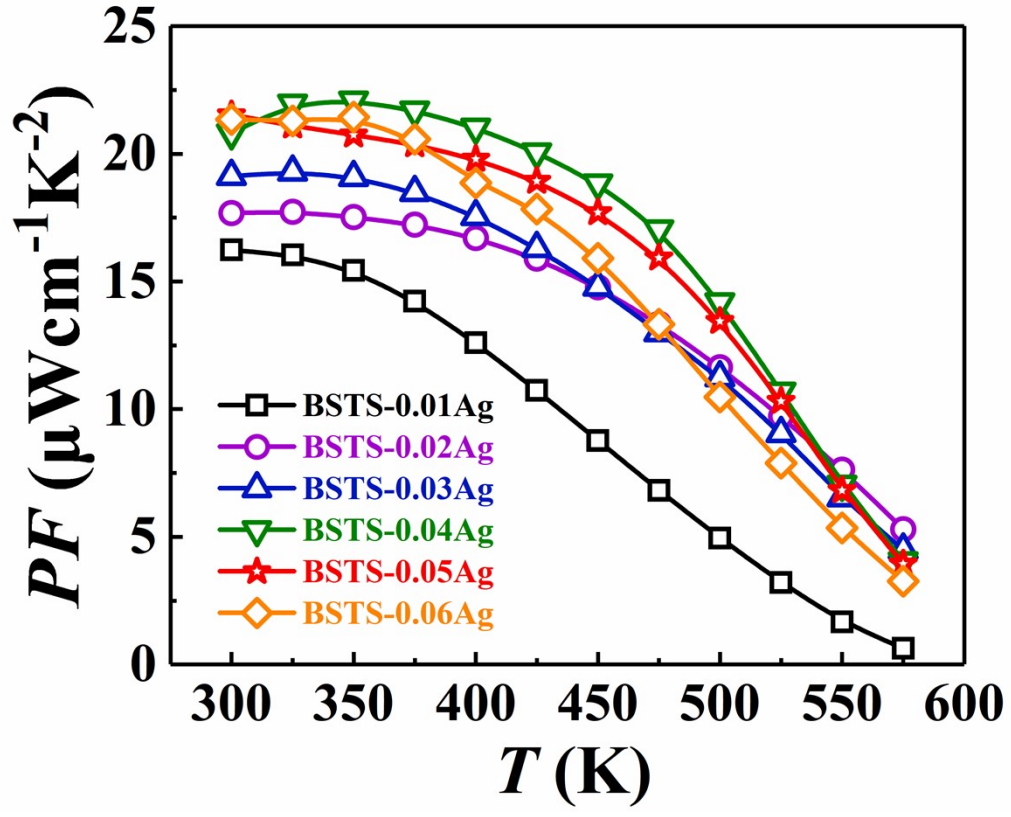


Fig S19. Power factor of the Ag doped BiSbTe₂Se.

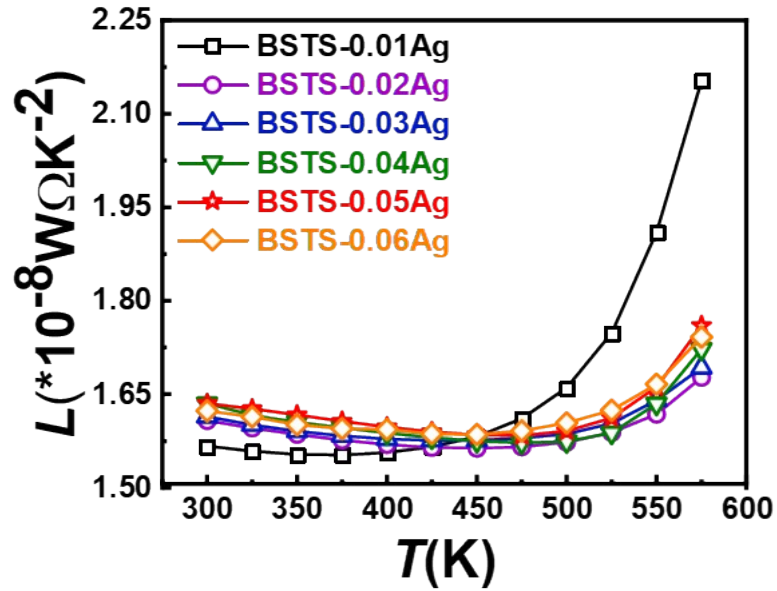


Fig S20. The Lorentz number, for all the samples derived from the equation $L = 1.5 + \exp [-|S|/116]$.

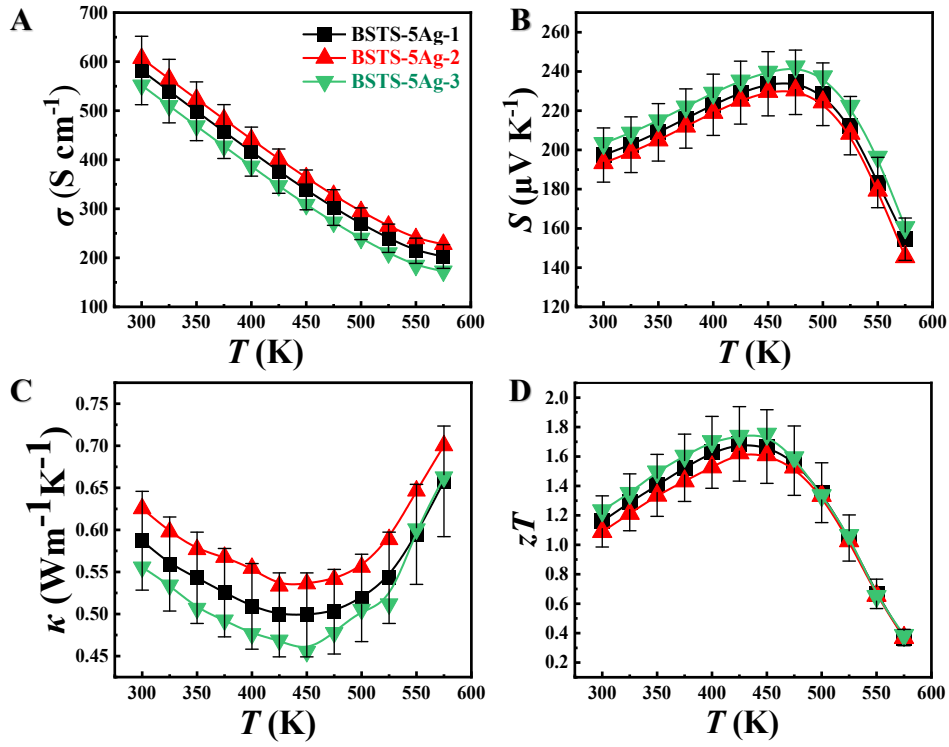


Fig S21. Repeat data for 5Ag BiSbTe₂Se sample (A) Electrical conductivity. (B) Seebeck coefficient (S). (C) Thermal conductivity (κ) and (D) thermoelectric Fig of merit (zT).

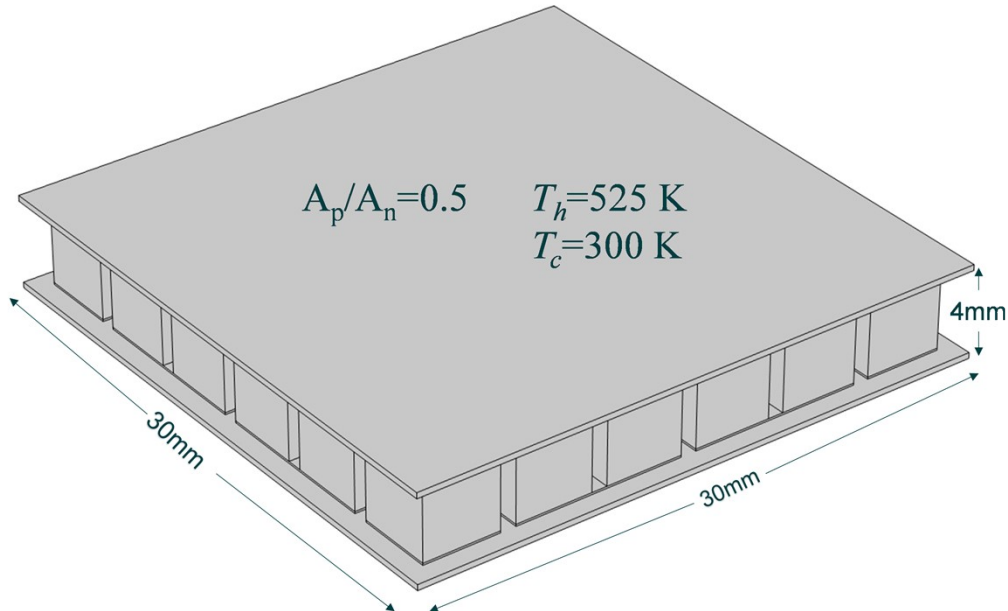


Fig S22. Schematic TE device of dimension of $30 \times 30 \times 4\text{ mm}^3$ with $A_p/A_n=0.5$.

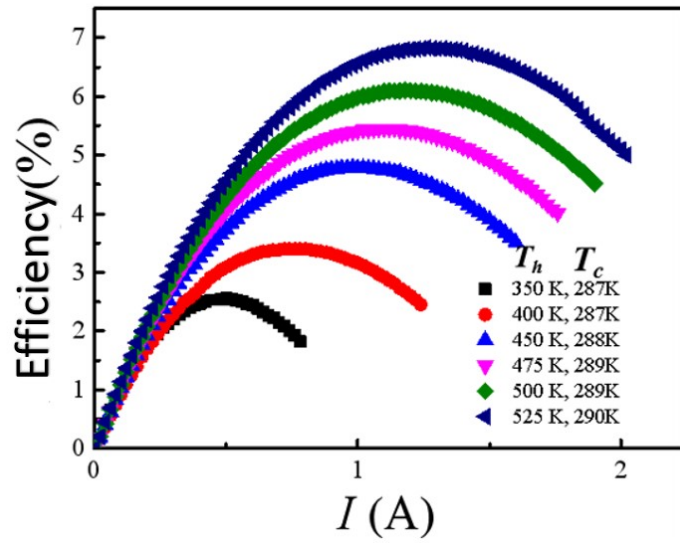


Fig S23. Performance of TE module. (A) Current dependence of efficiency for TE device with $A_p/A_n=1$

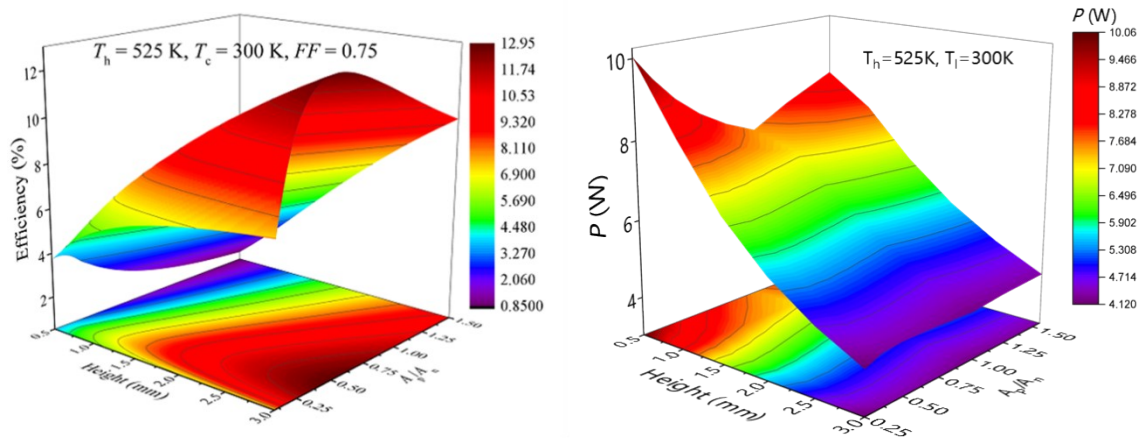


Fig S24. 3D plot relates the calculated maximum (A) conversion efficiency and (B) output power.

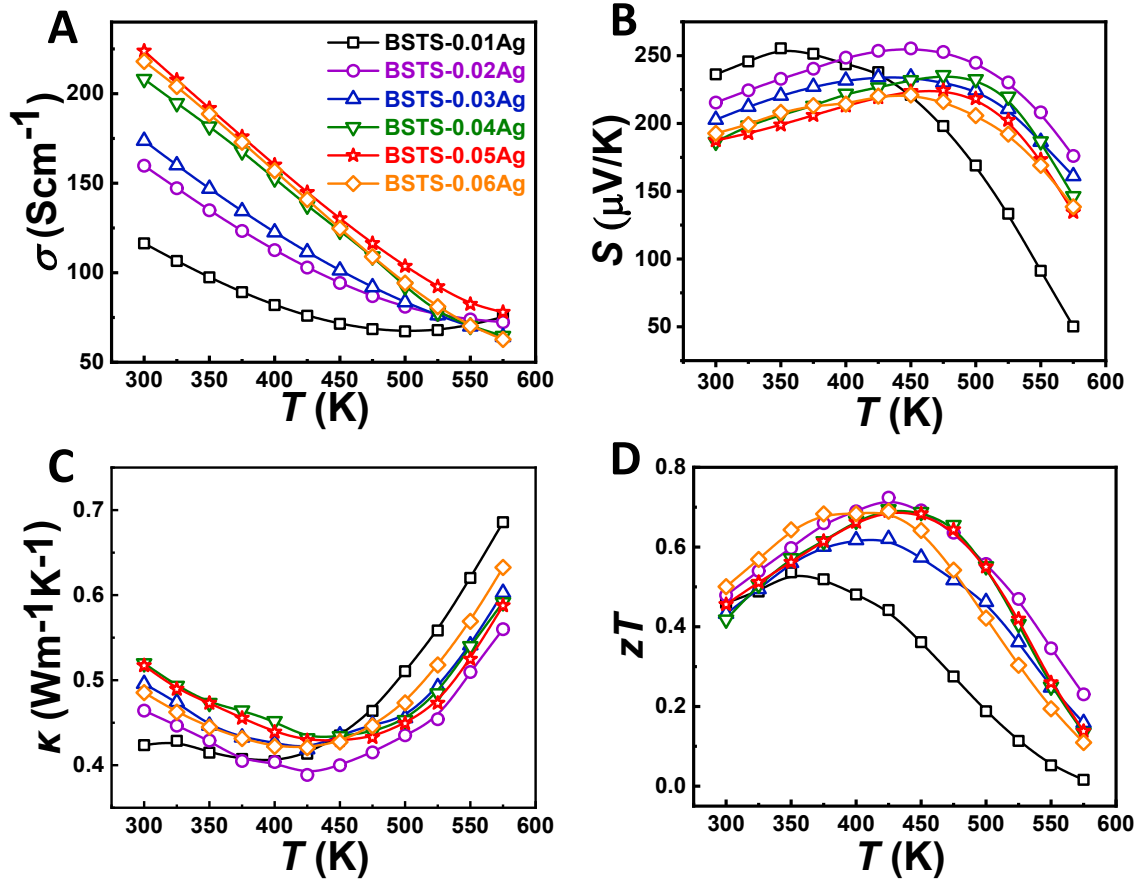


Fig S25. Out of-plane thermoelectric properties of $\text{BiSb}_{1-x}\text{Ag}_x\text{Te}_2\text{Se}$ ($x = 0.01 - 0.06$) (A-D). Temperature variation of (A) electrical conductivity (σ). (B) Seebeck coefficient (S). (C) Total thermal conductivity (κ) (D) thermoelectric Fig of merit (zT).

Table S1. Elemental composition for BiSb_{0.95}Ag_{0.05}Te₂Se through EDS.

EDS Spots	Bismuth		Antimony		Silver		Tellurium		Selenium	
	wt%	at%	wt%	at%	wt%	at%	wt%	at%	wt%	at%
Spot 1	24.77	15.03	19.24	20.04	0.03	0.05	40.79	40.54	15.15	24.34
Spot 2	24.87	15.00	18.59	19.24	0.03	0.04	40.16	39.66	15.15	24.34
Spot 3	23.99	14.31	15.41	15.77	3.22	3.71	40.48	39.53	16.90	26.67
spot 4	28.28	17.19	14.49	15.12	3.66	14.31	37.19	37.02	16.39	26.37
spot 5	25.77	15.54	38.85	38.36	3.71	4.33	38.85	38.36	16.05	25.60

Table S2. Physical properties used to calculate k_l based on various phonon scattering processes.

Parameters	Values
Debye temperature θ_D (K)	164 ¹⁷
Longitudinal sound velocity v_l (ms ⁻¹)	2800 ¹⁷
Transverse sound velocity v_T (ms ⁻¹)	1600 ¹⁷
Sound velocity v (ms ⁻¹)	1778
Average atomic mass of Bi ₂ Te ₃ M_{BT} (kg)	2.66×10 ⁻²⁵
Average atomic mass of Sb ₂ Te ₃ M_{ST} (kg)	2.07×10 ⁻²⁵
Average atomic volume of Bi ₂ Te ₃ V_{BT} (m ³)	3.48×10 ⁻²⁹
Average atomic volume of Sb ₂ Te ₃ V_{ST} (m ³)	3.13×10 ⁻²⁹
Sample density ρ (g cm ⁻³)	6.94
Grain size d (um)	30
Magnitude of Burger's vector B_D (Å)	12
average radius of the precipitates (nm)	15
Number of stacking faults crossing a line of unit length (m ⁻¹)	2×10 ²⁰
Poisson's ratio r	0.14 ¹⁸
Grüneisen parameter γ	1.5 ¹⁹
Bulk modulus K (GPa)	37.4 ¹⁷

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