Supplementary Information

Retarding Ostwald Ripening through Gibbs Adsorption and Interfacial Complexions Leads to High-Performance SnTe Thermoelectrics

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Experimental Section

Materials fabrication: Polycrystalline $SnAg_{0.05}Te-x\%CdSe$ (x = 0, 2, 4, 6, 8, 10, and12; x is in mole ratio), SnTe-6%CdSe, SnTe and SnAg_{0.05}Te samples were prepared by melting the stoichiometric compositions of high-purity elements Sn (> 99.5%, Aladdin), Te (99.99%, Aladdin), Ag (99.95%, Aladdin), Cd (99.99%, Aladdin), and Se (99.999%, Aladdin), which were sealed in the graphite-coated quartz tubes under a vacuum (~ 10^{-4} torr). The raw materials were slowly raised to 1223 K in 10 h, then dwelled for 10 h, and subsequently quenched in cold water. After annealing at 953 K for 100 h, the obtained ingots were hand-ground into fine powders in an Argon-filled glove box and further consolidated using spark plasma sintering (SPS-331Lx, Japan) at 843 K for 8 min under a uniaxial pressure of ~ 45 MPa. Finally, dense sintered (>98% of theoretical density) cylinder-shaped pellets with a thickness of $\sim 4 \text{ mm}$ and a diameter of 20 mm were obtained. SnAg_{0.05}Te-6%CdSe and Ag-free SnTe-6%CdSe underwent further thermal annealing at 953 K for up to 200 h, so as to examine their aging stability of both precipitation morphology and thermoelectric properties. In order to fabricate the single-leg module and junction of p-type SnAg_{0.05}Te-6%CdSe and Ni electrode, the SnAg_{0.05}Te-6%CdSe powders and the Ni powders were sequentially loaded into a graphite die and sintered together by SPS at 843 K for 8 min under 45 MPa. The junctions were cut along the pressure direction into a block with the cross section of 3.0 mm \times 3.0 mm and the height of \sim 6.5 mm for the contact resistance and the thermoelectric conversion efficiency measurements.

Thermoelectric properties measurements: The electrical transport properties including electrical resistivity (ρ) and Seebeck coefficient (*S*) were measured on a Namicro-3L system in a high vacuum atmosphere from room temperature to 600 K. The typical dimensions of the required SPSed samples are about $2 \times 2 \times 8 \text{ mm}^3$. Heating and cooling cycles allow repeatable electrical transport properties for the synthesized products. The measuring uncertainty of ρ and *S* was ~ 5%. The Hall coefficient ($R_{\rm H}$) was investigated under a reversible magnetic field (1.5 T) using the van der Pauw method across the temperature range of 300 K to 600 K during heating and cooling. The hole concentration ($n_{\rm H}$) and Hall carrier mobility ($\mu_{\rm H}$) were determined according

to the relations $n_{\rm H} = 1/(eR_{\rm H})$ and $\mu_{\rm H} = \sigma R_{\rm H}$, respectively, where *e* represents the electron charge. The total thermal conductivity was calculated using $\kappa = D\rho C_p$, where the thermal diffusivity (D) was measured on a Netzsch LFA 427 instrument by the laser flash method, the density (ρ) was estimated by the Archimedes principle, and the specific heat capacity (C_p) was derived from the measured values of Blachnik and Igel by $C_p(k_B/\text{atom}) = (3.07 + 0.00047(T/K - 300))$ for SnTe.^{1, 2} Given the individual uncertainty of each parameter, the measurement uncertainty of thermal conductivity κ was estimated to be within 10%. The combined uncertainty for all measurements involved in zT determination is below 20%. The electrical contact resistance was examined using four voltage probe method under a direct current electrical load (see Figure S31a). The single-leg module performance was measured by mini-PEM instrument (Advance Riko) under vacuum, using a nominal hot-side temperature from 50 °C up to 300 °C in sampling interval of 25 K. The hot-side and cold-side of the thermoelectric leg were weld by tin-based solder, together with copper wires soldered on the copper substrates (Figure S31b). The output power under varied loads would be determined through P = VI, here, V means the measured terminal voltage and I denotes the electrical current.

Materials characterizations: The phase compositions and crystal structure of all samples were identified through room-temperature powder X-ray diffraction (XRD) analysis (Ultima IV, Rigaku, Japan) using Cu K_{α} radiation ($\lambda = 1.5418$ Å, 40 kV, 40 mA), with a scan speed of 2°/min and a step size of 0.01°. In order to obtain the lattice parameter, the X-ray diffraction patterns were refined via FULLPROF software suite based on the Rietveld method. The X-ray photoelectron spectroscopy (XPS) was conducted on Thermo ESCALAB 250XI using Al K_{α} as the X-ray source (1486.74 eV) with an energy resolution of 0.43 eV. The carbon 1s peak (binding energy 284.8 eV) was used as a reference to calibrate the binding energies of the other core level spectra. The temperature-dependent in situ XRD was collected on Rigaku SmartLab SE under an argon gas atmosphere to preclude oxidation of the powder sample. The temperature was boosted stepwise with a heating rate of 30 K/min from 293 K to 773 K at 100 K intervals. The thin specimens for scanning transmission electron microscopy (STEM)

investigations were prepared by conventional methods including cutting, grinding, dimpling, polishing and Ar ion-milling (Gatan PIPS Model691). Atomic resolution STEM-HAADF imaging and energy dispersive X-ray mapping (EDX) experiments were performed on a JEOL ARM200F transmission electron microscope with a probe aberration corrector and an Oxford X-MaxN 100TLE spectrometer, operated at 200 keV. To exclude the influence during specimen preparation, a control TEM specimen was prepared by a dual beam focused ion beam (FIB) system (Helios NanoLab 600i, FEI) with a Ga ion beam at 30 kV. The structural characterizations were performed on a FEI Titan 80-300 transmission electron microscope with an imaging aberration corrector at 300 kV. Both TEM characterizations show similar core/shell structure and interfacial complexions. Atomic-scale composition analysis was conducted using atom probe tomography (APT). Site-specific specimens were fabricated by the in situ lift-out method³ using a dual-beam SEM/FIB instrument (Helios NanoLab650, FEI). To prevent Ga⁺ damage during milling, a low-energy (5 kV) cleaning procedure was carried out to remove the surface damage. APT measurements were performed on a local electrode atom probe (LEAPTM 4000X Si, CAMECA) by applying 10-ps, 10-pJ ultraviolet (wavelength = 355 nm) laser pulses with a detection rate of 1 ion per 100 pulses on average, a pulse repetition rate of 200 kHz at a base temperature of 40 K, and an ion flight path of 160 mm. The detection efficiency is limited to 50% due to the open area left between the microchannels on the detector plates. The data reconstruction and analysis were processed using the IVASTM 3.8.0. The nano-mechanical properties of all bulk samples were measured in an Agilent G200 Tester equipped with a standard Berkovich indenter with a load of 20 mN. Nano-hardness was determined from the measured load versus depth curves under the loading/unloading process. The nanoindentation tests were carried out 6 times for each sample to ensure the repeatability of the measuring data. The uncertainty in nanoindentation measurement is within 10%.

Density-functional-theory calculation: DFT calculations were performed by Vienna Ab initio Simulation Package (VASP)⁴ with the projector augmented wave (PAW) method.⁵ The exchange-functional was treated using the Perdew-Burke-Ernzerhof

(PBE)⁴ formulation, in combination with the DFT-D correction.⁶ The cut-off energy of the plane-wave basis was set at 500 eV. For the optimization of both geometry and lattice size, the Brillouin zone integration was performed with $3 \times 3 \times 3$ and $1 \times 1 \times 1$ Γ k-point sampling for the conventional cell of SnTe and the doped structures respectively. The self-consistent calculations apply a convergence energy threshold of 10^{-5} eV. The equilibrium geometries and lattice constant were optimized with maximum stress on each atom within 0.02 eV/Å.

1. XRD analyses of SnAg_{0.05}Te-x%CdSe



Figure S1. (a) Room-temperature powder XRD patterns of SnTe, and SnAg_{0.05}Te*x*%CdSe (x = 0 - 12) samples. (b) Enlarged (200) peak showing the peak shift with CdSe content. (c) Refined lattice parameter *a* and crystal cell volume *V* versus CdSe content in SnAg_{0.05}Te-*x*%CdSe (x = 0 - 12) based on Rietveld refinement method. The red dashed line is fitting of *a* on the basis of Vegard's law for a solid solution. (d) In situ XRD patterns as a function of temperature for SnAg_{0.05}Te-6%CdSe from 293 K to 773 K. Note that all the SnTe-based alloys show split of the (200) peak but it should not be related to the precipitates because the *x*=0% sample also shows this phenomenon. The position of the satellite peak shifts with the main (200) peak and does not fit with the expected diffraction angle of CdTe. The origin of peak split is interesting for future work but the lack in understanding of this phenomenon has no impact on the conclusion of this work.



2. Rietveld refinements for SnAg_{0.05}Te-*x*%CdSe

Figure S2. Rietveld refinement plots of $SnAg_{0.05}Te-x\%CdSe$ (x = 0 - 12) with the observed patterns in red, calculated patterns in black, and the differences between the observed and calculated intensities as a solid line at the bottom of the figure.



3. XPS characterizations of SnAg_{0.05}Te-6%CdSe sample

Figure S3. XPS spectra of wide scan (a) for $SnAg_{0.05}Te-6\%CdSe$ sample and high-resolution scan for (b) Sn 3d, (c) Ag 3d, (d) Cd 3d, (e) Te 3d, and (f) Se 3d.

As shown in Figure S3a, the wide scan of $SnAg_{0.05}$ Te-6%CdSe sample illustrates the characteristic energy peaks of Sn 3d, Ag 3d, Cd 3d, Se 3d, and Te 3d, indicating that Ag and Cd were effectively doped into the matrix lattice, and therefore forming chemical bonds with other elements. The corresponding high-resolution scans are presented in Figure S3b–f.

The coexistence of Sn^{2+} and Sn^{4+} in $\text{Sn } 3d_{5/2}$ core-level spectra is evidenced by a shoulder observed on the predominant peaks at 585.5 eV (Figure S3b), which is assigned to Sn^{4+} species. In Figure S3e, the Te 3d spectrum clearly reveals the presence of two different oxidation states (Te²⁻ and Te⁴⁺) for tellurium atoms. The main spin doublets ($3d_{5/2}$ and $3d_{3/2}$), present at 572.8 and 583.2 eV, respectively, are in good agreement with the reported values for Te²⁻.⁷ Additional peaks of higher binding energies in the Te 3d region correspond to Te⁴⁺. According to the known chemistry of tellurium-related compounds,⁸ the observed Te (II) and Te (IV) surface oxides obey the

following evolution mechanisms: $Te^{2-\rightarrow}Te^{0\rightarrow}Te^{4+}$. There is no measurable Te^{0} accumulation at the surface when the rate $v_2 > v_1$. Meanwhile, the particles containing Te^{4+} , as a final oxidation product, would readily leave the surface. This provides a feasible explanation for the reduction of the Te concentration (29.38 at. %) at the surface relative to Sn (48.14 at. %), in which the chemical compositions are calculated based on the core-level peak area and their relative sensitivity factor. Assuming surface composition remains homogenous, the above atomic concentration of Sn also fits well with the proposed value (i.e., 46.08 at. %), which demonstrates the occurrence of Sn self-compensation in our present work.

4. SEM characterizations of as-sintered SnAg_{0.05}Te-6%CdSe and SnTe-6%CdSe



Figure S4. SEM images with composition mappings by EDS for as-sintered (a) SnTe-6%CdSe and (b) SnAg_{0.05}Te-6%CdSe. No CdTe precipitates or Cd-rich phases are observed for as-sintered both SnAg_{0.05}Te-6%CdSe and SnTe-6%CdSe within the detection resolution of SEM measurement, and the corresponding composition mappings by EDS confirm the homogeneity for the matrix phase. Such single-phaselike morphologies observed by SEM before annealing can be understood by the existence of metastable supersaturated solid solution that contains many nanoscale precursors of precipitates. A similar phenomenon was also observed in other bulk thermoelectrics such as GeTe⁹ and PbTe.^{10, 11}

5. SEM characterizations of SnAg_{0.05}Te-6%CdSe and SnTe-6%CdSe annealed at 953 K for 100 h



Figure S5. (a) SEM image of SnTe-6%CdSe sample showing the coarsening of CdTe precipitates, which can be confirmed by EDS mapping analysis. (b) SEM image of SnAg_{0.05}Te-6%CdSe sample revealing a high density of nano-precipitates with an average size of 0.28 μ m, and the corresponding EDS mapping results verify that these nanoprecipitates are enriched in Cd.



Figure S6. Precipitate size distributions for the case of (a) SnTe-6%CdSe and (b) $SnAg_{0.05}Te-6\%CdSe$.

6. SEM characterizations of SnAg_{0.05}Te-6%CdSe and SnTe-6%CdSe annealed at 953 K for 200 h



Figure S7. (a) SEM image of SnTe-6%CdSe sample after annealing at 953 K for 200 h, showing coarser CdTe precipitates (~3.37 μ m) than that of the sample annealed for 100 h at 953 K. This morphological evolution of CdTe precipitates upon annealing at elevated temperatures results from the effect of Ostwald ripening on the sample SnTe-6%CdSe. (b) SEM image of SnAg_{0.05}Te-6%CdSe sample, revealing a highly stable Cdrich nano-precipitates (~0.22 μ m) under the long-duration annealing conditions.



Figure S8. Precipitate size distributions for the case of (a) SnTe-6%CdSe and (b) $SnAg_{0.05}Te-6\%CdSe$.

7. STEM characterizations of SnAg_{0.05}Te-6%CdSe



Figure S9. (a) Coherent interface between the (001) planes of SnTe and CdTe along the $[1\overline{1}0]$ direction. (b) Geometric phase analysis (GPA) of the area of (a).

8. APT characterizations of SnAg_{0.05}Te-6%CdSe and Gibbsian interfacial excess of Ag at interface



Figure S10. (a) APT reconstruction of the annealed $SnAg_{0.05}Te-6\%CdSe$ sample and (b) corresponding composition profile of Sn, Te, Cd, Se, and Ag.



Figure S11. Ladder diagram determined from the cuboid region of interest across the CdTe/SnTe interface. The Gibbsian interfacial excess of Ag at the interface can be calculated according to $\Gamma_{Ag} = N_{excess}/(\eta A)$, where N_{excess} can be obtained from the ladder

diagram indicated by the red arrow, A is the interfacial area of the selected region (40 nm \times 30 nm), and η is the APT detection efficiency (50% in case of LEAP 4000X Si).



9. Thermal transport properties of SnAg_{0.05}Te-x%CdSe samples

Figure S12. Temperature dependence of (a) thermal diffusivity (*D*), (b) electrical thermal conductivity, and (c) the ratio of κ_L/κ_{tot} as a function of CdSe fractions for SnAg_{0.05}Te-*x*%CdSe samples.

10. Modeling studies on thermal transport

Based on the Callaway-Klemens model, the relationship between lattice thermal conductivity of a disordered alloy \Box_{L}^{alloy} and that of the pure compound \Box_{L}^{pure} is described as follows:¹²

$$\frac{\kappa_{\rm L}^{\rm alloy}}{\kappa_{\rm L}^{\rm pure}} = \frac{\arctan(u)}{u} \tag{1}$$

where the scaling factor u is expressed by:^{13, 14}

$$u^{2} = \frac{\pi \Theta_{\rm D} \Omega}{2 h v_{\rm s}^{2}} \kappa_{\rm L}^{\rm pure} \Gamma$$
⁽²⁾

where Θ_D is the Debye temperature, Ω is the average volume per atom, \hbar is the reduced Planck's constant, v_s is the average sound velocity given by a weighted harmonic mean of the longitudinal and transverse sound velocities, and Γ is a total imperfection scaling parameter defined as:¹⁵

$$\Gamma = x \left(1 - x \right) \left[\left(\frac{\Delta M}{M} \right)^2 + \varepsilon \left(\frac{\Delta \alpha}{\alpha} \right)^2 \right]$$
(3)

where ΔM and $\Delta \alpha$ are the difference in mass and atomic radius between two constituents, M and α are the average mole mass and radius of all atoms in the unit cell, and ε stands for the phenomenological fitting parameter, which can be determined by:⁷

$$\varepsilon = \frac{2}{9} \left[\frac{6.4 \times \gamma \left(1 + r \right)}{1 - r} \right]^2 \tag{4}$$

here γ is the Grüneisen parameter, r is the Poisson ratio.

11. Calculated elastic properties of all the samples

The average sound velocity (v_s) , bulk modulus (B), shear modulus (G) and Young's modulus (E) are, respectively, given by:¹⁶⁻¹⁸

$$v_{\rm s} = \left(\frac{1}{3} \left[\frac{2}{v_{\rm t}^3} + \frac{1}{v_{\rm l}^3}\right]\right)^{-1/3}$$
(5)

$$B = \rho \left(v_1^2 - \frac{4v_t^2}{3} \right) \tag{6}$$

$$G = \rho v_{\rm t}^2 \tag{7}$$

$$E = \frac{9BG}{3B+G} = \frac{\rho v_t^2 \left(3v_1^2 - 4v_t^2\right)}{\left(v_1^2 - v_t^2\right)}$$
(8)

here, v_1 and v_t are longitudinal and transverse sound velocities obtained from ultrasonic measurements, respectively, and ρ represents the as-SPSed sample density.

The Grüneisen parameter (γ) and Poisson ratio (r) can be expressed as:¹⁹

$$\gamma = \frac{3}{2} \left(\frac{1+r}{2-3r} \right) \tag{9}$$

$$r = \frac{1 - 2(v_{\rm t}/v_{\rm l})^2}{2 - 2(v_{\rm t}/v_{\rm l})^2}$$
(10)

The Debye temperature (Θ_D) is determined from the sound velocity:²⁰

$$\Theta_{\rm D} = \frac{h}{k_{\rm B}} \left[\frac{3N}{4\pi V} \right]^{1/3} \nu_{\rm s} \tag{11}$$

where *h* is Planck's constant, $k_{\rm B}$ is the Boltzmann constant, *N* is the number of atoms in a unit cell, *V* is the unit-cell volume, and $v_{\rm s}$ is the average sound velocity.



Figure S13. Composition-dependent sound velocity of $SnAg_{0.05}Te-x\%CdSe$ (x = 0 - 12).

Table S1. Elastic properties for $SnAg_{0.05}Te-x\%CdSe$ at room temperature, including shear (*G*), bulk (*B*) and Young's (*E*) modulus, Grüneisen parameter (γ), Debye temperature (Θ_D), Debye frequency (ω_D), and Poisson ratio (*r*).

Composition	G	B	E	γ	Θ_{D}	$\omega_{\rm D}$	r
	(GPa)	(GPa)	(GPa)		(K)	(THz)	
<i>x</i> =0	12.9	20.2	32.0	1.44	148	25.7	0.24
<i>x</i> =2	12.8	17.2	30.7	1.30	146	25.8	0.26
<i>x</i> =4	12.6	20.9	31.5	1.50	146	25.1	0.27
<i>x</i> =6	13.7	21.2	33.7	1.43	152	25.2	0.27
<i>x</i> =8	12.9	15.9	30.4	1.22	147	25.3	0.27
<i>x</i> =10	12.9	18.8	31.5	1.37	148	25.0	0.28
<i>x</i> =12	13.5	19.4	32.8	1.36	151	25.2	0.27

12. Analysis of carrier transport coefficients



Figure S14. Comparison of the Hall carrier concentration-dependent Hall carrier mobility ($\mu_{\rm H}$) at 300 K with those reported in the literature.²¹⁻²³

Compared to the theoretical line, the slightly degraded carrier in $SnAg_{0.05}Te-x\%CdSe$ system is an inevitable consequence of heavy alloying (Figure S14), essentially, which is likely attributed to the high-density point defects and the increased population of lower mobility holes coming from the heavier Σ band due to valence-band convergence.



13. Electrical transport properties of SnAg_{0.05}Te-6%CdSe

Figure S15. Temperature-dependent thermoelectric properties of $SnAg_{0.05}Te-x\%CdSe$ (x = 0 - 10) samples: (a) electrical resistivity, (b) Seebeck coefficient, (c) power factor. (d) Comparison of the Hall carrier concentration-dependent Seebeck coefficient at 300 K with literature data.^{14, 21-26} The solid Pisarenko line is calculated based on the two-valance-band model considering both light hole and heavy hole valence band. The red circle is used to guide the eye.

The electrical transport properties including electrical resistivity (ρ), Seebeck coefficient (*S*), and power factor (PF) are depicted in Figure S15a–c, respectively. Note that extra Sn (~ 5%) is added to tune the carrier concentration ($n_{\rm H}$) in this work, i.e., Sn self-compensation.²⁶ It can be seen that both ρ and *S* in all the samples increase monotonically with elevating *T* up to 873 K, exhibiting a degenerate semiconducting nature. Regardless of *T*, the positive sign of *S* discloses holes as the major carriers, namely, p-type conduction. After doping with Ag, the ρ and *S* substantially rise in the full range of temperature for the sample with x = 0 compared to pristine SnTe. In

addition, the Hall measurement at 300 K shows a slight increase of $n_{\rm H}$ from ~ 3.31 × 10^{20} cm⁻³ in SnTe to ~ 3.42 × 10^{20} cm⁻³ in SnAg_{0.05}Te (The details of the room-temperature TE transport properties are listed in Table S2). Meanwhile, Hall carrier mobility ($\mu_{\rm H}$) is remarkably decreased after Ag incorporation, leading to increased electrical resistivity. The enhanced Seebeck coefficient at the same carrier concentration level and the reduced carrier mobility can be attributed to band convergence of light *L* and heavy Σ valence bands induced by Ag doping in SnTe.²⁷

With further increasing CdSe fraction in SnAg_{0.05}Te, the room-temperature ρ enhances noticeably in samples from x = 0 to 6, accompanied by a reduced $n_{\rm H}$ from ~ 3.42 to 1.43×10^{20} cm⁻³. This shows that CdSe serves as an electron donor to the SnAg_{0.05}Te lattice despite the nominally isovalent alloying. Similar effects were also found in SnTe-CdTe reported earlier and mainly attributed to the increase in the formation energy of single Sn-vacancy due to the presence of Cd alloying.^{26, 27} Moreover, further alloying with CdSe does not markedly alter ρ due to the limited solubility of Cd in SnTe. The SnAg_{0.05}Te-6%CdSe sample shows the highest *S* throughout the measuring temperature range of 300 – 873 K (Figure S15b). Specifically, the room-temperature *S* value of 44 μ V K⁻¹ for the *x* = 6 sample is higher than that of 31 μ V K⁻¹ for the CdSe-free SnAg_{0.05}Te (refer to *x* = 0). A maximum *S* approaching 180 μ V K⁻¹ at 873 K is achieved for SnAg_{0.05}Te-*x*%CdSe compounds without observable bipolar conduction. Owing to the compromise between *S* and ρ , the maximum power factor *S*²/ ρ of ca. 21 μ W cm⁻¹ K⁻² is achieved in SnAg_{0.05}Te-4%CdSe while the CdSe-free SnAg_{0.05}Te shows a value of 17 μ W cm⁻¹ K⁻² (Figure S15c).

To explicitly clarify the modified electronic transport, we plot the theoretical Pisarenko relationship between $n_{\rm H}$ and S at 300 K (see Figure S15d). The solid grey line in Figure S15d depicts a two-valence-band model predication using the density of state (DOS) effective mass ($m^*_{\rm DOS}$) of 0.168 $m_{\rm e}$ and 1.92 $m_{\rm e}$ ($m_{\rm e}$ being the unit mass of electron, 9.11 × 10⁻³¹ kg) for the L and Σ valence bands, respectively, and the energy separation ($\Delta E_{\rm L-\Sigma}$) of 0.35 eV.²⁸ The experimental S versus $n_{\rm H}$ for SnAg_{0.05}Te- x° /CdSe and data points obtained from literature (e.g., Ag,²⁵ Cd,²⁶ and Se²⁴ doped SnTe) are also included. The data of pristine, Sn self-compensated, and Se-alloyed SnTe match the

predicted line, indicating a negligible effect on the band structure and related m_{DOS}^* . In contrast, *S* values of CdSe-alloyed SnAg_{0.05}Te are considerably higher than those predicted by the Pisarenko curve, denoting the increase of m_{DOS}^* after the dual incorporation of Ag and Cd since *S* is proportional to m_{DOS}^* . Moreover, our samples also exhibit *S* values far above the corresponding data from (Cd, Ge)²² or (Cd, Se)²³ co-doped SnTe at a given $n_{\rm H}$. This conspicuous deviation of $n_{\rm H}$ -dependent *S* supports the enhanced valence band convergence in SnAg_{0.05}Te-x%CdSe compared to solely Ag-doped or CdSe-alloyed SnTe.

Table S2. The Seebeck coefficient (*S*), Hall carrier concentration ($n_{\rm H}$), Hall carrier mobility ($\mu_{\rm H}$), electrical resistivity (ρ), total thermal conductivity ($\kappa_{\rm tot}$), lattice thermal conductivity ($\kappa_{\rm L}$), and measure density (*d*) of SnAg_{0.05}Te-*x*%CdSe system (x = 0 - 10) at room temperature (300 K).

Composition	<i>S</i> (μV	$n_{\rm H}$ (10 ²⁰	$\mu_{\rm H}$ (cm ² V ⁻	ρ (mΩ	κ_{tot} (W m ⁻	$\kappa_{\rm L}$ (W m ⁻	Measured density
	K-1)	cm ⁻³)	$^{1}s^{-1}$)	cm)	${}^{1}K^{-1}$)	${}^{1}K{}^{-1}$)	(g cm ⁻³)
SnTe	28	3.31	146	0.13	9.41	3.60	6.41
<i>x</i> =0	31	3.42	103	0.18	7.14	3.31	6.46
<i>x</i> =2	34	2.77	98	0.23	5.24	2.49	6.47
<i>x</i> =4	40	2.47	100	0.25	4.15	1.87	6.46
<i>x</i> =6	44	1.43	130	0.33	3.23	1.74	6.45
<i>x</i> =8	37	3.88	60	0.27	3.23	1.13	6.32
<i>x</i> =10	34	3.62	57	0.30	2.91	0.83	6.40



Figure S16. Temperature-dependent weighted carrier mobility (μ_w). The μ_w follows a power law of $T^{-3/2}$ over the entire measured temperature range, indicating acoustic-phonon deformation potential scattering. The green curve is used to guide the eye.



Figure S17. DFT calculated electronic band structures of (a) pure SnTe, (b) $Sn_{31}AgTe_{32}$, and (c) $Sn_{29}AgCd_2Se_2Te_{30}$. The shadows in (a–c) represent the band gap. (d) The plots of total density of states (DOS).

We conducted first-principles density functional theory (DFT) calculations to examine the origin of enhanced Seebeck coefficient in SnAg_{0.05}Te-x%CdSe. Figure S17a-c illustrates the calculated band structures of pure SnTe, Sn₃₁AgTe₃₂ and Sn₂₉AgCd₂Se₂Te₃₀, respectively, in which the valence band maximum (VBM) and conduction band minimum (CBM) both locate at the L point. For pure SnTe, the direct band gap (E_g) at L and the energy separation between the primary L valence band and the secondary Σ valence band ($\Delta E_{L-\Sigma}$) are 0.05 eV and 0.35 eV, respectively, which is in good agreement with the previous reports.^{29, 30} With increasing Ag and CdSe contents, the calculated band gap increases to 0.15 eV in Sn₃₁AgTe₃₂, and further increases to 0.27 eV in Sn₂₉AgCd₂Se₂Te₃₀. Although the DFT calculations cannot precisely predict the E_g , the tendencies upon Ag and CdSe alloying should be reliable. This widened $E_{\rm g}$ can suppress the bipolar diffusion of charge carriers, maintaining a high Seebeck coefficient at high temperatures and reducing the bipolar thermal conductivity ($\kappa_{\rm b}$) as $\kappa_{\rm b} \propto \exp\left(-E_{\rm g}/2k_{\rm B}T\right)$, where $k_{\rm B}$ denotes the Boltzmann's constant and T is the absolute temperature. Additionally, incorporation of Ag and CdSe shrinks the energy separation between L and Σ valence band and enables a stronger band convergence at a given Fermi level. The overall effective band degeneracy N_v can be as high as 12–16 given the high N_v value of 4 for L and 12 for Σ bands, giving rise to a high m_{DOS}^* according to $m_{\text{DOS}}^* = N_{\text{V}}^{2/3} m_{\text{b}}^*$, where m_{b}^* is the average single valley

effective mass.³¹ Besides, the DFT calculations show that either Ag doping or Ag/CdSe co-doping causes a remarkable flattening of L valence band, which leads to the increased m_b^* further enhancing the m_{DOS}^* . Consequently, the most increase in density of states (DOS) near the Fermi level is achieved for Ag/CdSe co-doped SnTe (compared with the pure and single Ag-doped system) shown in Figure S17d.



Figure S18. Calculated partial density-of-states (PDOS) of (a) pure SnTe, (b) $Sn_{31}AgTe_{32}$, and (c) $Sn_{29}AgCd_2Se_2Te_{30}$. The vertical line denotes the Fermi level.

We further calculated the projected density of states (PDOS) to profoundly understand the role of (Cd, Ag) on this band convergence effect (see Figure S18). For pure SnTe, the VBM and CBM derive mostly from Te 5p and Sn 5p states, respectively, as shown in Figure S18a. For Ag-doped SnTe, the Ag 4d state not only contributes to the deep low-lying valence bands but also adds component near the second VBM (along the Σ line), which likely lifts the heavy Σ band position. With regard to the Ag-doped and CdSe alloyed SnTe, the conspicuous contribution from Cd 5s orbital is witnessed in the vicinity of the Fermi level (Figure S18c), corresponding to the hump of total DOS. The impurity band induced by isoelectronic substitution of Se on the Te site demonstrates a negligible role in band modification. Given all that, these band results along with experimentally observed high solubility of doping agents are responsible for the evident band convergence and much-improved S.

15. Analysis of quality factor and *zT* value



Figure S19. Thermoelectric figure of merit (zT) as a function of reduced Fermi level (η) and quality factor (B).



Figure S20. Power factor (PF) and total thermal conductivity (κ_{tot}) at 873 K for SnAg_{0.05}Te-*x*%CdSe.



Figure S21. Comparisons of zT values as a function of temperature for SnTe systems, including this work and other reported polycrystalline samples.^{23, 25-27, 32-38}





Figure S22. The repeated measurements of thermoelectric properties for $SnAg_{0.05}$ Te-6%CdSe sample, showing a highly reproducible and stable performance. Temperature dependence of (a) electrical resistivity, (b) Seebeck coefficient, (c) total thermal conductivity, and (d) *zT* values. The error zones in (d) correspond to 10% error. Note that all the samples are prepared with the same synthesis condition.

17. Theoretical conversion efficiency



Figure S23. Theoretical conversion efficiency as a function of hot-side temperature for SnAg_{0.05}Te-6%CdSe compared to Cd-doped,²⁶ Ag-doped,²⁵ and CdSe-alloyed SnTe²³ alloys. Herein, the η is determined using Snyder's model³⁹ that takes into account the strongly *T*-dependent parameters *S*(*T*), $\rho(T)$, and $\kappa(T)$.



18. Thermoelectric properties of as-sintered SnAg_{0.05}Te-6%CdSe and SnTe-6%CdSe

Figure S24. Comparison of thermoelectric performances between as-sintered SnTe-6%CdSe and SnAg_{0.05}Te-6%CdSe samples: (a) electrical resistivity, (b) Seebeck coefficient, (c) power factor, (d) total and lattice thermal conductivity, (e) figure of merit zT, and (f) corresponding thermoelectric conversion efficiency.



19. Thermoelectric properties of SnAg_{0.05}Te-6%CdSe and SnTe-6%CdSe annealed at 953 K for 100 h

Figure S25. Comparison of thermoelectric performances between SnTe-6%CdSe and SnAg_{0.05}Te-6%CdSe samples annealed at 953 K for 100 h: (a) electrical resistivity, (b) Seebeck coefficient, (c) power factor, (d) total and lattice thermal conductivity, (e) figure of merit zT, and (f) corresponding thermoelectric conversion efficiency.



20. Thermoelectric properties of SnAg_{0.05}Te-6%CdSe and SnTe-6%CdSe annealed at 953 K for 200 h

Figure S26. Comparison of thermoelectric performances between SnTe-6%CdSe and SnAg_{0.05}Te-6%CdSe samples annealed at 953 K for 200 h: (a) electrical resistivity, (b) Seebeck coefficient, (c) power factor, (d) total and lattice thermal conductivity, (e) figure of merit zT, and (f) corresponding thermoelectric conversion efficiency.

21. Annealing-time-dependent thermoelectric properties for SnAg_{0.05}Te-6%CdSe and SnTe-6%CdSe



Figure S27. Annealing time dependent electrical resistivity (ρ_{300K}), Seebeck coefficient (S_{300K}), average power factor ($PF_{avg, 300-873K}$), lattice thermal conductivity ($\kappa_{L, 300K}$), weighted mobility ($\mu_{w, 300K}$) and figure of merit (zT_{873K}) for (a,b) SnTe-6%CdSe and (c,d) SnAg_{0.05}Te-6%CdSe.

For the SnTe-6%CdSe system, we find that its thermoelectric performance is limited by precipitate coarsening (Ostwald ripening) during the annealing process (Figure S24–27). Specifically, the Ostwald ripening/coarsening obviously increases the lattice thermal conductivity and the electrical resistivity, thereby having a detrimental effect on the weighted mobility and zT value. The zT value decreases with increasing annealing time (Figure S28a). The maximum value of zT is 1.04 at 873K for the assintered sample (i.e., metastable supersaturated solid solution alloys). Long-term thermal annealing consumes small precipitates and thus reduces the scattering strength of phonons with medium wavelengths, resulting in a significant enhancement in the lattice thermal conductivity. The unchanged Seebeck suggests that the Fermi level of the annealed sample is unaltered, and therefore this enlarged room-temperature electrical resistivity upon annealing is likely a result of the increased detrimental phase/grain boundary scattering. Based on this argument, continuous degeneration of nanostructuring effect (quantized via weighted mobility) should be mainly responsible for the reduction of thermoelectric properties with annealing time.

In contrast to the Ag-free sample, the transport properties that determine zT are all stabilized for SnAg_{0.05}Te-6%CdSe system annealed at 953 K for a period up to 200 h, indicating that Ag-added samples have strong resistance to Ostwald ripening. As shown in Figure S28b, the peak zT value remains constant (>1.42) with annealing time. As we know, the materials system takes shorter time to reach its equilibrium state at higher annealing temperatures (953 K)⁴¹. Such a difference of the annealing-time-dependent evolution of microstructure and thermoelectric properties between Ag-free SnTe-6%CdSe and SnAg_{0.05}Te-6%CdSe further demonstrates reliable effectiveness of suppression of Ostwald ripening via interface segregation under the long-duration annealing conditions.



Figure S28. Temperature dependence of thermoelectric figure of merit (*zT*) for (a) SnTe-6%CdSe and (b) SnAg_{0.05}Te-6%CdSe at different annealing period from 0 to 200 h.



22. Histogram of hardness among the reported thermoelectric material systems

Figure S29. Indentation hardness at the max load of pristine SnTe and SnAg_{0.05}Te-10%CdSe sintered pellets in comparison with other state-of-the-art TEs.^{15, 32, 42-46}



23. The contact resistance of the Ni/SnAg_{0.05}Te-6%CdSe junction

Figure S30. (a) Top: SEM image on the Ni/SnTe interface. Middle: resistance line scanning across the Ni/SnTe interface for electrical contact resistivity measurement. Bottom: corresponding EDS mapping for Ni. (b) 3D plots of repeatedly measured interfacial electrical resistances at Ni/SnTe electrodes.

Junction design: On the basis of the metal-semiconductor contact theory, the contact resistance ρ_c is closely related with the barrier height of the depletion layer between metal and semiconductor couple,⁴⁷ in which the barrier height could be described by the work function Φ (Φ_m for metal and Φ_{ps} for p-type semiconductor). The work function of 5.15 eV for Ni approaching that for SnTe (~ 5.10 eV),⁴⁸ namely, small Φ difference and, thus, an Ohmic contact is formed at the interfaces ($\Phi_m > \Phi_{ps}$).

24. Measurement systems for contact resistivity and conversion efficiency



Figure S31. (a) Practical view of the contact resistivity measurement. (b) Experimental setup to measure the conversion efficiency of a single TE leg.

Note that: The output voltage V_{out} versus current *I* in Figure 5c uncovers that the *I-V* curves present a good linear relation, where the *y*-intercept and slope intend the open circuit voltage (V_{oc}) and the single-leg's internal resistance (R_{in}), respectively. The maximum power density ($P_{out, max}$) was reached while the external electrical load was matched with R_{in} . It is worth noting that the $P_{out, max}$ was calculated through the tested maximum power divided by the leg cross-sectional area of 9 mm².

Discussion: Next, we also need to further improve the output power of the device via optimizing internal resistance (R_{in}). Despite the low contact resistance obtained in this work, resistance contributions from both Sn-Pb-based solder layer and wires should take critical responsibility for extra electrical loss. On one hand, it is necessary to replace the Ag-based solder with higher electrical conductivity. On the other hand, the preparation of several couples of p-n pairs is also expected to decrease the ratio of contact resistance to the internal resistance of materials, and thus enhancing the output power density and energy conversion efficiency.

References

- 1. R. Blachnik and R. Igel, Zeitschrift für Naturforschung B, 1974, 29, 625-629.
- 2. Y. Pei, X. Shi, A. LaLonde, H. Wang, L. Chen and G. J. Snyder, *Nature*, 2011, 473, 66-69.
- 3. K. Thompson, D. Lawrence, D. J. Larson, J. D. Olson, T. F. Kelly and B. Gorman, *Ultramicroscopy*, 2007, **107**, 131-139.
- 4. J. P. Perdew, K. Burke and M. Ernzerhof, *Physical review letters*, 1996, 77, 3865-3868.
- 5. G. Kresse and D. Joubert, *Physical Review B*, 1999, **59**, 1758-1775.
- S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *The Journal of Chemical Physics*, 2010, 132, 154104.
- D. An, S. Chen, Z. Lu, R. Li, W. Chen, W. Fan, W. Wang and Y. Wu, ACS applied materials & interfaces, 2019, 11, 27788-27797.
- V. S. Neudachina, T. B. Shatalova, V. I. Shtanov, L. V. Yashina, T. S. Zyubina, M. E. Tamm and S. P. Kobeleva, *Surface Science*, 2005, 584, 77-82.
- 9. J. Li, C. Zhang, Y. Feng, C. Zhang, Y. Li, L. Hu, W. Ao and F. Liu, *Journal of Alloys and Compounds*, 2019, **808**, 151747.
- P. Y. Deng, K. K. Wang, J. Y. Du and H. J. Wu, *Advanced Functional Materials*, 2020, 30, 2005479.
- S. N. Girard, K. Schmidt-Rohr, T. C. Chasapis, E. Hatzikraniotis, B. Njegic, E. M. Levin, A. Rawal, K. M. Paraskevopoulos and M. G. Kanatzidis, *Advanced Functional Materials*, 2013, 23, 747-757.
- X. Qian, H. Wu, D. Wang, Y. Zhang, J. Wang, G. Wang, L. Zheng, S. J. Pennycook and L.-D. Zhao, *Energy & Environmental Science*, 2019, 12, 1969-1978.
- H. Wang, A. D. LaLonde, Y. Pei and G. J. Snyder, *Advanced Functional Materials*, 2013, 23, 1586-1596.
- G. Tan, S. Hao, R. C. Hanus, X. Zhang, S. Anand, T. P. Bailey, A. J. E. Rettie, X. Su, C. Uher, V. P. Dravid, G. J. Snyder, C. Wolverton and M. G. Kanatzidis, *ACS Energy Letters*, 2018, 3, 705-712.
- 15. D. An, S. Chen, X. Zhai, Y. Yu, W. Fan, T. Zhang, Y. Liu, Y. Wu, W. Wang and G. J. Snyder, *Journal of Materials Chemistry A*, 2020, **8**, 12156-12168.
- 16. O. L. Anderson, *Journal of Physics and Chemistry of Solids*, 1963, 24, 909-917.
- 17. T. Górecki, Materials Science and Engineering, 1980, 43, 225-230.
- M. Manikandan, A. Amudhavalli, R. Rajeswarapalanichamy and K. Iyakutti, *Solid State Communications*, 2019, 291, 36-42.
- 19. D. S. Sanditov and V. N. Belomestnykh, *Technical Physics*, 2011, 56, 1619-1623.
- K. Kurosaki, A. Kosuga, H. Muta, M. Uno and S. Yamanaka, *Applied Physics Letters*, 2005, 87, 061919.
- M. Zhou, Z. M. Gibbs, H. Wang, Y. Han, L. Li and G. J. Snyder, *Applied Physics Letters*, 2016, 109, 042102.
- J. Tang, B. Gao, S. Lin, X. Wang, X. Zhang, F. Xiong, W. Li, Y. Chen and Y. Pei, ACS Energy Letters, 2018, 3, 1969-1974.
- 23. B. Gao, J. Tang, F. Meng and W. Li, *Journal of Materiomics*, 2019, 5, 111-117.
- 24. M. Hong, Y. Wang, S. Xu, X. Shi, L. Chen, J. Zou and Z.-G. Chen, *Nano Energy*, 2019, **60**, 1-7.
- 25. D. Sarkar, T. Ghosh, A. Banik, S. Roychowdhury, D. Sanyal and K. Biswas, *Angewandte Chemie International Edition*, 2020, **59**, 11115-11122.

- G. Tan, L. D. Zhao, F. Shi, J. W. Doak, S. H. Lo, H. Sun, C. Wolverton, V. P. Dravid, C. Uher and M. G. Kanatzidis, *Journal of the American Chemical Society*, 2014, 136, 7006-7017.
- X. Qi, Y. Huang, D. Wu, B. Jiang, B. Zhu, X. Xu, J. Feng, B. Jia, Z. Shu and J. He, *Journal of Materials Chemistry A*, 2020, 8, 2798-2808.
- Q. Zhang, B. Liao, Y. Lan, K. Lukas, W. Liu, K. Esfarjani, C. Opeil, D. Broido, G. Chen and Z. Ren, *Proceedings of the National Academy of Sciences of the United States of America*, 2013, 110, 13261-13266.
- T. Hussain, X. Li, M. H. Danish, M. U. Rehman, J. Zhang, D. Li, G. Chen and G. Tang, *Nano Energy*, 2020, **73**, 104832.
- 30. J. Tang, B. Gao, S. Lin, J. Li, Z. Chen, F. Xiong, W. Li, Y. Chen and Y. Pei, Advanced Functional Materials, 2018, 28, 1803586.
- S. Sarkar, X. Zhang, S. Hao, X. Hua, T. P. Bailey, C. Uher, C. Wolverton, V. P. Dravid and M. G. Kanatzidis, *ACS Energy Letters*, 2018, 3, 2593-2601.
- R. Al Rahal Al Orabi, J. Hwang, C.-C. Lin, R. Gautier, B. Fontaine, W. Kim, J.-S. Rhyee, D. Wee and M. Fornari, *Chemistry of Materials*, 2016, 29, 612-620.
- H. Wu, C. Chang, D. Feng, Y. Xiao, X. Zhang, Y. Pei, L. Zheng, D. Wu, S. Gong, Y. Chen, J. He,
 M. G. Kanatzidis and L.-D. Zhao, *Energy & Environmental Science*, 2015, 8, 3298-3312.
- W. Li, L. Zheng, B. Ge, S. Lin, X. Zhang, Z. Chen, Y. Chang and Y. Pei, *Advanced materials*, 2017, 29, 1605887.
- 35. J. Tang, Z. Yao, Z. Chen, S. Lin, X. Zhang, F. Xiong, W. Li, Y. Chen and Y. Pei, *Materials Today Physics*, 2019, **9**, 100091.
- A. Banik, U. S. Shenoy, S. Anand, U. V. Waghmare and K. Biswas, *Chemistry of Materials*, 2015, 27, 581-587.
- Z. Chen, X. Guo, J. Tang, F. Xiong, W. Li, Y. Chen and R. Ang, ACS applied materials & interfaces, 2019, 11, 26093-26099.
- S. Li, J. Xin, A. Basit, Q. Long, S. Li, Q. Jiang, Y. Luo and J. Yang, *Advanced science*, 2020, 7, 1903493.
- 39. G. J. Snyder and A. H. Snyder, *Energy & Environmental Science*, 2017, **10**, 2280-2283.
- 40. M. Wood, J. J. Kuo, K. Imasato and G. J. Snyder, *Advanced materials*, 2019, **31**, 1902337.
- Y. Wu, Z. Chen, P. Nan, F. Xiong, S. Lin, X. Zhang, Y. Chen, L. Chen, B. Ge and Y. Pei, *Joule*, 2019, 3, 1276-1288.
- 42. M. S. Darrow, W. B. White and R. Roy, *Journal of Materials Science*, 1969, 4, 313-319.
- 43. P. Qin, Z.-H. Ge and J. Feng, *Journal of Materials Research*, 2017, **32**, 3029-3037.
- 44. F. Ren, E. D. Case, E. J. Timm and H. J. Schock, *Journal of Alloys and Compounds*, 2008, **455**, 340-345.
- 45. K. Tyagi, B. Gahtori, S. Bathula, M. Jayasimhadri, S. Sharma, N. K. Singh, D. Haranath, A. K. Srivastava and A. Dhar, *Solid State Communications*, 2015, **207**, 21-25.
- 46. L.-D. Zhao, B.-P. Zhang, J.-F. Li, M. Zhou, W.-S. Liu and J. Liu, *Journal of Alloys and Compounds*, 2008, **455**, 259-264.
- 47. W. Liu, Q. Jie, H. S. Kim and Z. Ren, Acta Materialia, 2015, 87, 357-376.
- 48. Z. Fu, M. Liu and Z. Yang, *Physical Review B*, 2019, 99.