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Efficient power generation near room temperature in earth-abundant thermoelectric tin sulfide

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Abstract

Tin monosulfide (SnS), an earth-abundant IV–VI semiconductor, has emerged as a promising platform for low-temperature thermoelectrics owing to its highly tunable electronic structure. Here, we show that Na/Ag co-doped SnS single crystals induce a favorable reconstruction of the valence-band, forming a modulated triple-band structure that enhances the density-of-states effective mass while retaining high carrier mobility and enabling an ultrahigh room-temperature power factor of $\sim 101 \mu\text{W cm}^{-1} \text{K}^{-2}$. Combined with intrinsically low thermal conductivity arising from the lattice distortion, the optimized crystal reaches a zT value of ~ 1.06 at 300 K and ~ 2.0 at 573 K, delivering $\sim 3.3\%$ conversion efficiency and $\sim 0.31 \text{ W cm}^{-2}$ output power density in a single-leg module under 243 K temperature gradient. These results indicate the highly effective multiband-engineered tin sulfide thermoelectrics for near-room-temperature energy conversion.

Thermoelectric (TE) devices offer a unique solid-state route for heat-to-electricity conversion, enabling compact and maintenance-free energy harvesting via the Seebeck effect. Conversely, the Peltier effect provides on-chip and electronics cooling without the need for refrigerant^{1,2}. Despite these inherent advantages, the widespread deployment of thermoelectrics has been hindered by the sluggish progress in developing the conversion efficiency of the semiconductor materials, which is determined by the dimensionless figure of merit, $zT = \sigma S^2 T / (\kappa_l + \kappa_e)$, where T is the absolute temperature^{3,4}. The three transport parameters, electrical conductivity (σ), Seebeck coefficient (S), and the thermal conductivity from the electronic part (κ_e), are strongly interdependent, making the optimization challenging. Therefore, gaining zT typically focuses on minimizing the independent variable of lattice thermal conductivity κ_l , while simultaneously maximizing the power factor ($PF = \sigma S^2$)^{6,7}.

In recent years, investigations on high-performance TE materials operating near room temperature (RT) have intensified, as evidenced by the substantial progress in several systems, including $\text{Mg}_3(\text{Bi}, \text{Sb})_2$ -based alloys^{8,9}, Heuslers^{10,11}, and other emerging chalcogenides^{12,13}. Parallel efforts in flexible and microscale TE platforms have further expanded the scope of thermoelectrics for wearable and on-chip cooling applications¹⁴. However, to date, the feasibility of commercialized devices still relies predominantly on Bi_2Te_3 -based materials, whose dependence on tellurium presents critical challenges due to its scarcity, high cost, and toxicity^{15,16}. This urgency to move away from tellurium has motivated the exploration of alternative systems based on earth-abundant and environmentally benign elements capable of delivering competitive performance.

In this regard, layered tin chalcogenides, especially tin selenide (SnSe), have emerged as highly attractive candidates delivering record high ZT value^{17–19}. SnS , while structurally analogous, offers practical advantages including lower toxicity, lower cost, and greater elemental abundance^{20,21}. Aliovalent doping by substitutional cations (Na^+ and Ag^+) has been proven effective for tailoring the carrier density and enhancing p-type TE efficiency^{22–25}. On the other hand, isovalent doping at the S site by Se promotes the enhancement of PF through band structure modification and κ_l reduction by lowering the phonon group velocity^{26,27}. However, in conventional polycrystalline SnS , the peak thermoelectric performance typically appears at elevated temperatures, mainly due to strong carrier scattering at grain boundaries that limits carrier mobility (μ) near RT. This effect is further reinforced by the structural phase transition from the low-symmetry Pnma phase to the high-symmetry Cmcm phase at high temperature, which enhances μ and shifts optimal performance toward higher temperatures^{25,27}.

In contrast, single-crystalline counterpart eliminates grain-boundary scattering and expose the intrinsic transport behavior of the lattice, enabling superior thermoelectric performance near RT. For example, $\text{SnS}_{0.9}\text{Se}_{0.1}$, optimized by controlled sulfur enrichment through SnS_2 addition, exhibits a power factor of $\sim 58 \mu\text{W cm}^{-1} \text{K}^{-2}$ at 300 K and reaches a peak zT of ~ 1.6 at 573 K²⁸. However, these strategies primarily increased carrier concentration (n), while the associated reduction in μ limited performance near RT.

This limitation motivated us to develop single-crystalline SnS that restructures the valence band, preserving effective carrier transport even under a high effective mass, m^* , as illustrated in Fig. 1a. Na^+ is first introduced to regulate hole concentration, providing a direct handle on electrical conductivity. Building upon this optimized carrier background, Ag^+ is introduced as a secondary dopant to engineer the valence-band structure. Pristine SnS exhibits four valence bands (VBs), separated by momentum space $\text{Y}-\Gamma-\text{Z}-\text{U}$, with the maxima located relatively close to the Fermi level. At higher Ag concentrations, the band evolution becomes more pronounced, where VB1 and VB3 begin to merge into a single dispersive feature, as confirmed by angle-resolved photoemission spectroscopy (ARPES). A similar band-merging phenomenon in SnSe, known as a “pudding-mold” band structure arising from multiband synglisis, was reported by Qin *et al.*¹⁸. This merging flattens the valence-band maximum, enhancing the effective mass while preserving high mobility by suppressing intervalley scattering, with additional mobility gains from convergence of the light band (VB4) at the $\text{Y}-\Gamma$ valleys^{19,27}. The evolution toward this modulated triple-valence-band configuration in SnS promotes higher μ while simultaneously enhancing the density-of-states (DOS) effective mass, m_d^* . This strategy effectively mitigates the coupling effect between μ and m_d^* , yielding a high weighted mobility ($\mu_w \approx \mu (m_d^*/m_e)^{3/2}$) of $\sim 1286 \text{ cm}^2 \text{V}^{-1} \text{S}^{-1}$ at RT. Within this temperature range, κ_l exhibits a modest reduction arising from the structural defects, specifically Sn–S bond-angle distortions and direction-dependent phonon softening, which enhance phonon scattering while leaving σ unaffected. Fig. 1B demonstrates the significant enhancement of μ_w/κ_l in $\text{Sn}_{0.99-x}\text{Na}_{0.01}\text{Ag}_x\text{S}$ single crystals, delivering a high quality factor ($B \propto \mu_w/\kappa_l$) at RT. The pronounced increase in μ_w/κ_l with Hall carrier concentration (n_H) indicates a synergistic balance between charge transport and phonon scattering.

This work represents a notable breakthrough in single-crystalline SnS thermoelectrics, particularly given that the raw constituent elements are eco-friendly and cost-effective²⁹. Furthermore, it establishes a new pathway for realizing high-performance sulfide-based thermoelectrics, demonstrating that the poor performance at RT can be effectively overcome

through the band-structure engineering strategies developed here. In this study, our p-type $\text{Sn}_{0.96}\text{Na}_{0.01}\text{Ag}_{0.03}\text{S}$ achieved a record zT peak of ~ 2 at 573 K (see Fig. 1c), surpassing those of previously reported single crystals^{20,21,27,28} and establishing this system as the best-performing tin sulfide-based thermoelectrics to date.

Enhanced thermoelectric transport properties

Figure 2 summarizes the thermoelectric transport properties measured along the crystallographic b-axis, which exhibits the highest performance in this system^{20,21}. High-quality single crystals were synthesized using a modified Bridgman method and subsequently cut into well-defined geometries for transport measurements (see Supplementary Fig. 1). Phase purity and crystallographic orientation were confirmed by powder X-ray diffraction and Laue back-reflection analysis (Supplementary Figs. 2 and 3), which verified the orthorhombic Pnma structure and accurately resolved the principal crystal axes. Ag incorporation induces a pronounced evolution of S (Fig. 2a), which increases from ~ 224 to $\sim 246 \mu\text{V K}^{-1}$ at RT as Ag concentration rises from 0 to 0.04, despite the simultaneous rise in measured n_{H} . Moreover, σ at RT improved gradually up to $\sim 1700 \text{ S cm}^{-1}$ for $x = 0.03$ (Fig. 2b), which is the highest value reported to date among SnS single crystals^{27,28}. The modest decrease of σ with temperature reflects the expected acoustic-phonon transport, consistent with $T^{-1.5}$ behavior of μ_{w} shown in Fig. 2b inset. Despite the large Ag nominal (x) in this compound, the positive trend of σ and n_{H} confirmed the successful cationic substitution in the crystals. However, as more dopant (at $x = 0.04$) was introduced, the electron donor from the Ag precipitate started to contribute^{13,30}, as revealed by the elemental mapping (see Supplementary Fig. 4), and the impurity scattering became more dominant, resulting in a reduction of both n_{H} and μ_{w} in this sample. Overall, the substantial improvement of σ and S resulted in the enhancement of PF through this Ag incorporation (Fig. 2c). Consequently, the maximum PF reached $\sim 101 \mu\text{W cm}^{-1} \text{ K}^{-2}$ at 300 K for $x = 0.03$, a value essentially higher than the high performance reported for the SnS and SnSe single crystal^{18,28}.

For thermal transport measurements, the total thermal conductivity (κ_{tot}) was determined from the measured thermal diffusivity, heat capacity, and density (Supplementary Fig. 5 and Supplementary Table 1). The heat capacity remains essentially unchanged upon Ag incorporation ($x = 0.03$), as confirmed with low-temperature heat-capacity measurements (see Supplementary Discussion 1). As shown in Fig. 2d, κ_{tot} decreases with increasing temperature for all compositions due to increased phonon–phonon scattering (Umklapp). Ag incorporation

leads to a slight change of κ_{tot} across the entire temperature range, though the variation remains modest compared to the SnS crystal ($x = 0$). The electronic contribution to thermal transport was evaluated by calculating the Lorenz number (L) using the single parabolic band (SPB) model and estimating the electronic thermal conductivity ($\kappa_e = L\sigma T$), as shown in Supplementary Fig. 6. Applying the Wiedemann–Franz relation ($\kappa_l = \kappa_e - \kappa_{\text{tot}}$), the extracted κ_l reveals a clear reduction with increasing Ag concentration, particularly for $x = 0.03$. This suppression arises from enhanced phonon scattering due to mass fluctuation and local lattice strain introduced by Ag substitution^{31,32}, consistent with Callaway’s simulation (Supplementary Methods) of κ_l . The observed T^{-1} further confirms Umklapp scattering as the dominant heat transport mechanism³³.

Modifications in the crystal structure

To confirm the TE properties associated with crystal structure modifications, we investigated the structural evolution using high-resolution synchrotron radiation (SR) powder X-ray diffraction (XRD) with quantitative structural analysis, through Rietveld refinement as shown in Supplementary Fig. 7. The lattice parameters were evaluated by Le Bail fit to decorrelate the information with respect to the structure (see results in Supplementary Fig. 8 and Supplementary Tables 2 and 3). A key indicator of structural change is the angle (θ) between Sn–S bond and the a -axis, calculated from the refined atomic positions. As shown in Fig. 3a, θ progressively decreases with increasing Ag content, confirming a systematic modification of the crystal structure. Qin et al. reported similar structural response in Pb- and Sr-doped SnSe^{18,19}, exhibiting enhanced in-plane electrical transport associated with increased crystal symmetry arising from θ reduction.

Further structural insight with Sn K-edge X-ray absorption near-edge structure (XANES) of Sn_{0.96}Na_{0.01}Ag_{0.03}S shows a subtle shift of the spectrum edge toward higher energy relative to Ag-free SnS (Fig. 3b). This behavior indicates only a slight modification of the local Sn electronic environment by dopant incorporation, consistent with a small increase in Debye-Waller factor (σ^2) in Sn_{0.96}Na_{0.01}Ag_{0.03}S sample (See fitting results in Supplementary Figs. 9–11 and Supplementary Table 4). Figs. 3D compares the extended X-ray absorption fine structure (EXAFS) spectra at both the Sn and Ag K-edges for the Sn_{0.96}Na_{0.01}Ag_{0.03}S sample. Both Fourier transforms of the EXAFS signal show strong similarities, suggesting the successful substitution of Ag on the Sn site. Based on such observations, both signals have been fitted using SnS as a structural model, allowing an isotropic and linear expansion of

interatomic distances. In this model, a contraction of $\sim 3.7\%$ of Ag–S bond distance with respect to Sn–S distances is observed (see Supplementary Table 4). This contraction is consistent with the reduction in unit-cell volume determined by X-ray diffraction.

Raman spectroscopy provides further evidence of lattice dynamical changes induced by Ag incorporation into $\text{Sn}_{0.99-x}\text{Na}_{0.01}\text{Ag}_x\text{S}$ sample. Figures 3d and 3e show the Raman spectra and their extracted peak positions for the out-of-plane (A_g^1 and A_g^3) and in-plane (A_g^2 and B_{3g}) vibrational modes as a function of Ag content, with schematic illustrations of the corresponding vibrational modes shown in Fig. 3f. Upon increasing Ag concentration, all four Raman-active modes exhibit a systematic red shift, indicating phonon softening associated with the progressive introduction of chemical defects^{33,34}. Notably, the in-plane vibrational modes show only a slight degree of softening, whereas the red shifts from the out-of-plane modes are more pronounced. This anisotropic phonon renormalization indicates enhanced vibrational anisotropy at higher Ag content, with a stronger in-plane vibrational character. Such behavior corroborates the structural distortions and is expected to shorten the phonon mean free path, thereby suppressing κ_l while maintaining high electrical transport properties^{35–37}. In addition, the microstructure analysis of $\text{Sn}_{0.96}\text{Na}_{0.01}\text{Ag}_{0.03}\text{S}$ crystal via scanning transmission electron microscopy (STEM) reveals local structural characteristics (see Supplementary Fig. 12), in which the magnified image of high-angle annular dark field (HAADF) STEM shows the displacement of Sn atoms. The distortions are expected to introduce spatial fluctuations in local strain gradients, leading to systematic θ deviations in similar layered crystal systems (38, 39).

Electronic band structure modification and multi-valley transport

To elucidate the role of electronic band structure in governing the electrical transport properties of $\text{Sn}_{0.99-x}\text{Na}_{0.01}\text{Ag}_x\text{S}$, we performed density functional theory (DFT) calculations, as displayed in Fig. 4a. The corresponding unfolded band structures were constructed with the 144-atom supercells for direct accommodation with empirical compositions (see details in Supplementary Discussion 2). Relative to the pristine SnS band structure ($x = 0$) (Supplementary Fig. 13), the band structure of $\text{Sn}_{70}\text{Na}_1\text{Ag}_1\text{S}_{72}$ shows a convergence of the valence band (VB) along the Γ –Y direction, where the energy offset (ΔE) is reduced by half, from 0.142 to 0.064 eV (Supplementary Table 5). With higher Ag incorporation in $\text{Sn}_{70}\text{Na}_1\text{Ag}_2\text{S}_{72}$, the band features broaden due to enhanced band mixing around the band edge. Additionally, DFT calculations, performed using the crystal structure information (CIF) obtained from Rietveld refinement, reveal the emergence of band convergence between Na-

doped SnS ($x = 0$) and $\text{Sn}_{0.96}\text{Na}_{0.01}\text{Ag}_{0.03}\text{S}$ ($x = 0.03$), as shown in Supplementary Fig. 14, confirming the contribution of the modified crystal structure to the observed band modulation.

ARPES measurements were performed at RT using a photon energy of 92 eV to experimentally probe the evolution of the valence band structure in $\text{Sn}_{0.99-x}\text{Na}_{0.01}\text{Ag}_x\text{S}$ for selected compositions $x = 0, 0.01$, and 0.03 , as shown in Fig. 4b, with the corresponding Brillouin zone illustrated in Supplementary Fig. 15a. The energy dispersion (E) along the Γ –Z momentum path (k) was resolved to examine the first valence band maximum (VBM), which predominantly governs electrical transport properties of SnS. For all compositions, the VBM lies close to the Fermi energy (E_F), indicating that Na-doped SnS is already degenerated. With the introduction of substitutional Ag, the three valence bands become clearly distinguishable. At $x = 0.03$, the VBM is shifted away from the Z-point, confirming the k alignment from this extremum.

Ag incorporation also induces noticeable flattening of the VBM, resulting in an increased band effective mass (m^*/m_e) at higher Ag concentration. By fitting the second derivative of the ARPES intensity maps using the $E(k)$ dispersion relation, m^*/m_e were extracted for different Ag contents (Supplementary Fig. 15b). The Na-doped SnS sample ($x = 0$) exhibits $m^*/m_e \approx 0.39$, which increases to ~ 0.68 in $\text{Sn}_{0.96}\text{Na}_{0.01}\text{Ag}_{0.03}\text{S}$. This trend is consistent with the Pisarenko plot of n_H vs S based on the single parabolic band (SPB) model (supplementary Fig. 16), where Ag-rich samples fall along the theoretical line corresponding to a larger DOS effective mass ($m_d^* = N_v^{2/3}m^*$) of $1.97m_e$. Consequently, the high S of $\sim 244 \mu\text{V K}^{-1}$ at 300 K in $\text{Sn}_{0.96}\text{Na}_{0.01}\text{Ag}_{0.03}\text{S}$ is attributed to simultaneous enhancements of both N_v and m^*/m_e . This agrees with the Mott relation $S \propto m_d^* T n^{-2/3}$ (40), which indicates that a moderate increase in n_H does not suppress S due to enhanced m_d^* .

To correlate the band modulation with the experimentally measured transport properties, we analyzed the relationships among S , n_H , and Hall carrier mobility (μ_H , calculated using the free-electron model $\sigma = en\mu$, where e is the elementary charge) using multiband transport simulations comparing four-band and three-band models by acoustic deformation potential^{41,42}. Details of the calculations are provided in Supplementary Discussion 2, and the corresponding parameters are provided in Supplementary Tables 5–7. As shown in Fig. 4c, the plot reveals that the experimental S of Ag-doped samples lie close to the curve corresponding to the modulated three-band configuration, where these enhanced S arise from band flattening associated with band merging. Introducing Ag substantially increases μ_H , aligning the values with the predictions of the modulated three-band model, as shown in Fig. 4d. Eventually, the

reduced ΔE between two extrema along the Y– Γ –Z direction results in a maximum μ_H of $\sim 327 \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$ in $\text{Sn}_{0.96}\text{Na}_{0.01}\text{Ag}_{0.03}\text{S}$. Room-temperature Hall measurements further revealed the doping optimization, where both μ_H and n_H were simultaneously enhanced, suggesting decoupling of these typically interdependent parameters. These simulations demonstrate that the enhanced electrical transport properties in $\text{Sn}_{0.96}\text{Na}_{0.01}\text{Ag}_{0.03}\text{S}$ originate from the multiband configuration induced by band convergence and merging, highlighting the significant influence on the performance^{42–44}.

Figure of merit (zT) and single-leg module performance

Through this electronic band structure evolution, a record zT was achieved, as shown in Fig. 5a, where $\text{Sn}_{0.96}\text{Na}_{0.01}\text{Ag}_{0.03}\text{S}$ crystals attained a zT of ~ 1.06 at 300 K and a zT peak of ~ 2 at 573 K. Moreover, the zT average of ~ 1.57 exceeds the latest reported value of p-type SnS single crystal^{27,28}. Notably, the zT maximization at RT arises from the modulated three-band configuration, as supported by the zT simulations shown in Supplementary Fig. 17. The reproducibility of the TE performance across different synthesis batches confirms the material stability and reliability within temperature range of 300–573 K (Supplementary Fig. 18). Despite the restricted operating temperature window, the achieved zT peak is substantially superior, establishing $\text{Sn}_{0.96}\text{Na}_{0.01}\text{Ag}_{0.03}\text{S}$ as one of the best-performing tin-sulfide and sulfide-based TE materials reported to date^{30,36,37,45–49}, as summarized in Fig. 5b. Overall, this work demonstrates that effective decoupling of σ , S , and κ firmly enables $\text{Sn}_{0.99-x}\text{Na}_{0.01}\text{Ag}_x\text{S}$ as a leading earth-abundant TE material for low-temperature applications.

Additionally, a TE generator based on this SnS material was demonstrated using a single-leg module. Fig. 5c presents the current (I) vs power (P), under different temperature gradients (ΔT), with an inset schematic of a single-leg module. As shown in Fig. 5d, the single-leg module achieved a high η of $\sim 3.3 \%$ under an applied ΔT of 243 K, which is currently outperforming $\text{SnS}_{0.9}\text{Se}_{0.1}$ performance under this ΔT (see the benchmark in Supplementary Fig. 19). The limitation of Sn-based solder suggests the outlook for the contact optimization for better η . Notably, a high output power density (P_d) of $\sim 0.31 \text{ W cm}^{-2}$ directly reflects the ultrahigh PF achieved in this sample⁵⁰. These results validate the effectiveness of enhancing TE η by maximizing PF in earth-abundant tin sulfide systems.

Conclusions

In summary, the multiband engineering via Na and Ag co-doping enables a remarkable advancement in the TE performance of earth-abundant SnS single crystals. DFT calculations

and ARPES, respectively, confirm valence-band convergence and band flattening along the Γ –Z momentum space, validating the emergence of a multi-valley transport mechanism that enhances S , while maintaining high σ even at elevated n_H . Comprehensive structural characterizations reveal modifications of the orthorhombic Pnma phase of SnS induced by substitutional Ag incorporation into the SnS lattice. Crystal structure analysis further identifies lattice distortion associated with enhanced crystal symmetry, originating from a reduction in the distortion angle (θ) and anisotropic phonon renormalization, thereby establishing effective carrier–phonon decoupling. As a result, the optimized $\text{Sn}_{0.96}\text{Na}_{0.01}\text{Ag}_{0.03}\text{S}$ single crystal achieved a record-high PF of $\sim 101 \mu\text{W cm}^{-1} \text{K}^{-2}$ at 300 K and zT peak of ~ 2 at 573 K. The study confirms that intrinsic property optimization enables low-cost, environmentally benign SnS to emerge as a competitive and sustainable material platform for low-temperature TE applications.

Methods

Single crystal synthesis

Purified Sn pellets (99.99 wt.% pure) and Na ingot (99.99 wt.% pure) from Ultimate Materials Technology, S powder (99.98 wt.% pure) from Sigma Aldrich, and Ag powder (99.999 wt.% pure) from Thermofischer Puratronics were weighed carefully and calculated according to the stoichiometry of (Ag or $x = 0, 1, 2, 3$, and 4 at. %) $\text{Sn}_{0.99-x}\text{Na}_{0.01}\text{Ag}_x\text{S}$. All weighted precursors were prepared inside the carbon-coated quartz tube and sealed under ~ 50 mTorr vacuum with an outer larger quartz tube to avoid oxidation from the high-temperature synthesis inside the furnace. The mixed materials were annealed to 1273 K using a slow heating ramp and held at this temperature for 3 days. Subsequently, the samples were cooled to room temperature inside the furnace. The resulting polycrystalline SnS ingots were crushed, ground, and sieved through a 200-mesh screen to ensure compositional uniformity. Approximately 20 g SnS fine powder was then transferred into a 13 mm inner-diameter carbon-coated conical quartz tube and double-sealed with a larger outer quartz tube. For single-crystal growth, the sealed samples were placed in a vertical furnace. The sample was held in the hot zone and heated to 1273 K for 24 hours, then maintained at this temperature for an additional 2 days to ensure complete melting, followed by transfer to the cold zone at 1073 K using a pulling parameter corresponding to a cooling rate of 1 K h^{-1} . The entire single-crystal growth process

required approximately 14 days to obtain a crystal with a length of ~5 cm. After growth, the crystals were naturally cooled to room temperature inside the furnace for 1 day.

Material characterizations

The phase purity of the as-synthesized crystals was characterized using powder X-ray diffraction (XRD) performed on a Bruker D2 diffractometer equipped with Cu K α radiation (λ = 1.5406 Å). Crystal orientation was examined using electron backscattered diffraction (EBSD) combined with field-emission scanning electron microscopy (FESEM; JEOL JSM-7800F) and Laue X-ray diffraction. High-angle annular dark-field scanning transmission electron microscopy combined with high-resolution electron energy-loss spectroscopy (HAADF-STEM-EELS) was performed using a JEOL JEM-2100F transmission electron microscope equipped with aberration correction. STEM specimens were prepared by focused ion beam (FIB) milling at iTek Technology Co., Ltd.

Raman spectroscopy and fitting procedure

Raman spectra were measured using a custom-built confocal fiber microscope integrated with a HORIBA iHR550 spectrometer, equipped with a Sincerity BI-NIR CCD camera (wavelength range: 400–1075 nm) and a 532 nm diode laser as the excitation source. The scattered signals were collected using a photomultiplier detector (PicoQuant PMA192; wavelength range: 230–920 nm). Measurements were performed on the basal plane of small SnS bulk crystals with dimensions of approximately 4 x 4 mm² in size. For each sample, spectra were acquired from up to five different locations with an exposure time of approximately 90 s per spot. The final Raman spectrum was obtained by averaging the spectra collected from different spots. Raman peak positions were determined by Gaussian fitting using OriginLab software, yielding fitting quality with residuals corresponding to $R^2 \approx 0.99$.

Synchrotron radiation measurements

Most synchrotron-based experiments were carried out at the Taiwan Photon Source (TPS) of the National Synchrotron Radiation Research Center (NSRRC), Taiwan. High-energy (20 keV) synchrotron X-ray diffraction was used to collect powder diffraction data. For Rietveld refinement, crystal powders were prepared by hand grinding and sieved through a 400-mesh

screen to ensure uniform particle size for all samples. For elemental mapping, bulk single-crystal specimens were analyzed using nano-focused X-ray fluorescence (XRF) at TPS beamline 21A with a polychromatic X-ray source covering an energy range of 5–30 keV. X-ray absorption spectroscopy (XAS) measurements at the Sn K-edge were conducted at TPS beamline 44A1 in transmission mode using ground SnS powder as the specimen. An energy scan operating in step mode was employed to acquire optimized absorption spectra at the Ag K-edge in fluorescence detection.

XRD refinement and XAS fitting

PXRD patterns were refined by Rietveld analysis using the FullProf and WinPlotr software packages^{51,52}. The shape of the diffraction peaks was modeled using a Thompson–Cox–Hastings pseudo-Voigt profile function. Zero-point shift and asymmetry parameters were systematically refined, and the background contribution was manually estimated. Lattice parameters, atomic positions, and isotropic displacement parameters (i.e., Debye–Waller factors: Biso) were finally refined. For extracting the EXAFS fitting parameters, reduction and modelling of the data from XAS measurement were realized using the IFEFFIT code as implemented in the Athena and Artemis software⁵³.

Band structure measurement via angle-resolved photoemission spectroscopy (ARPES)

ARPES measurements were performed at beamline BL21B1 of the Taiwan Light Source (TLS) and beamline BL39A1 of the Taiwan Photon Source (TPS) at the National Synchrotron Radiation Research Center (NSRRC). Photoemission spectra were collected using hemispherical analyzers (Scienta R4000 at TLS and DA30L at TPS) with a $\pm 15^\circ$ collection angle and an angular resolution of 0.5° . The base pressure during measurements was better than 9.1×10^{-11} torr. Single-crystal samples were cleaved in situ and immediately transferred to the measurement chamber. The beam spot sizes were approximately 120 μm at TLS BL21B1 and 10 μm at TPS BL39A1. All spectra were acquired at room temperature using linearly horizontal polarized light with a photon energy of 92 eV. After collecting the ARPES spectra, the band effective mass (m^*) is calculated with this relation:

$$\frac{1}{m^*} = \frac{1}{\hbar^2} \frac{d^2 E}{dk^2} \quad (1)$$

where $\hbar$ is the reduced Planck constant and $E(k)$ is the energy dispersion as a function of wave vector k . The fitting was performed using the second derivative of the ARPES spectra, in which the local minima correspond to the extrema of the valence-band dispersion.

Thermoelectric transport measurement

For the electronic transport property measurement, the cut specimens were prepared with parallelepiped shapes (3 x 3 x 10 mm³). The electrical conductivity σ and Seebeck coefficient S were simultaneously measured under a Helium gas atmosphere on an Analyser ZEM-3 (ULVAC) with an estimated ~5% measurement uncertainty for each parameter. The Hall measurement was performed using the Quantum Design physical property measurement system (PPMS) AC transport 5-point probe with a variable magnetic field from -5 to 5 T. The Hall carrier concentration (n_H) and Hall mobility (μ_H) were calculated with the measured Hall coefficient (R_H) by using $n_H = 1/(eR_H)$ and $\mu_H = \sigma R_H$, where e represents the electron charge.

From measured σ and S , the weighted mobility can be calculated by the following equation⁵⁴:

$$\mu_W = \frac{3h^3\sigma}{8\pi e(2m_e k_B T)^{3/2}} \left[\frac{\exp\left[\frac{|S|}{k_B/e} - 2\right]}{1 + \exp\left[-5\left(\frac{|S|}{k_B/e} - 1\right)\right]} + \frac{\frac{3}{\pi^2} \frac{|S|}{k_B/e}}{1 + \exp\left[5\left(\frac{|S|}{k_B/e} - 1\right)\right]} \right] \quad (2)$$

where h , k_B , and m_e are Planck's constant, Boltzmann's constant, and mass of an electron, respectively.

For the thermal transport property measurement, a ~2 mm thickness square-shaped specimen (6 x 6 mm²) was prepared. The measurements of thermal diffusivity (D) and specific heat (C_p) were performed by using a laser flash method (LFA 457, NETZSCH) with pyroceram as the reference and standard calibration. The thermal conductivity is calculated from Dulong-Petit Law using $\kappa_{tot} = DC_p\rho$, where the density (ρ) is obtained from the conventional Archimedes method using a Mettler Toledo balance. The lattice thermal conductivities were calculated from the equation $\kappa_l = \kappa_{tot} - \kappa_e$. The electronic thermal conductivity (κ_e) was

defined from the Wiedemann–Franz law as $\kappa_e = L \sigma T$, where L is the Lorenz number calculated by single parabolic model (SPB). The uncertainty of thermal conductivities with these measurement systems was estimated to be $\sim 5\%$.

From σ , S , κ_{tot} , and T , the figure of merit, zT is defined. The average thermoelectric figure of merit (zT_{avg}) over the temperature range was estimated using the integral approximation:

$$zT_{\text{avg}} = \frac{1}{T_h - T_c} \int_{T_c}^{T_h} zT(T) dT \quad (3)$$

Where T_h and T_c are the hot-side and the cold-side temperatures, respectively.

Lorenz number estimation

An estimation of the Lorenz number (L) is using the model given by

$$L = \left(\frac{k_B}{e}\right)^2 \left(\frac{(r + 7/2)F_{r+5/2}(\eta)}{(r + 3/2)F_{r+1/2}(\eta)} - \left[\frac{(r + 5/2)F_{r+3/2}(\eta)}{(r + 3/2)F_{r+1/2}(\eta)} \right]^2 \right) \quad (4)$$

where k_B is the Boltzmann constant, r is the scattering factor, $F_i(\eta)$ is the Fermi-Dirac integral, η is the reduced Fermi level. For degenerate semiconductor, the transport will be dominated by acoustic phonon scattering mechanism ($r = -1/2$). Here, L value is obtained from the calculated η with the measured Seebeck coefficient at any temperature. The detail for the SPB calculation is provided in the Supplementary Method.

Single-leg thermoelectric device fabrication and power generation measurement

For device fabrication, a thermoelectric leg with nominal dimensions comparable to those used for electrical transport measurements was sectioned along the b-axis from the as-grown SnS single crystal. The surface of the SnS leg and the copper electrodes were polished and metallized with a Ni(P) layer via electroless plating to serve as a diffusion barrier. The metallized components were subsequently joined using a Sn-3Ag-0.5Cu (SAC305) solder paste under constant pressure to achieve a robust, void-free interface. Copper wires were

soldered onto the copper electrodes for the measurements of the current and voltage. The power generation performance of the fabricated single-leg device was characterized using a Mini-PEM system (Advance Riko). The device was evaluated at several temperature differences (ΔT), while maintaining the cold-side temperature (T_c) approximately at 295 K. The current-voltage (I - V) characteristics were measured by varying an external load resistor (R_L), as shown in supplementary Fig. 20. The output power (P) was calculated as $P = IV$. The output heat flow at the cold side (Q_c) was measured by using a flow calorimeter. Theoretically, Q_c is described by the sum of heat conduction ($K\Delta T$), Peltier heat (ST_cI), and Joule heat ($0.5I^2R$), where R is the internal resistance of the leg. The heat source at the hot side (Q_h) was then determined from the energy balance equation:

$$Q_h = P + Q_c \quad (5)$$

Finally, the conversion efficiency (η) was calculated using the standard definition as:

$$\eta = \frac{P}{Q_h} \quad (6)$$

The output power density was calculated as $P_d = P_{\max}/A$ where the maximum output power ($P_{\max}$) obtained from the maximum ΔT , and A is the cross-sectional area of the single-leg device. The fabricated single-leg sample had approximate dimensions of 8 x 3 x 2 mm³.

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Author contributions

M.Y.F., A.G., and S.M.V. designed the experiments, analyzed the data, and wrote the manuscript. M.Y.F. and W.C.L. carried out material synthesis and basic characterization. D.L.N. and A.G. performed the density functional theory (DFT) calculations and simulations. C.P. and E.G. conducted XRD refinement and XAS fitting. C.Y.H., C.C.C., and C.M.C. performed the ARPES measurements and analysis. W.C.L., H.H.M.J., S.S., K.H., and C.N.L. carried out single-leg device fabrication. B.H.C. and H.J.W. performed device conversion efficiency measurements. Z.L.Y. and Y.P.C. conducted PPMS measurements and data analysis. M.H.L. and M.W.C. performed TEM characterization. Z.L.Y. and Y.P.C. carried out STS measurements and analysis. K.H.C. and L.C.C. provided resources and supervision. All authors discussed the results and commented on the manuscript.

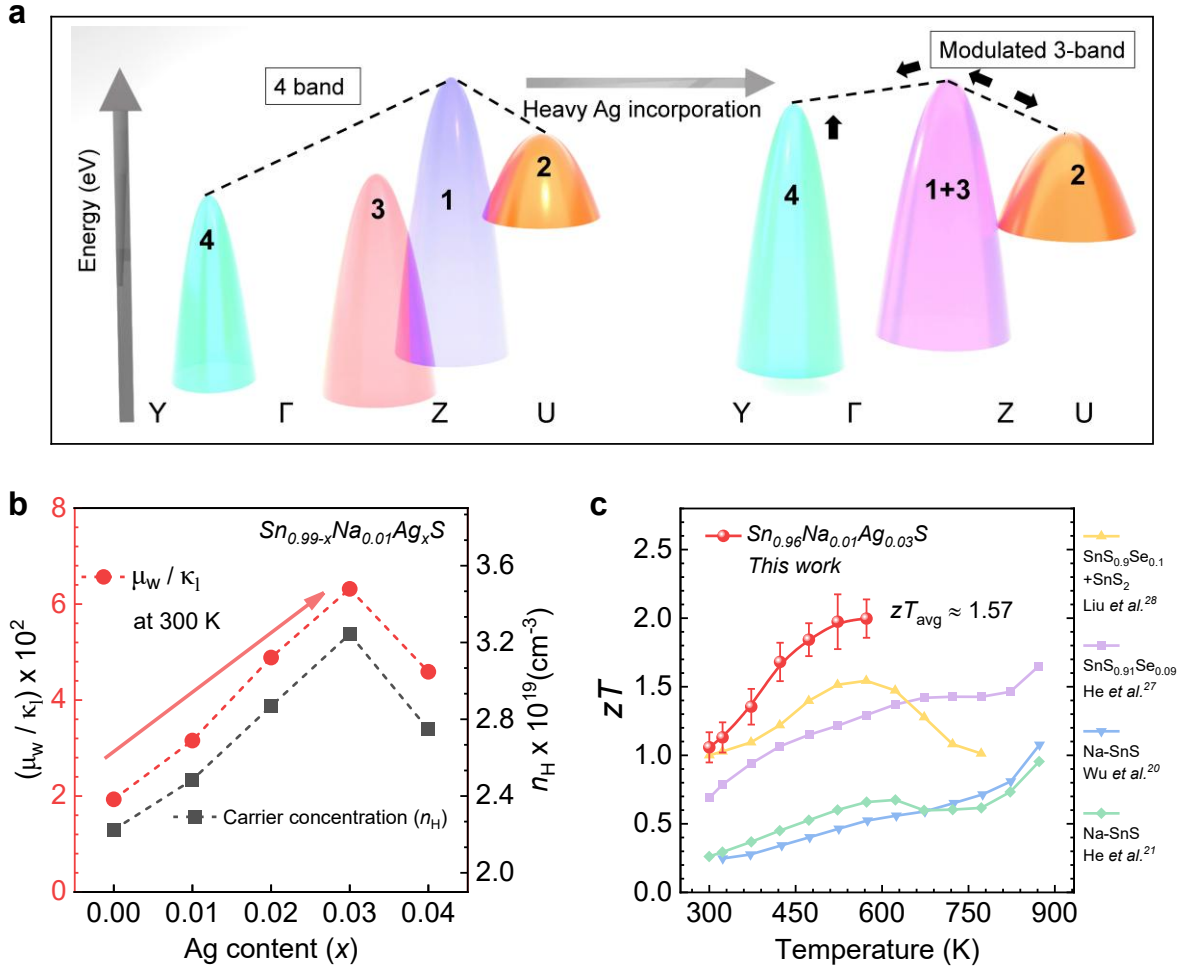


Fig. 1 | Multivalence band reconstruction and optimization of TE properties in $\text{Sn}_{0.99-x}\text{Na}_{0.01}\text{Ag}_x\text{S}$ single crystal. **a**, Schematic illustration of the electronic band evolution in SnS under Ag incorporation (x). **b**, The calculated μ_w/κ_l under the variation of Ag content (x) and carrier concentration (n_H). **c**, Temperature-dependent zT compared with those reported in SnS single crystals (20, 21, 27, 28).

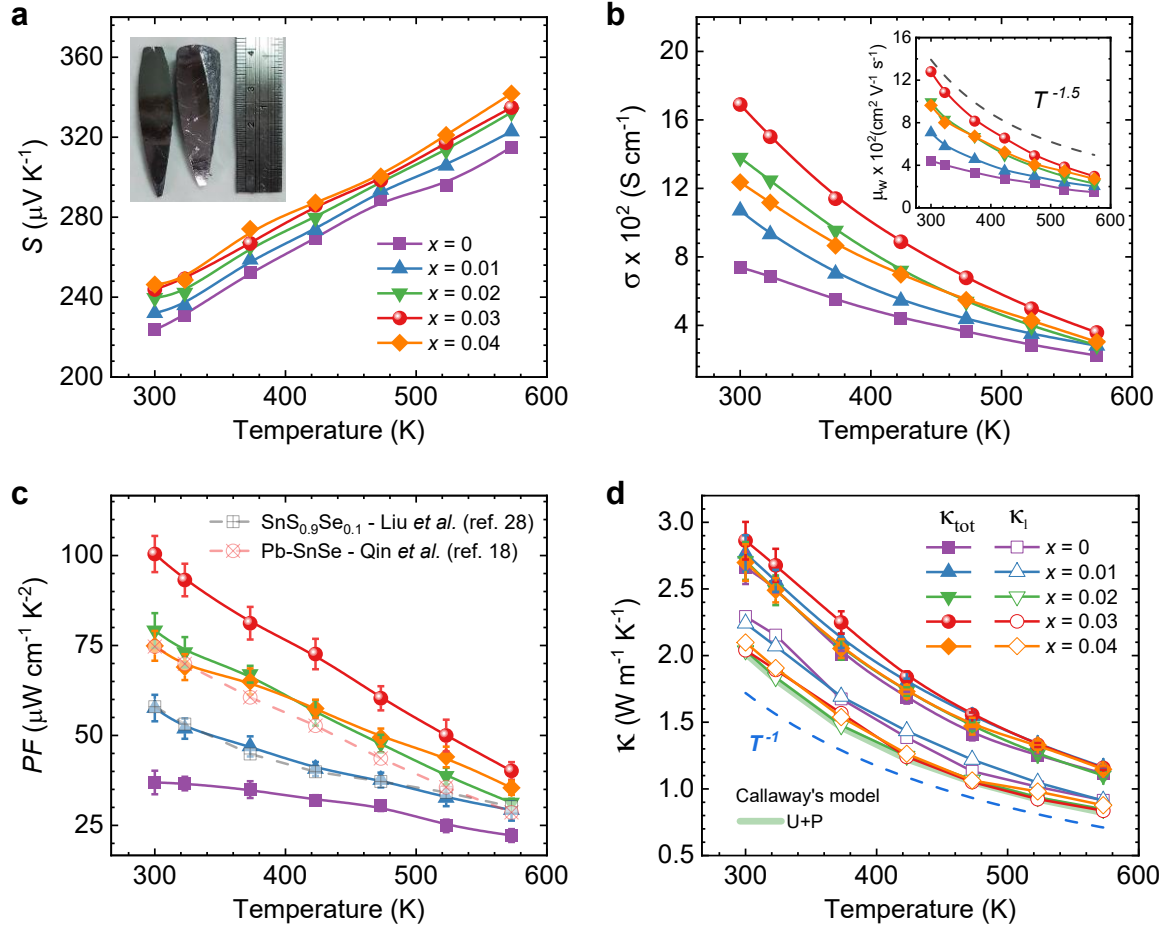


Fig. 2 | Temperature-dependent TE transport properties of $\text{Sn}_{0.99-x}\text{Na}_{0.01}\text{Ag}_x\text{S}$ single crystals with different Ag contents (x). **a**, Seebeck coefficient (S); the inset shows a Bridgeman-grown single-crystal for $x = 0.03$. **b**, Temperature-dependent electrical conductivity (σ) and calculated weighted mobility (μ_w) shown in the inset. **c**, Power factor (PF) compared with benchmark values reported for SnSe and SnS single crystals^{18,28}. **d**, Total thermal conductivity (κ_{tot}) and lattice thermal conductivity (κ_l) obtained by subtracting κ_{tot} from the electronic contribution (κ_e); dashed lines represent the T^{-1} dependence typical of phonon scattering, and the thick transparent green line is the κ_l simulation by using Callaway's model with Umklapp (U) and point defects (P) parameters.

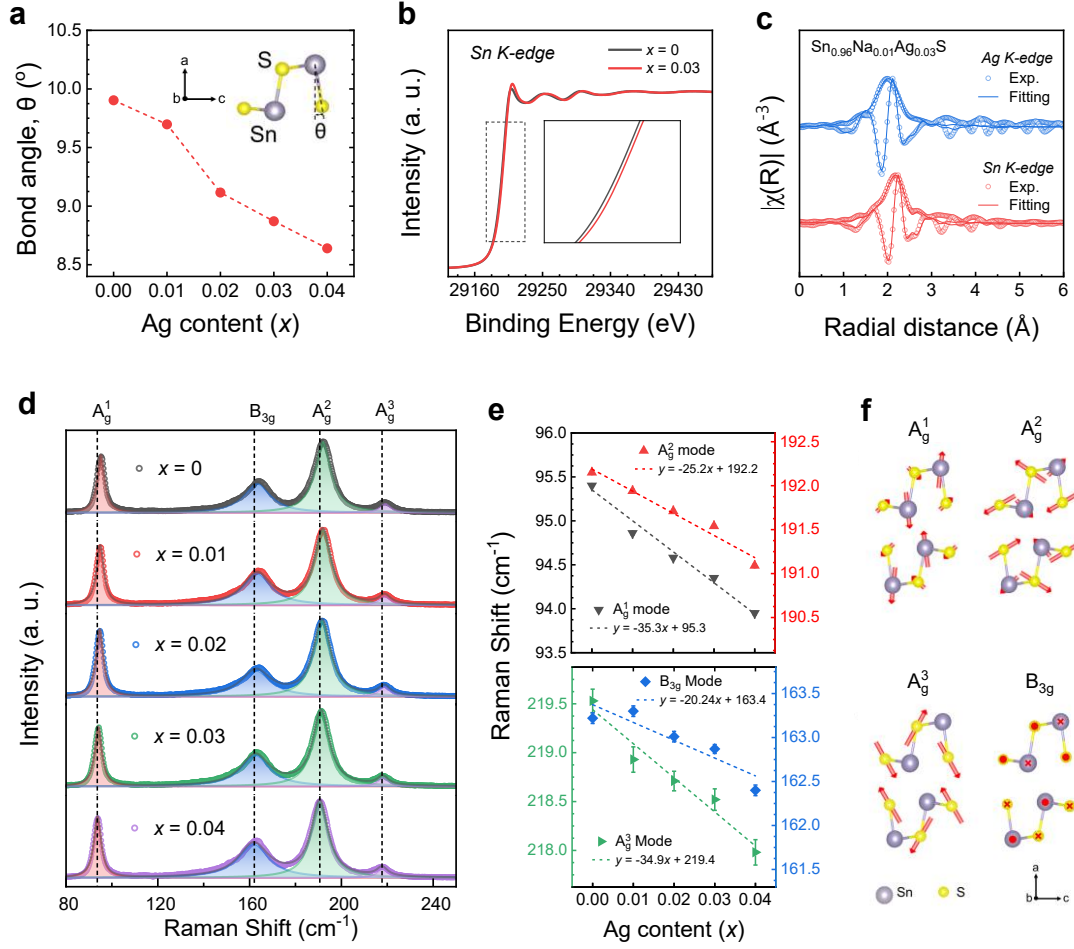


Fig. 3 | Crystal structure modification in Ag-doped SnS crystal. **a**, The Sn-S bond angle (θ) of $\text{Sn}_{0.99-x}\text{Na}_{0.01}\text{Ag}_x\text{S}$ Pnma phase at 300 K with increasing Ag content (x). **b**, Sn K-edge XANES spectra comparing samples without Ag ($x = 0$) and with Ag ($x = 0.03$). **c**, Fourier-transformed EXAFS at Sn and Ag K-edge for $\text{Sn}_{0.96}\text{Na}_{0.01}\text{Ag}_{0.03}\text{S}$ sample. **d**, Raman spectra of $\text{Sn}_{0.99-x}\text{Na}_{0.01}\text{Ag}_x\text{S}$ single crystals ($x = 0$ – 0.04) with peak fitting of the characteristic vibrational modes (A_g^1 , B_{3g} , A_g^2 , and A_g^3), resolved using a Gaussian function. **e**, The Raman shift of the dominant peaks out-of-plane (A_g^1 and A_g^3) and in-plane (A_g^2 and B_{3g}) modes as a function of Ag content (x). **f**, The corresponding vibrational models, with arrows representing the direction of atomic vibrations.

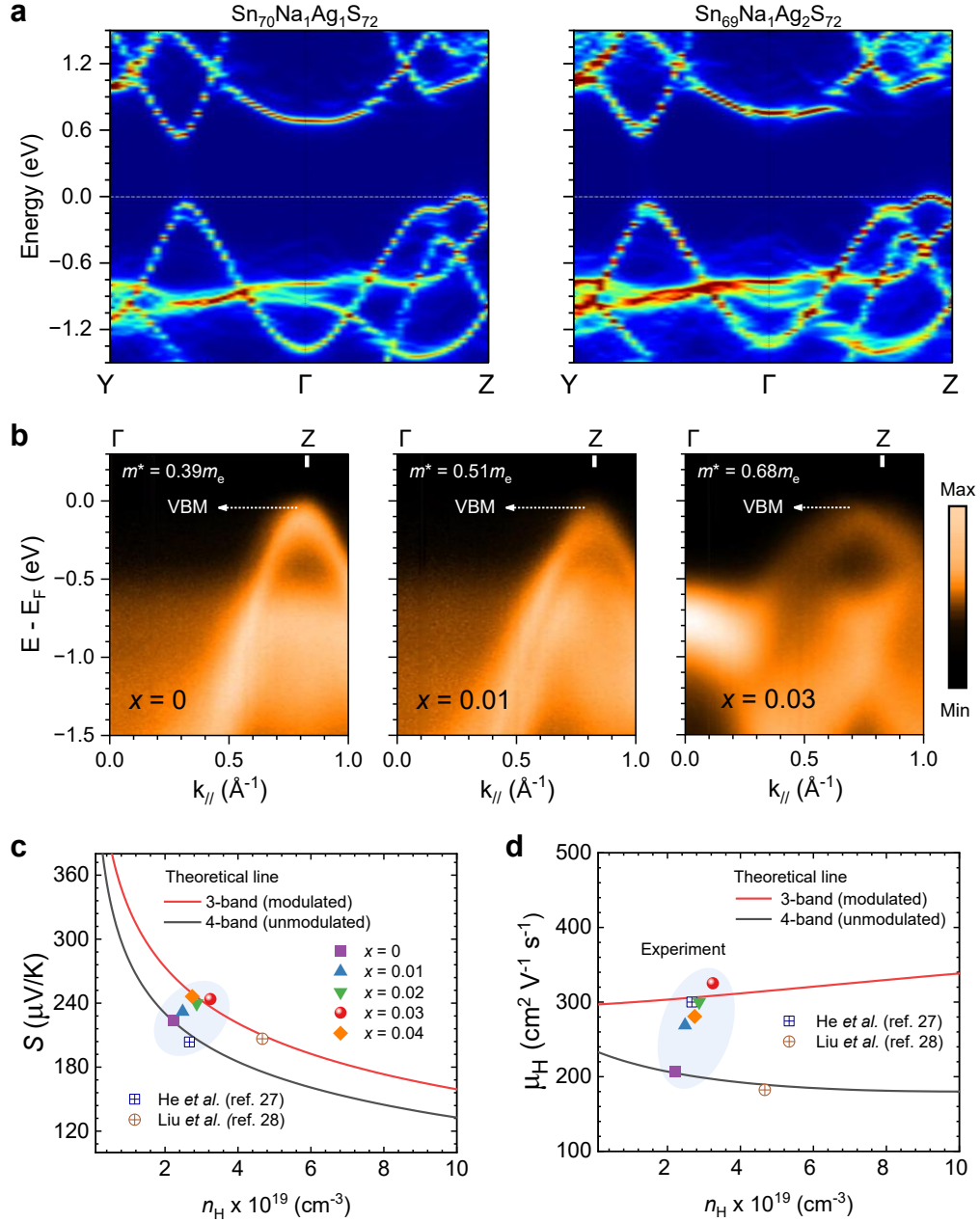


Fig. 4 | Band structure evolution of $\text{Sn}_{0.99-x}\text{Na}_{0.01}\text{Ag}_x\text{S}$ single crystals and electrical transport analysis. **a**, Unfolded band structures with 144-atom supercells to account for the substitutional incorporation of Na and Ag. **b**, ARPES band maps measured at 300 K with 92 eV photon energy for $x = 0$, $x = 0.01$, and $x = 0.03$ samples, focusing on the valence band maximum (VBM) along the Γ –Z direction. **c**, Pisarenko plot of n_H vs S , compared with the theoretical plot from the multiple band model at 300 K. **d**, Pisarenko plot of n_H vs Hall mobility (μ_H), with benchmarks from the latest report of SnS single crystals were included^{27,28}.

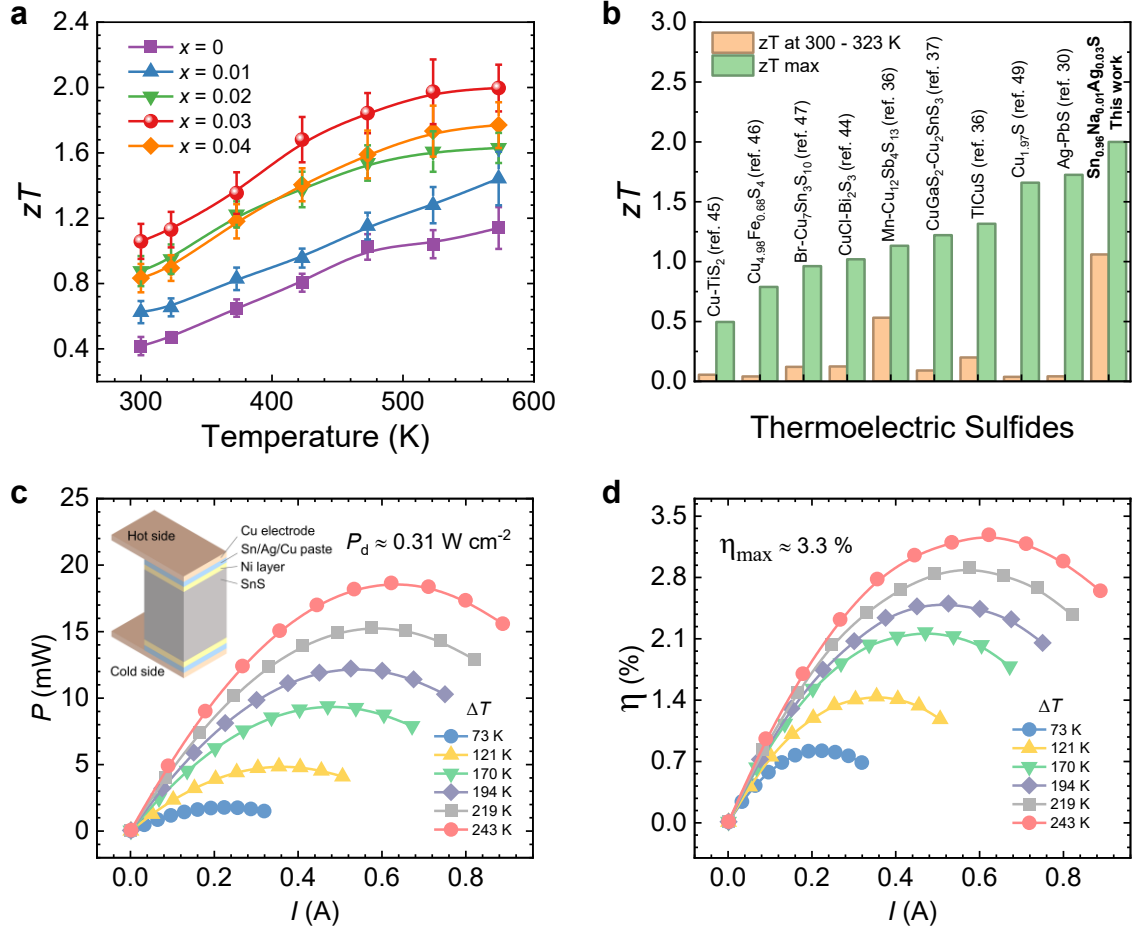


Fig. 5. | Figure of merit (zT) value and device performance $\text{Sn}_{0.99-x}\text{Na}_{0.01}\text{Ag}_x\text{S}$ single crystals demonstrating state-of-the-art sulfide-based TE performance. a, Temperature-dependent zT . b, Benchmark comparison of room-temperature zT and zT peak values with those of previously reported sulfide-based TE materials^{30,36,37,45–49}. c, Input current (I) versus output power (P) for different temperature gradients (ΔT) with an inset schematic of the fabricated single-leg module. d, Input current (I) versus conversion efficiency (η) under different temperature gradients (ΔT).

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