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High Thermoelectric Performance in the New Cubic Semiconductor AgSnSbSe_3 by High Entropy Engineering

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ABSTRACT: We investigate the structural and physical properties of the $\text{AgSn}_m\text{SbSe}_{m+2}$ system with $m=1-20$ (i.e. SnSe matrix and $\sim 5-50\%$ AgSbSe_2) from length scales ranging from atomic, nano and macro. We find the 50:50 composition, with $m=1$ (i.e. AgSnSbSe_3), forms a stable cation disordered cubic rock-salt p-type semiconductor with a special multipeak electronic valence band structure. AgSnSbSe_3 has an intrinsically low lattice thermal conductivity of $\sim 0.47 \text{ W m}^{-1}\text{K}^{-1}$ at 673 K owing to the synergy of cation disorder, phonon anharmonicity, low phonon velocity, and low-frequency optical modes. Furthermore, Te alloying on the Se sites creates a quinary high entropy NaCl-type solid solution $\text{AgSnSbSe}_{3-x}\text{Te}_x$ with randomly disordered cations and anions. The extra point defects and lattice dislocations lead to glass-like lattice thermal conductivities of $\sim 0.32 \text{ W m}^{-1}\text{K}^{-1}$ at 723 K and higher hole carrier concentration than AgSnSbSe_3 . Concurrently, the Te alloying promotes greater convergence of the multiple valence band maxima in $\text{AgSnSbSe}_{1.5}\text{Te}_{1.5}$, the composition with the highest configurational entropy. Facilitated by these favorable modifications, we achieve a high average power factor of $\sim 9.54 \mu\text{W cm}^{-1}\text{K}^{-2}$ (400-773 K), a peak thermoelectric figure of merit ZT of 1.14 at 723 K and a high average ZT of ~ 1.0 over a wide temperature range of 400-773 K in $\text{AgSnSbSe}_{1.5}\text{Te}_{1.5}$.

■ INTRODUCTION

Thermoelectric materials enable reliable conversion from heat to electrical power, thus thermoelectric technology may have applications for improving energy utilization and management.¹ The energy conversion efficiency of thermoelectric modules is determined by the materials' dimensionless thermoelectric figure of merit ZT . $ZT = S^2\sigma T/\kappa = S^2\sigma T/(\kappa_e + \kappa_L)$, where S , σ , κ , and T are the Seebeck coefficient, electrical conductivity, thermal conductivity and absolute temperature, respectively. κ_e and κ_L are the respective contributions to the total thermal conductivity contributed by electrons and phonons. Maximizing ZT is constrained by the complex relationships among S , σ and κ_e . Because κ_{lat} is independent of the electronic properties, traditional strategies to optimize the figure of merit generally begin by seeking materials with already low thermal conductivity and then attempting to reduce it further. Established routes to achieve low κ_{lat} include: (1) enhancing phonon scattering through the introduction of point defects,² nanostructures³ and all-scale hierarchical architec-

tures;⁴⁻⁵ and (2) exploring new materials with inherently low lattice thermal conductivity, typically originating from complex crystal structures and strong lattice anharmonicity.⁶ Examples of the second approach include In_4Se_3 ,⁷ Ag_9GaSe_6 ,⁸ $\text{Sb}_2\text{Si}_2\text{Te}_6$,³ AgCuTe ,⁹ $\text{Ba}_5\text{Cu}_8\text{In}_2\text{S}_{12}$ ¹⁰ and SnSe .¹¹⁻¹⁴

SnSe is a rapidly emerging thermoelectric compound. Much of the attention drawn to SnSe focuses on its intrinsically low lattice thermal conductivities ($\sim 0.21, 0.24, 0.20 \text{ W m}^{-1}\text{K}^{-1}$ at 973 K along the a, b and c axis directions in single crystals, respectively), which originates from its unique crystal structure.¹¹ SnSe crystallizes in the orthorhombic space group ($Pnma$) at room temperature, adopting a layered structure with two-atomic SnSe slabs stacking along the a axis linked by the weaker intralayer Sn-Se bonding. At high temperature the material undergoes a phase transition from $Pnma$ to $Cmcm$.¹⁵ The $Cmcm$ phase preserves the layered motif, but the Sn coordination environment changes. The phase transition induces non-uniform changes to the lattice parameter generating

strains and extended defects (including microcracks) that degrade the mechanical properties of SnSe and make it unsuitable for long-term power generation applications at temperatures near the phase transition. To avoid having to deal with the phase transition, we explored a chemical modification route to stabilize a rock-salt SnSe structure over the orthorhombic structure by synthesizing rational compositional derivatives.

Specifically, we investigated the $\text{AgSn}_m\text{SbSe}_{m+2}$ ($m=1-20$) series. We hypothesized alloying orthorhombic SnSe with sufficient quantity of the cubic AgSbSe_2 will eventually stabilize the rock salt structure, Figure 1. Phase and microstructure analyses illustrate a 50:50 mixture forms a new pure rock-salt phase (i.e. AgSnSbSe_3). AgSnSbSe_3 has higher average power factor $S^2\sigma$ ($\text{PF}_{\text{ave}} \sim 4.60 \mu\text{Wcm}^{-1}\text{K}^{-2}$) and average ZT ($\text{ZT}_{\text{ave}} \sim 0.47$) than polycrystalline SnSe ($\text{PF}_{\text{ave}} \sim 0.97 \mu\text{Wcm}^{-1}\text{K}^{-2}$, $\text{ZT}_{\text{ave}} \sim 0.14$) in the temperature range of 400-823 K. The new compound has a special electronic structure with multiple valence band peaks near the Fermi energy, a difficult to find and highly desired electronic structure feature that enhances the Seebeck coefficients. Moreover, we simultaneously optimized the electrical and thermal transport properties of AgSnSbSe_3 by alloying the anion site with Te to create a five-element high entropy system, $\text{AgSnSbSe}_{3-x}\text{Te}_x$. Te alloying further improves the charge carrier concentration and the density of states effective hole mass m^* of AgSnSbSe_3 while retains the overall structure NaCl-type, as shown in Figure 1. Additionally, enhanced point defects and dislocations created by random Se/Te anion disorder strengthen phonon scattering, leading to very low lattice thermal conductivities. Owing to the enhanced electronic and thermal properties, the highest configurational entropy $\text{AgSnSbSe}_{1.5}\text{Te}_{1.5}$ composition achieves a peak ZT of 1.14 at 723 K, a high average power factor (PF_{ave}) of $9.54 \mu\text{Wcm}^{-1}\text{K}^{-2}$ and a high ZT_{ave} of ~ 1.0 between 400-773 K.

■ RESULTS AND DISCUSSION

1. AgSnSbSe_3 a new rock salt compound

Synthesis, structure, and phase analysis of $\text{AgSn}_m\text{SbSe}_{m+2}$. We prepared polycrystalline ingots with nominal compositions of $\text{AgSn}_m\text{SbSe}_{m+2}$ ($m=1, 2, 4, 6, 8, 10, 12$ and 20) by melting stoichiometric quantities of each element at 1173 K for 20 h followed by annealing at 823 K for 20 h (see Experimental section in Supporting Information for details). Figure 2a shows the powder X-ray diffraction (PXRD) patterns obtained for samples of SnSe and $\text{AgSn}_m\text{SbSe}_{m+2}$. The Bragg peaks of pristine SnSe are well indexed in the orthorhombic space group of $Pnma$. After AgSbSe_2 alloying, the intensity of the Bragg peaks belonging to orthorhombic SnSe (i.g. (311), (511), (203), etc.) gradually decline with decreasing m value (increasing AgSbSe_2) and are undetectable when $m=1$ (i.e. AgSnSbSe_3). Instead, this sample is indexed as a cubic NaCl-type structure (space group $Fm\bar{3}m$) (Figure 2b), similar to the $\text{Sn}_{0.4}(\text{AgSb})_{0.6}\text{Se}$ compound.¹⁶ Our PXRD results therefore indicate 50 mol% AgSbSe_2 stabilizes the rock salt cubic phase of SnSe, with cell parameter $a=5.8580(1) \text{ \AA}$.

Microstructure of $\text{AgSn}_m\text{SbSe}_{m+2}$. Look beyond the PXRD analysis, we conducted electron microscopy studies to analyze the micro and nano scale structure of our $\text{AgSn}_m\text{SbSe}_{m+2}$ materials. Back-scattered electron microscopy with energy dispersive X-ray spectrometry (BSE/EDS) analysis shows that SnSe (bright contrast) and AgSnSbSe_3 (dark contrast) coexist in samples with m values as low as 2 (equivalently, $\sim 33\%$ AgSbSe_2 in SnSe), and the fraction of the AgSnSbSe_3 phase decreases with increasing m value (Figure S1-S3 of Supporting Information). However, the images obtained for AgSnSbSe_3 ($m=1$) show uniform contrast and a homogeneous distribution of elemental Ag, Sn, Sb and Se with no detection of any secondary phases (Figure 2c and Figure S4 in supporting Information), indicating the AgSnSbSe_3 composition is in fact a single-phase compound. This is also confirmed by transmission electron microscopy (TEM), Figure 2d, in which the selected area electron diffraction (SAED) pattern (lower inset) can be well indexed to [121] zone axis of the rock-salt (NaCl) crystal structure without spot splitting or additional spots.

Differential thermal analysis (DTA) of AgSnSbSe_3 (i.e. $m=1$) (Figure S5 in supporting Information) shows a single melting peak and a single crystallization peak at $\sim 920 \text{ K}$, indicating AgSnSbSe_3 is thermodynamically stable and melts congruently.

The above results provide strong evidence that the 50:50 mixture of AgSbSe_2 and SnSe forms a single phase rock-salt compound, which is a solid solution with Ag, Sn and Sb atoms randomly distributed over the Na sites of the NaCl lattice, Figure 3a. In addition, we also prepared samples with $m < 1$, presented as $\text{AgSn}_y\text{SbSe}_{y+2}$ ($y=0.75, 0.50$ and 0.25). The corresponding XRD patterns (Figure S6 in Supporting Information) show these samples are also single-phase with a rock-salt structure. Accordingly, we propose a tentative pseudo-binary phase diagram for the SnSe- AgSbSe_2 system in Figure S7 in Supporting Information.

Electronic band structure of AgSnSbSe_3 . To assess the electronic structure of AgSnSbSe_3 , we used first-principles density functional theory (DFT). Due to the imaginary vibrational frequencies that can derive from special quasirandom structure (SQS) structures, we used a cation-ordered configuration (Figure 3b) to approximate the experimental sample, and additional details for these calculations are given in the experimental section. The electronic band structure calculated along the L- Γ -K directions is presented in Figure 3c. The DFT calculations suggest that AgSnSbSe_3 is a narrow gap semiconductor with an indirect band gap of $\sim 0.17 \text{ eV}$. Importantly, AgSnSbSe_3 has a complex multipeak valence band structure, including three valence band maxima. The first valence band maximum (VBM) locates at L point, while the second and the third VBM are lying along Γ -L and Γ -K direction. The energy difference between the first and second VBM is about 0.24 eV and the energy difference between the second and the third VBM is only about 0.03 eV. These energy differences are small and similar to the well-known VBM difference in SnSe¹² (about 0.06 eV), suggesting the potential for convergence of multiple valence band maxima.¹⁷ Furthermore,

the orbital projected density of states (DOS) of AgSnSbSe_3 are shown in Figure 3d. The first VBM at ~ -0.02 eV is mainly contributed from Sn 5p and Se 4p orbitals with small admixture of Sb 5p and Ag 4d orbitals. The second VBM at ~ -0.15 eV is mainly contributed from the strong hybridization between Sn 5s, Sn 5p and Ag 4d orbitals and some overlap between Se 4p and Sb 5p orbitals. The third at ~ -0.18 eV is mainly contributed from Sn 5s, Sn 5p, Ag 4d, Sb 5s, Sb 5p and Se 4p orbitals.

2. Thermoelectric performance of $\text{AgSn}_m\text{SbSe}_{m+2}$

Electronic transport properties of $\text{AgSn}_m\text{SbSe}_{m+2}$. Figures 4a-b depict the temperature dependent electrical conductivities and Seebeck coefficients for our $\text{AgSn}_m\text{SbSe}_{m+2}$ ($m=1-12$) samples. The electrical conductivities and Seebeck coefficients both increase gradually with the decrease of m (increasing AgSbSe_2). As the AgSbSe_2 fraction increases from ~ 7 to 50 percent ($m = 12-1$), the room temperature electrical conductivity rises from 4.1×10^{-3} to 93 Scm^{-1} , while the Seebeck coefficients are enhanced from 51 to $179 \mu\text{VK}^{-1}$. The electrical conductivity of the $m=20$ sample is too low to be measured on the ZEM-3 system, likely suggesting a low number of carriers $< 10^{15} \text{ cm}^{-3}$.

Hall effect measurements (see Experimental section in Supporting Information for details) indicate holes as the dominant carrier in all samples. The $m=12$ (7.5% AgSbTe_2) sample has the lowest charge carrier concentration of $1.7 \times 10^{15} \text{ cm}^{-3}$ at ~ 300 K (Table S1 in Supporting Information), in agreement with its low electrical conductivity, Figure 4a. The charge carrier concentration in this sample is about two orders of magnitude lower than in pure SnSe ($1.65 \times 10^{17} \text{ cm}^{-3}$ at ~ 300 K). The AgSnSbSe_3 ($m=1$) sample, however, has both the highest hole concentration ($2.8 \times 10^{19} \text{ cm}^{-3}$ at 300 K) and electrical conductivities. The hole mobility μ in this sample was estimated at $\sim 20 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. The ability to achieve such a high carrier concentration in AgSnSbSe_3 , without extrinsic dopants is reminiscent of the behavior of SnTe. In this case the high hole density may arise from non-stoichiometry such as Sn vacancies or an non-ideal Ag:Sb=1 ratio similar to SnTe.¹⁸⁻¹⁹

The power factors $S^2\sigma$ of the $\text{AgSn}_m\text{SbSe}_{m+2}$ samples are depicted in Figure 4c and increase with decreasing m value. AgSnSbSe_3 has a peak power factor of $5.2 \mu\text{Wcm}^{-1}\text{K}^{-2}$ at 723 K and the highest average power factor ($\text{PF}_{\text{ave}} \sim 4.60 \mu\text{Wcm}^{-1}\text{K}^{-2}$) in the temperature range of 400 to 823 K. The PF_{ave} of AgSnSbTe_3 is about 4 times higher than pure SnSe ($\text{PF}_{\text{ave}} \sim 1.06 \mu\text{Wcm}^{-1}\text{K}^{-2}$) in the same temperature range.

Thermal transport properties of $\text{AgSn}_m\text{SbSe}_{m+2}$. All samples of $\text{AgSn}_m\text{SbSe}_{m+2}$ have very low thermal conductivities κ ($0.6 \pm 0.1 \text{ Wm}^{-1}\text{K}^{-1}$) at room temperature, about half the value of pristine SnSe ($1.2 \text{ Wm}^{-1}\text{K}^{-1}$ at 300 K), Figure 4d. After subtracting the electronic thermal conductivity estimated by the Wiedemann-Franz Law,²⁰ the estimated lattice thermal conductivities (κ_L) show only a weak temperature dependence, Figure 4e. For example, the κ_L value of AgSnSbSe_3 (i.e. $m=1$) decreases slightly from $\sim 0.59 \text{ Wm}^{-1}\text{K}^{-1}$ (323 K) to $\sim 0.47 \text{ Wm}^{-1}\text{K}^{-1}$ (673 K) and then increases to $\sim 0.51 \text{ Wm}^{-1}\text{K}^{-1}$ (823 K). This small variation is well within the experimental error, which is about 10%.

The lattice thermal conductivity of the AgSnSbSe_3 compound ($\sim 0.53 \text{ Wm}^{-1}\text{K}^{-1}$ at 623 K) is comparable to the ultra-low lattice thermal conductivities of InTe ,²¹ $\text{Cu}_2\text{Se}_{0.5}\text{S}_{0.5}$,²² SnSe ²³ and AgCrSe_2 .²⁴

ZT values of $\text{AgSn}_m\text{SbSe}_{m+2}$. The temperature dependent ZT values for $\text{AgSn}_m\text{SbSe}_{m+2}$ samples are plotted in Figure 4f. AgSnSbSe_3 has the best thermoelectric performance with a peak ZT of ~ 0.69 at 773 K, and more importantly, an ZT_{ave} of ~ 0.47 in the temperature range of 400-823 K. This is nearly three times higher than undoped SnSe ($\text{ZT}_{\text{ave}} \sim 0.14$) and ~ 0.14 higher than the undoped AgSbSe_2 ($\text{ZT}_{\text{ave}} \sim 0.33$ from 400 to 723 K).

3. Phonon propagation in AgSnSbSe_3

To understand the physical origin of the low lattice thermal conductivity, we used first-principles DFT to calculate phonon dispersions for the ordered AgSnSbSe_3 , Figure 3b. The calculated phonon dispersions are shown in Figure 5a. The frequency of the zone-boundary transverse acoustic mode (TA) along Γ -X, Γ -Y, and Γ -Z directions are ~ 28 , 42 and $\sim 24 \text{ cm}^{-1}$ respectively, indicating that the TA modes along the Γ -X and Γ -Z directions are softer than along the Γ -Y direction. Similarly, the transverse acoustic modes (TA') and the longitudinal acoustic (LA) modes along the Γ -X and Γ -Z directions are stiffer than along the Γ -Y direction. Such anisotropic TA, TA' and LA modes indicate strong phonon anharmonicity in AgSnSbSe_3 .

To quantitatively evaluate the phonon anharmonicity, we calculated the Grüneisen parameters of the acoustic modes for the ordered model of AgSnSbSe_3 . Figure 5b shows the Grüneisen parameters plotted along the same high symmetry directions, and indicates all values of γ are large (> 3) and comparable to those of SnSe.¹¹ Furthermore,

the average Grüneisen parameters ($\bar{\gamma}$),²⁵ evaluated by $\bar{\gamma} = \sqrt{\langle \gamma_i^2 \rangle}$ are 1.75, 3.32 and 2.06 for TA, TA' and LA modes, respectively. Such large Grüneisen parameters are also comparable to 3.91, 2.20 and 1.61 of $\text{Cu}_{17.6}\text{Fe}_{17.6}\text{S}_{32}$,²⁶ and suggest the AgSnSbTe_3 lattice is strongly anharmonic.

Consistent with the high lattice anharmonicity, calculated average phonon velocities in each direction (Γ -X, Γ -Y, and Γ -Z) are 2350, 2188 and 2428 m/s, are lower than typical velocities (~ 3000 m/s) found in usual solid state materials.^{3, 27} Moreover, the low-frequency optical modes from the Ag and Se atoms play an important role in suppressing the lattice thermal conductivity of AgSnSbSe_3 . As shown in the projected phonon density of states (PDOS) in Figure 5c, the Ag atoms exhibit a clear peak near 30 cm^{-1} , and the Se atoms (red circle line) present a significant peak at 42 cm^{-1} . These very low frequency transverse optical modes can enhance Umklapp scattering processes and strongly reduce the phonon mean free path.²⁸⁻²⁹

4. Effect of Te alloying on the phase, entropy, microstructure and band structure of AgSnSbSe_3

Synthesis and phase composition of $\text{AgSnSbSe}_{3-x}\text{Te}_x$. We employed high entropy engineering³⁰⁻³² to further enhance the thermoelectric performance of AgSnSbSe_3 . We prepared the Te alloyed high entropy system $\text{AgSnSbSe}_{3-x}\text{Te}_x$

($x=0-3$) using the same synthetic procedure for AgSnSbSe_3 . Figure 6a shows the powder XRD patterns of the $\text{AgSnSbSe}_{3-x}\text{Te}_x$ samples which are indexed to the cubic $\text{NaCl } Fm\bar{3}m$ space group. All reflections, e.g. (200), (220) and (222) facets, shift to lower diffraction angles with increasing x , showing the increase in unit cell size with increasing Te content. The unit cell parameters (Figure 6b) increase linearly with increasing content of Te owing to the larger ionic radius of Te^{2-} (2.21Å) compared to Se^{2-} (1.98Å). The variation of the lattice parameters follows the Vegard's law (green dotted line) between AgSnSbSe_3 ($x=0$) and AgSnSbTe_3 ($x=3$), implying the series $\text{AgSnSbSe}_{3-x}\text{Te}_x$ are continuous solid solutions. By adding the tellurium, we obtained a quinary system which remains single-phase with the NaCl structure type (Figure 1). Therefore, our final system possesses three cations randomly disordered on the Na site and two anions randomly disordered on the Cl site. This arrangement qualifies for the system to be called a high entropy alloy.³³⁻³⁴

Higher entropy from Te alloying. Considering an N-species system, the ΔS (ΔS , the difference between the actual and ideal entropies of mixing) of the high entropy system $\text{AgSnSbSe}_{3-x}\text{Te}_x$ is given by:³⁵

$$\Delta S = \kappa_B \sum_{i=1}^N x_i \ln(x_i) \quad (1)$$

Where κ_B is the Boltzmann constant, x_i is the composition of each species, and $\sum_{i=1}^N x_i = 1$. Accordingly, we calculated the configurational entropy ΔS for $\text{AgSnSbSe}_{3-x}\text{Te}_x$ by using:

$$\Delta S = -3\kappa_B \left(\frac{x}{3} \ln \frac{x}{3} + \frac{3-x}{3} \ln \left(\frac{3-x}{3} \right) \right) \quad (2)$$

The calculated ΔS as a function of composition (x) is plotted in Figure S8 in Supporting Information, one can see that the ΔS increases from 0 $\text{Jmol}^{-1}\text{K}^{-1}$ at $x=0$ to maximum value 17.3 $\text{Jmol}^{-1}\text{K}^{-1}$ at $x=1.5$, then continuously decreases to 0 $\text{Jmol}^{-1}\text{K}^{-1}$ at $x=3$. Such a high ΔS in $\text{AgSnSbSe}_{1.5}\text{Te}_{1.5}$ indicates substantial lattice distortion and severe alloying point defect scattering of phonons.³²

Micro and nano-structure of $\text{AgSnSbSe}_{3-x}\text{Te}_x$. Back-scattered electron BSE/EDS characterization (Figure S9 in Supporting Information) of $\text{AgSnSbSe}_{1.5}\text{Te}_{1.5}$ shows a uniform contrast and homogeneous distribution of Ag, Sn, Sb, Se and Te. The low magnification TEM image (Figure 6c) of $\text{AgSnSbSe}_{1.5}\text{Te}_{1.5}$ shows a clean surface without any detectable precipitates or clusters. The corresponding STEM/EDS elemental maps (Figure S10 in Supporting Information) also show that the Ag, Sn, Se and Te elements distribute homogeneously in $\text{AgSnSbSe}_{1.5}\text{Te}_{1.5}$. Figures 6d-f show the selected area electron diffraction (SAED) patterns for the sample projected along the $[101]$, $[121]$ and $[100]$ zone axes, respectively. Reciprocal lattice points are assigned to the cubic structure of $Fm\bar{3}m$ space group, which further supports that $\text{AgSnSbSe}_{1.5}\text{Te}_{1.5}$ retains the

rock-salt structure of AgSnSbSe_3 . The high-resolution TEM (HRTEM) image (Figure 6g) shows clear lattice fringes with an interplanar spacing of 3.01Å and an intersection angle of 90°, in good agreement with the expected values of the (002) and (020) facets of rock-salt $\text{AgSnSbSe}_{1.5}\text{Te}_{1.5}$.

Importantly, the TEM images shown in Figures 6c and Figure S11 reveal many dislocation arrays distributed along the grain boundary in addition to intra-grain dislocations. Because such features are not observed in the samples with only Se anions, the dense dislocations are ascribed to the lattice distortions caused by Te alloying. We calculated the lattice distortions coefficients ξ caused by Te alloying as:³⁶

$$\xi = \left[\sum_{i=1}^n c_i \left(1 - \left(\frac{r_i}{\bar{r}} \right)^2 \right) \right]^{1/2} \quad (3)$$

Where c_i and r_i are the atomic fraction and the Goldschmidt radius of the i th element, respectively. The $\bar{r}$ is the average atomic radius calculated using the Vegard's law:

$$\bar{r} = \sum_{i=1}^n c_i r_i \quad (4)$$

The calculated lattice distortion coefficients ξ for $\text{AgSnSbSe}_{3-x}\text{Te}_x$ samples are presented in Figure S12. The ξ value estimated for the $\text{AgSnSbSe}_{1.5}\text{Te}_{1.5}$ is ~ 0.12 when the AgSnSbSe_3 is taken as a reference ($\xi=0$). Such a high ξ value (for instance, the ξ for $\text{Al}_{0.1}\text{CrFeCoNi}$ ³⁶ high-entropy alloy with dense dislocations is only ~ 0.02) indicates the Te alloying generates high atomic misfits and causes additional lattice distortion than already present in AgSnSbSe_3 itself.³⁷

Electronic band structure of $\text{AgSnSbSe}_{1.5}\text{Te}_{1.5}$ and AgSnSbTe_3 . To address the changes Te alloying imparts on the electronic structure of AgSnSbSe_3 , we used DFT to calculate the electronic band structure for $\text{AgSnSbSe}_{1.5}\text{Te}_{1.5}$ and AgSnSbTe_3 . Our calculations indicate $\text{AgSnSbSe}_{1.5}\text{Te}_{1.5}$ (Figure 7a) and AgSnSbTe_3 (Figure 7b) are indirect band gap semiconductors similar to AgSnSbSe_3 . The calculated band gaps of AgSnSbSe_3 , $\text{AgSnSbSe}_{1.5}\text{Te}_{1.5}$ and AgSnSbTe_3 are 0.17, 0.02 and 0.01 eV, respectively. Such a trend indicates that Te alloying reduced the band gap of AgSnSbSe_3 to nearly form a semimetal.

In addition, Te alloying retains the complex multipeak valence band structure of AgSnSbSe_3 . $\text{AgSnSbSe}_{1.5}\text{Te}_{1.5}$ and AgSnSbTe_3 have about 6 valence band maxima, with the energy separation between the uppermost two valence bands is ~ 0.28 eV and ~ 0.14 eV for $\text{AgSnSbSe}_{1.5}\text{Te}_{1.5}$ and AgSnSbTe_3 , respectively. Figure 7c and 7d show the orbital projected DOS of $\text{AgSnSbSe}_{1.5}\text{Te}_{1.5}$ and AgSnSbTe_3 , respectively. We see the topmost VBM (at ~ -0.02 eV) originates mainly from Sb 5p, Te 5p and Se 4p with small contributions from Sn 5p and Ag 4d for $\text{AgSnSbSe}_{1.5}\text{Te}_{1.5}$. On the other hand, Sb 5p with small admixture of Ag 4d, Sn 5p and Te 5p mainly contribute to the topmost VBM for AgSnSbTe_3 , respectively. For $\text{AgSnSbSe}_{1.5}\text{Te}_{1.5}$, the second VBM at ~ -0.25 eV is largely from the strong combination between Ag 4d, Sn 5p, Sb 5p, Te 5p and Se 4p, as well as from interactions between Sn 5s and Sb 5s orbitals. While the second

VBM on AgSnSbTe₃, at ~ -0.17 eV, is mainly contributed from Sb 5p, Sn 5s, and Te 5p with small admixture of Ag 4d, Sn 5p and Sb 5s.

Importantly, owing to the strong hybridization between Ag 4d, Sn 5p, Sb 5p, Te 5p and Se 4p orbitals at around -0.25 eV, a relatively flat valence band emerges in AgSnSbSe_{1.5}Te_{1.5} along the Γ -L and Γ -L line with the energy difference between 2 and 6 VBM is about 0.05 eV. This indicates a greater degree of band convergence in AgSnSbSe_{1.5}Te_{1.5} than AgSnSbSe₃ and AgSnSbTe₃. The convergence of multiple VBM associated with the presence of a flat band in AgSnSbSe_{1.5}Te_{1.5} would cause high DOS effective mass thus high Seebeck coefficients.³⁸⁻³⁹

5. Enhanced thermoelectric performance of AgSnSbSe_{3-x}Te_x

Electrical transport properties. The electrical conductivity of AgSnSbSe_{3-x}Te_x increases with increasing Te content (Figure 8a) from ~ 92.9 to 574.1 Scm⁻¹ for $x=0-3$ samples. Hall measurements reveal that the enhancement of electrical conductivity is mainly from an increased carrier concentration (Table S2 in Support Information), which may arise from the large changes to the electronic structures after the addition of Te, as we discussed above.⁴⁰

The Seebeck coefficients (Figure 8b) for AgSnSbSe_{3-x}Te_x samples are positive, reflecting p-type conduction and decrease with rising Te content (i.e. x value) due to the increased carrier concentration. The room temperature Seebeck coefficients decrease from 179.2 to 98.1 μ VK⁻¹ as x is raised from 0 to 3. The room temperature Seebeck coefficients plotted against the charge carrier concentration are shown in Figure 8c. The Pisarenko plots (green dotted line) for AgSnSbSe₃ were estimated using a single parabolic band model⁴¹ with an effective mass of $1.0m_e$, which can help us to analyze the change in Seebeck coefficient caused by band convergence and band flattening. From the Pisarenko plot, we can see the experimental Seebeck coefficients of the Te alloyed samples do not follow the trend predicted from the single band model, and are much larger, especially for compositions with x from 1.3 to 2.0. This enhancement in Seebeck coefficient is attributed to the enhancement in DOS effective mass (m^*), Figure 8d, which we ascribe to the better band convergence and flat/heavy valence band discussed above.

As a result, Te alloying leads to a large enhancement in the power factor over the whole temperature range (Figure S13 in Supporting Information). The room temperature power factor is ~ 7.1 μ Wcm⁻¹K⁻² for the AgSnSbSe_{1.5}Te_{1.5}, which rises to a maximum of ~ 9.9 μ Wcm⁻¹K⁻² at ~ 723 K. More importantly, its average power factor PF_{ave} reaches ~ 9.54 μ Wcm⁻¹K⁻² in the temperature range of 400-773 K, more than double the value of AgSnSbSe₃ (~ 4.60 μ Wcm⁻¹K⁻²).

Thermal transport properties. As we illustrate in Figure 9a, the total thermal conductivities κ of the AgSnSbSe_{3-x}Te_x samples decrease with increasing Te content (i.e. x value) and reach minimum values in $x=1.0$ sample. For instance, the room temperature κ for AgSnSbSe₃ (i.e. $x=0$) is ~ 0.63 Wm⁻¹K⁻¹, which decreases to ~ 0.54 Wm⁻¹K⁻¹ for AgSnS-

bSe₂Te (i.e. $x=1$) and then increases to ~ 0.81 Wm⁻¹K⁻¹ for AgSnSbTe₃ (i.e. $x=3$). To better understand the thermal transport properties of the Te alloyed samples, we estimated the electronic thermal conductivities κ_e using the Wiedemann-Franz law (Figure S14 in Supporting Information). The κ_e values increase with increasing x values, in agreement with the enhancement in electrical conductivities. Figure 9b shows the lattice thermal conductivities κ_L for AgSnSbSe_{3-x}Te_x decrease sharply with rising Te content from $x=0$ to $x=1.5$ and then increase with further Te, indicating Se/Te disorder plays an important role in suppressing κ_L . The κ_L values for the samples at different temperatures show U-shaped curves with the minimum values obtained at nearby $x=1.5$ (Figure 9c), indicating the feasibility of high entropy engineering in reducing thermal conductivity.³¹

As we discussed above, the increase in configurational entropy would strengthen the point defect scattering because of the atomic mass differences (mass fluctuation), as well as the differences in size and interatomic coupling force (strain field fluctuation) between the host atoms and the hetero-atoms.⁴² To assess the strength of these mechanisms in AgSnSbSe_{3-x}Te_x, we calculated the theoretical disorder scattering parameter Γ_{total} using the model proposed by Slack⁴³ and Abeles,⁴⁴ $\Gamma_{total} = \Gamma_M + \Gamma_S$, where Γ_M and Γ_S are the scattering parameters respectively corresponding to mass and strain field fluctuations (see Experimental section for more details). We find that the strain field fluctuations dominate the phonon scattering in the AgSnSbSe_{3-x}Te_x continuous solid solution system (Figure 9d), similar to the Se alloyed Bi₂Te_{3-x}Se_x compounds.⁴⁵ Furthermore, our calculated scattering parameters each show an inverted U-shaped relationship to the Te composition (x value), in which AgSnSbSe_{1.5}Te_{1.5} has the maximum disorder parameter, in agreement with the lower lattice thermal conductivity measured for these compositions (Figure 9c).

ZT values of AgSnSbSe_{3-x}Te_x. The above measurements indicate Te alloying simultaneously enhances the power factor and suppresses the thermal conductivity. As presented in Figure 10, AgSnSbSe_{1.5}Te_{1.5} reaches a peak ZT of ~ 1.14 at 723 K, which is about twice the value for AgSnSbSe₃ (ZT ~ 0.65 at 723 K). In addition, the figures of merit ZT for the Te alloyed samples are enhanced over a broad temperature range, and the AgSnSbSe_{1.5}Te_{1.5} exhibits a high ZT_{ave} of ~ 1.0 in the temperature interval of 400-773 K, over 2 times higher than that of AgSnSbSe₃ ($ZT_{ave} \sim 0.47$). Such a high ZT_{ave} indicates AgSnSbSe_{1.5}Te_{1.5} is a promising candidate for thermoelectric power generator with its thermal-electric conversion efficiency η determined by:²³

$$\eta = \frac{T_h - T_c}{T_h} \frac{\sqrt{1 + ZT_{ave}} - 1}{1 + ZT_{ave} + T_c/T_h} \quad (5)$$

where the T_h and T_c are the hot-side and cold-side temperatures of thermoelectric power generator, respectively.

CONCLUDING REMARKS

Equimolar mixtures of AgSbSe₂ and SnSe form a single-phase compound, AgSnSbSe₃, which crystallizes in the rock-salt crystal structure with the cations Ag, Sn and Sb

randomly distributed over the Na sites of the NaCl lattice. Our DFT calculations show that AgSnSbSe_3 has a special multippeak valence band structure with three valence band maxima around the Fermi level, strong phonon anharmonicity, low phonon velocity, as well as the interaction of low-frequency optical modes and acoustic modes. These features result in promising thermoelectric performance in AgSnSbSe_3 , with a peak ZT of ~ 0.69 at 773 K and a ZT_{ave} of ~ 0.47 (400 to 823 K). Te alloying can further stabilize a single-phase quinary system $\text{AgSnSnSe}_{3-x}\text{Te}_x$ which is a high entropy alloy that retains the rock-salt structure. The increase in configurational entropy leads to strong lattice distortions, point defects, and dense dislocations in the high entropy system, especially for $\text{AgSnSnSe}_{1.5}\text{Te}_{1.5}$, which has the lowest lattice thermal conductivity ($\sim 0.32 \text{ W m}^{-1}\text{K}^{-1}$ at 723 K). In addition, Te alloying contributes additional electronic bands near the chemical potential to yield a valence band structure with about 6 VBM and a relatively flat valence band at around Fermi level in $\text{AgSnSnSe}_{1.5}\text{Te}_{1.5}$, which leads to high DOS effective mass and Seebeck coefficient. The simultaneous optimization of the electrical and thermal transport properties yields an enhanced average power factor of $\sim 9.54 \mu\text{W cm}^{-1}\text{K}^{-2}$ (400–773 K), a high peak ZT of 1.14 at 723 K together with a high average ZT value of ~ 1.0 (400–773 K) in $\text{AgSnSnSe}_{1.5}\text{Te}_{1.5}$. The average ZT value is comparable to the optimized polycrystalline SnSe-based thermoelectric materials in the same temperature interval, suggesting $\text{AgSnSbSe}_{1.5}\text{Te}_{1.5}$ should be a promising candidate for further performance improvements.

■ ASSOCIATED CONTENT

Supporting Information

Experimental and Computational Details; Figure S1–S15; Table S1–S2.

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Notes

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Figure captions

Figure 1. Crystal structures for SnSe, AgSnSbSe₃ and AgSnSbSe_{1.5}Te_{1.5}, respectively.

Figure 2. (a) Powder X-ray diffraction (XRD) patterns of SnSe and AgSn_mSbSe_{m+2} (m=1, 2, 4, 6, 8, 10, 12, 20) samples. (b) PXRD patterns of AgSnSbSe₃ (m=1) and AgSbSe₂ samples, (green lines) the simulated XRD peaks of a cation disordered cubic AgSnSbSe₃ with a Fm $\bar{3}$ m space group. (c) The energy dispersive X-ray spectrometry elemental mapping (EDS) image of AgSnSbSe₃ (scale bar is 100 μ m). (d) Transmission electron microscopic (TEM) image of AgSnSbSe₃ (scale bar is 500 nm) with selected-area electron diffraction (SAED) pattern (upper inset) and high magnification TEM image (lower inset), indicating the sample forms a solid solution with the rock-salt (NaCl) crystal structure.

Figure 3. (a) Crystal structure of the disordered AgSnSbSe₃ and (b) the ordered AgSnSbSe₃ from cluster expansion calculations, (c) DFT calculated electronic band structure and (d) orbital projected density of states of the ordered AgSnSbSe₃.

Figure 4. Temperature dependent (a) electrical conductivities, (b) Seebeck coefficients and (c) power factors, (d) total thermal conductivities, (e) lattice thermal conductivities and (f) ZT values for SnSe, AgSbSe₂ and AgSn_mSbSe_{m+2} (m=1- 20) samples.

Figure 5. (a) Phonon dispersions, (b) Grüneisen dispersions and (c) projected phonon density of states (PDOS) of the ordered AgSnSbSe₃ structure (Figure 3b). It is noted that the transverse acoustic (TA and TA') modes are plotted as red and green, the longitudinal acoustic (LA) mode is plotted as blue lines in panel a, respectively. Correspondingly, the Grüneisen dispersions from TA, TA', and LA are also plotted as red, green, and blue lines in panel b.

Figure 6. (a) Powder XRD patterns of AgSnSbSe_{3-x}Te_x (x=0, 0.5, 1, 1.3, 1.5, 1.7, 2, 2.5 and 3) samples. (b) Lattice parameters as a function of x for the AgSnSbSe_{3-x}Te_x system. (c) Low magnification TEM image (scale bar=1000 nm), (d-f) SAED patterns and (g) HRTEM image for the AgSnSbSe_{1.5}Te_{1.5} sample (scale bar is 2 nm), indicating a pure phase with cubic crystal structure (space group: Fm $\bar{3}$ m).

Figure 7. Electronic band structures of (a) AgSnSbSe_{1.5}Te_{1.5} and (b) AgSnSbTe₃, orbital projected density of states of (c) AgSnSbSe_{1.5}Te_{1.5} and (d) AgSnSbTe₃.

Figure 8. (a) Electrical conductivities and (b) Seebeck coefficients for AgSnSbSe_{3-x}Te_x samples as functions of temperature. (c) Seebeck coefficients for AgSnSbSe_{3-x}Te_x samples as a function of hole concentration, the green dotted line is the theoretical Pisarenko plot for AgSnSbSe₃ considering $m^* = 1.0m_e$. (d) Density of states effective mass m^* for AgSnSbSe_{3-x}Te_x samples estimated from the single band model.

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