Supplementary information of

Engineering an atomic-level crystal lattice and electronic band structure for an extraordinarily high average thermoelectric figure of merit in n-type PbSe

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Figure S15. The (a) electrical conductivity (σ), (b) Seebeck coefficient (*S*), (c) total thermal conductivity (κ_{tot}), and (d) thermoelectric figure of merit (*ZT*) for the Cu_{0.0029}Pb(Se_{0.8}Te_{0.2})_{0.95} samples. Two independently synthesized samples were investigated. The sample was tested twice under the same conditions. These observations verify the reliability and cyclability of the excellent thermoelectric properties of the title sample.

Figure S16. The calculated temperature-dependent κ_{lat} of the Cu_{0.0029}Pb(Se_{0.8}Te_{0.2})_{0.95} samples from Fig. S15. Two independently synthesized samples were investigated. The sample was tested twice under the same conditions.

6. References

1. Methods

Reagents. Pb (powder, 99.95%, Alfa Aesar), Cu (powder, 99.9%, Aladdin), Se, and Te (powder, 99.999%, American Elements) were used as received.

Synthesis and Sample Preparation

To synthesize $Cu_xPb(Se_{0.8}Te_{0.2})_{0.95}$ (x = 0-0.0057) compounds, a mixture of an appropriate molar ratio of the starting reagents was ball milled using a planetary ball milling instrument (Focucy F-P400) in a steel jar with steel balls at 250 rpm for 2 h under an Ar atmosphere. The resulting powder was loaded in a graphite mold in an Ar-filled glovebox and consolidated at 823 K for 5 min under an axial pressure of 50 MPa in a vacuum using spark plasma sintering (SPS) instrument (SPS-211Lx, Fuji Electronic Industrial Co., Japan). Afterward, the cylindrical sample with a typical thickness of ~12 mm and a diameter of ~13 mm was obtained. The density of the samples was calculated from the geometrical dimensions and masses. All the samples have the relative density higher than 98% of the theoretical value (Table S1), indicating that the density negligibly affects the transport properties.

Powder X-ray Diffraction (PXRD), Scanning Electron Microscopy (SEM) and Thermal Analyses

PXRD data were obtained using a SmartLab Rigaku powder X-ray diffractometer (Cu K $\alpha \lambda = 1.5418$ Å graphite-monochromatized radiation) operating at 40 kV and 30 mA at room temperature. Backscattered electron (BSE) images and corresponding energy dispersive spectroscopy (EDS) elemental maps were collected from the polished surface of bulk SPS-processed pellets acquired on a JEOL JSM-7800F Prime field emission scanning electron microscope (FESEM) equipped with an Oxford X-Max^N 80 EDS detector. In-situ temperature-dependent PXRD patterns were collected on a Bruker D8 Advance powder X-ray diffractometer from 300 to 823 K with an Anton Paar XRK 900 reaction chamber under an Ar flow of 200 ml min⁻¹. Thermal analyses were conducted by a differential scanning calorimetry (DSC 214 Polyma, Netzsch) under an Ar flow at a heating rate of 10 K min⁻¹.

Charge and Thermal Transport Property Measurements

The SPS-processed samples were cut and polished into various shapes to measure charge and thermal transport properties. The bar-shaped samples with a typical dimension of $\sim 12 \times 2 \times 3 \text{ mm}^3$ were employed to measure Seebeck coefficient and electrical conductivity simultaneously by an Ulvac-Riko ZEM-3 M8 instrument under a low-pressure He atmosphere from room temperature to 823 K. The Hall effect measurements as a function of temperature were conducted on a Lakeshore 8407

system from 300 to 823 K under an Ar flow with a reversible 1.5 T magnetic field and 5 mA excitation current.

The thermal diffusivity of the samples coated with graphite was recorded by a Netzsch LFA 457 MicroFlash instrument. The thermal conductivity was calculated from the relation $\kappa = D C_p \rho$, where *D* is the thermal diffusivity, C_p is the heat capacity, and ρ is the mass density of the specimens. The temperature-dependent C_p was determined by the relation $C_p = [0.17078 + (2.64876 \times 10^{-5}) \times T]$ J g⁻¹ K⁻¹.¹ The ρ values were obtained using their geometrical dimensions and masses. The total thermal conductivity κ_{tot} is the sum of the lattice (κ_{lat}) and electronic thermal (κ_{ele}) conductivities. The κ_{ele} is in proportion to the electrical conductivity (σ) according to Wiedemann-Franz relation ($\kappa_{ele} = L \sigma T$), where *L* is the temperature-dependent Lorenz number and *T* is the absolute temperature.² The *L* as a function of temperature was obtained from single parabolic band (SPB) model (Figure S13).³ κ_{lat} was estimated by subtracting κ_{ele} from κ_{tot} .

Transmission Electron Microscopy (TEM)

Cross-sectional samples for scanning TEM (STEM) were prepared by focused ion beams (FIB, Helios G4, FEG, ThermoFisher Scientific) with a dual beam microscope using gallium ion milling. Defect structures and their chemical compositions were examined using a spherical aberration-corrected JEM ARM-200F microscope (Cold FEG Type, JEOL) equipped with an SDD-type EDS detector (Solid Angle 0.9-sr, X-MaxN 100TLE, Oxford), which are installed at the National Center for Inter-University Research Facilities (NCIRF) in Seoul National University. In high-angle annular darkfield (HAADF) STEM images, the point-to-point resolution was approximately 80 pm after spherical aberration-correction, and the angular range of an annular detector used was 68 to 280 mrad. All images were recorded by a high-resolution CCD detector using a 2k × 2k pixel device (UltraScan 1000, Gatan). For STEM-EDS analyses, chemical maps were recorded with a probe size of 0.13 nm and a probe current of 40 pA. The stabilization of dramatically variable local structures driven by even a subtle change in chemical compositions highlights the importance of direct observation of defect structures at the proper resolution and of careful inspection on the relationship between local structures and their effects on physical properties.

Atom Probe Tomography (APT)

APT needle-shaped specimens were processed using a dual-beam SEM/FIB (Nova 600 Nanolab, FEI) by the site-specific "lift-out"⁴ method. The specimens were investigated in a local electrode atom probe (LEAP 4000 X HR, Cameca) by applying 10 ps, 20 pJ ultraviolet (wavelength = 355 nm) laser pulses with a pulse repetition rate of 100 kHz. The detection rate was 5 ions per 100 pulses on average. The base

temperature is 43 K, and the ion flight path was 350 mm. The detection efficiency was limited to 38% because of the open area of the microchannel plate. The obtained APT data were processed by the commercial software package IVAS 3.8.8^{5,6}

2. Details in the Theoretical Calculations

2.1 Single Parabolic Band Model⁷⁻⁹ and Lorenz number¹⁰:

Pisarenko relation was calculated using single parabolic band model by assuming that acoustic phonons dominate scattering mechanism. According to the test data of carrier concentration and Seebeck coefficient (S), Pisarenko lines can be estimated based on the equations S1-S4:

$$S = \pm \frac{k_{\rm B}}{e} (\frac{2F_1(\eta)}{F_0(\eta)} - \eta)$$
(S1)

$$r_{\rm H} = \frac{3}{2} \frac{F_{1/2}(\eta) F_{-1/2}(\eta)}{2F_0^2(\eta)}$$
(S2)

$$F_n(\eta) = \int_0^\infty \frac{\chi^n}{1 + e^{\chi - \eta}} d\chi$$
(S3)

$$m_0 = \frac{h^2}{2k_{\rm B}T} \left[\frac{n \cdot r_H}{4\pi F_{1/2}(\eta)} \right]^{2/3}$$
(S4)

where $F_n(\eta)$ is the *n*th order Fermi integral, η is the reduced Fermi energy, *e* is the charge of an electron, $r_{\rm H}$ is the Hall factor, *h* is the Planck constant, $k_{\rm B}$ is the Boltzmann constant, *T* is the absolute temperature, and m_0 is the total density of states effective mass.

Because total thermal conductivity κ_{tot} is contributed by electrical (κ_{ele}) and lattice thermal conductivity (κ_{lat}), the subtraction of κ_{ele} from κ_{tot} is calculated by Wiedeman-Franz relation $\kappa_{lat} = \kappa_{tot} - \kappa_{ele}$ ($\kappa_{ele} = L \sigma T$), where σ and L is electrical conductivity and Lorenz number, respectively. L was calculated according to the equation (S5) combined with the equations (S1) and (S3).

$$L = \left(\frac{k_{\rm B}}{e}\right)^2 \left[\frac{3F_0(\eta)F_2(\eta) - 4F_1(\eta)^2}{F_0(\eta)^2}\right]$$
(S5)

2.2 Defect Formation Energy Calculations:

Defect formation energy calculations and electron density difference results were obtained by the Cambridge Sequential Total Energy Package (CASTEP) module.³ The

generalized gradient approximation (GGA) was used for the exchange-correlation functional within the Perdew-Burke-Ernzerhof (PBE) formulation.^{6, 11} The defect formation energy was calculated for $2 \times 2 \times 2$ supercells containing 64 atoms. All the atoms in the supercell were optimized for geometric structure until the forces on all atoms and their total energy difference were reduced less than 0.05 eV Å⁻¹ and 2×10^{-5} eV, respectively. The energy cutoff for the plane wave basis set was set at 400 eV. A 2 $\times 2 \times 2$ k-point set was used for integration over the Brillouin zone in the bulk structures.¹²

The formation energy $(\Delta H_{d,q})$ of the defect (d) with the charge state q is expressed by the equation (S6):

$$\Delta H_{d,q}(E_{F,\mu}) = E_{d,q} - E_p - \sum n_{\alpha}\mu_{\alpha} + q(E_F + E_V + \varepsilon)$$
(S6)

where $E_{d,q}$ and E_p are the total energy of the supercell with the defects with the charge state q obtained from CASTEP³ and the perfect host supercell, respectively. n_{α} is the number of exchanged atoms (α) in the defect supercell system, and μ_{α} is the corresponding chemical potential of the exchanged atoms (α). E_F is the Fermi level energy, and E_V corresponds to the valence band maximum energy, which were corrected by ε . The formation energy of the defect is a function of the E_F and μ_{α} of reactants.^{13, 14}

To define the relationship between $\Delta H_{d,q}(E_{F,\mu})$ and E_F , the boundary condition of μ_{α} needs to be given. Based on the thermodynamic limits on the achievable values of the chemical potentials, the μ_{α} can be obtained in Pb-rich and Pb-poor conditions by the method described in the relevant previous work.¹³ In Pb-rich condition, the $\mu_{Pb} = 0$ eV, $\mu_{Cu} = 0$ eV, $\mu_{Se} = \Delta E_{PbSe} = -1.12$ eV and $\mu_{Te} = \Delta E_{PbTe} = -0.77$ eV. In Pb-poor condition, $\mu_{Pb} = E_{PbSe} = -1.12$ eV, $\mu_{Cu} = \Delta E_{Cu2Se} = -0.02$ eV, $\mu_{Se} = 0$ eV and $\mu_{Te} = 0$ eV. Based on the above results, the relationship between the $\Delta H_{d,q}(E_{F,\mu})$ and the E_F in Pb-rich and Pb-poor conditions can be obtained.

We conducted DFT calculations for defect formation energy to better understand our STEM and APT results. We considered following possible extrinsic Cu locations: interstitial Cu (Cu_i) with four Se ligands (Cu_{i-Se}), Cu_i with one Te and three Se ligands (Cu_{i-Te}), and Cu replacing Pb (Cu_{Pb}). We also regarded plausible defects at the lattice point in rock-salt structure such as Te replacing Se (Te_{Se}), Pb vacancy (V_{Pb}), and Pb replacing Te (Pb_{Te}). Figures 6a and 6b show defect formation energy as a function of Fermi energy for the supercell under both the Pb-rich and Pb-poor conditions. The former better supports our system because we artificially stabilized anion vacancies. The results show that the Cu_{i-Se}, Cu_{i-Te}, and Te_{Se} defects are thermodynamically stable under Pb-rich condition. Importantly, the Cu_i slightly prefers Te to Se ligand, consistent with our experimental APT finding and the reported bond enthalpies.¹⁵ In our previous study,¹⁶ excess Pb in the composition Pb_{1.075}Se_{0.8}Te_{0.2} occupies vacant Te sites to form antisite defects (Pb_{Te}). However, when both Cu and Pb atoms are excess, the formation energy of both Cu_{i-Te} and Cu_{i-Se} is significantly lower than that of Pb_{Te}. Accordingly, Pb_{Te} antisite defect was not observed in the $Cu_{0.0029}Pb(Se_{0.8}Te_{0.2})_{0.95}$ sample by Cs-STEM.

2.3 Electronic Structure Calculations

To understand the electronic band structures of PbSe with Te alloying and Cu doping, we carried out first-principles electronic structure calculations within the density functional theory formalism. We utilized the projector augmented wave method ¹⁷ with the plane wave basis set, implemented in Vienna Ab-initio Simulation Package (VASP).^{18,19} For exchange correlation functional, we employed PBEsol²⁰ for crystal structure relaxations and the modified Becke-Johnson (MBJ) potential²¹ for electronic band structures. To describe the very small contents of Cu, we used $4 \times 4 \times 4$ supercell of the conventional unit cell of PbSe, which accommodates 512 lattice sites. The internal coordinates were optimized with force criterion of 0.01 eV A⁻¹, and lattice parameters are also relaxed.

3. Decoupling Charge and Thermal Transport Properties:

Conventional alloying and nanostructuring suppress κ_{lat} but also can severely damage $\mu_{\rm H}$ inevitably. To obtain maximal TE performance, a prime interest has been developing effective strategies to decouple naturally unavoidable close interrelationship between carrier mobility ($\mu_{\rm H}$) and $\kappa_{\rm lat}$. A greater ratio of $\mu_{\rm H}$ to $\kappa_{\rm lat}$ is a key parameter to increase ZT of materials, which is typically expressed by quality factor $B^{22, 23}$ The Cu_{0.0029}Pb(Se_{0.8}Te_{0.2})_{0.95} sample shows a *B* value of ~8.0 × 10³ at 300 K, far greater than the reported values for the state-of-the-art n-type PbSe systems despite the presence of complex multiscale defect structures including Vanion and dislocations (Figure 9c).²⁴⁻²⁸ The dashed line is given for comparison of B values, which is fitted based on data of pristine PbSe,²⁵ Pb_{0.9975}Sb_{0.0025}Se,²⁵ Pb_{0.9975}Bi_{0.0025}Se,²⁵ $Pb_{0.9955}Sb_{0.0045}Se-12\%GeSe$,²⁶ $Pb_{0.99}Sb_{0.01}Se-3\%CdSe$,²⁹ and $PbSe_{1-x}Te_x$ -Br (x = 0 and $(0.2)^{27}$ from the previous reports. The excess cation PbSe systems such as Zn_{0.01}PbSe_{0.998}Br_{0.002},³⁰ Cu_{0.0025}PbSe,²⁸ and the title material Cu_{0.0029}Pb(Se_{0.8}Te_{0.2})_{0.95} display unusually boosted B values. In contrast, $Pb_{0.95}Sb_{0.033}Se^{24}$ with dense dislocations driven by V_{cation} shows a very low *B* value because the involved defects strongly scatter charge carriers and phonons simultaneously, giving the considerably deteriorated $\mu_{\rm H}$ of ~60 cm² V⁻¹ s⁻¹. This observation represents the importance of designing proper defect structures for best TE performance.

4. Supporting Tables

Samples	Density (g cm $^{-3}$)	Relative density (%)
Pb(Se _{0.8} Te _{0.2}) _{0.95}	8.06	99.55
$Cu_{0.0014}Pb(Se_{0.8}Te_{0.2})_{0.95}$	8.07	99.59
$Cu_{0.0029}Pb(Se_{0.8}Te_{0.2})_{0.9}$	8.09	99.83
$Cu_{0.0043}Pb(Se_{0.8}Te_{0.2})_{0.9}$	8.06	99.51
$Cu_{0.0057}Pb(Se_{0.8}Te_{0.2})_{0.9}$	8.04	99.31

Table S1. Density of the $Cu_xPb(Se_{0.8}Te_{0.2})_{0.95}$ (x = 0-0.0057) samples after SPS process.

Table S2. The doping efficiency of the $Cu_xPb(Se_{0.8}Te_{0.2})_{0.95}$ (x = 0.0014 to 0.0043) samples at 300 and 723 K.

Samples	300 K	723 K
Cu _{0.0014} Pb(Se _{0.8} Te _{0.2}) _{0.95}	$0.08e^{-}$	$0.60e^{-}$
$Cu_{0.0029}Pb(Se_{0.8}Te_{0.2})_{0.9}$	0.16e ⁻	0.91e ⁻
Cu _{0.0043} Pb(Se _{0.8} Te _{0.2}) _{0.9}	0.10e ⁻	0.67e ⁻

5. Supporting Figures



Figure S1. (a) Backscattered electron (BSE) image for the SPS-processed $Cu_{0.0029}Pb(Se_{0.8}Te_{0.2})_{0.95}$ sample, showing the presence of microscale precipitates embedded in the surround bulk matrix. (b) The corresponding elemental map by SEM-EDS, obtained by overlaying the respective EDS signals directly arising from Pb (c), Cu (d), Se (e), and Te (f). It confirms that the microscale precipitates observed in (a) is Pb.



Figure S2. The powder X-ray diffraction (PXRD) patterns for the Pb(Se_{0.8}Te_{0.2})_{1-y} (y = 0, 0.025, and 0.05) samples.



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Figure S4. (a) The medium-magnification ABF-STEM image given in Fig. 2d in the main text. (b) The magnified ABF-STEM image focusing on the jointing area of three linear defects enclosed by black dotted lines in (a). The Burgers vector \vec{b} (yellow arrow) and complete Burgers loop (red dotted arrows) are presented.



Figure S5. The GPA of Fig. 2d in the main text revealing the propagation of lattice strains for (a) ε_{xx} , (b) ε_{yy} , and (c) ε_{xy} along the linear defects.



Figure S6. The (a) ABF- and (b) HAADF-STEM images recorded in the Cu-rich region viewed down the <110> zone axis. The location of Pb, Se, and Cu_i is indicated. Lines 1 and 2 are drawn to include Pb and Se atoms. (c) The intensity profile taken along the Lines 1 and 2 in (b) clearly distinguishes the position of Pb, Se, and Cu_i atoms. Cu_i is

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Figure S11. The estimated density of states effective mass (m_0) with respect to the Cu content in the Cu_xPb(Se_{0.8}Te_{0.2})_{0.95} (x = 0-0.0043) samples.



Figure S12. Crystal structures of the supercells (a) $Pb_{256}Se_{194}Te_{49}$, (b) $Cu_1Pb_{256}Se_{194}Te_{46}$, and (c) $Cu_2Pb_{256}Se_{194}Te_{46}$, representing the compositions of $Pb(Se_{0.8}Te_{0.2})_{0.95}$, $Cu_{0.004}Pb(Se_{0.8}Te_{0.2})_{0.95}$, and $Cu_{0.008}Pb(Se_{0.8}Te_{0.2})_{0.95}$, respectively. (d) The electronic band structure of $Pb_{256}Se_{194}Te_{49}$. The enlarged electronic bands near the Γ point for the supercells (e) $Pb_{256}Se_{194}Te_{49}$, (f) $Cu_1Pb_{256}Se_{194}Te_{4}$, and (g) $Cu_2Pb_{256}Se_{194}Te_{4}$. The calculated effective mass (m_0) and band gap (E_g) are given. E_F represents the Fermi energy.



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Figure S14. The calculated spectral thermal conductivity (κ_s) with respect to the phonon frequency at 300 K, based on various phonon scattering mechanisms involving point defect, dislocations, and nanostructures in the Cu_{0.0029}Pb(Se_{0.8}Te_{0.2})_{0.95} sample according to our STEM observations.



Figure S15. The (a) electrical conductivity (σ), (b) Seebeck coefficient (*S*), (c) total thermal conductivity (κ_{tot}), and (d) thermoelectric figure of merit (*ZT*) for the Cu_{0.0029}Pb(Se_{0.8}Te_{0.2})_{0.95} samples. Two independently synthesized samples were investigated. The sample was tested twice under the same conditions. These observations verify the reliability and cyclability of the excellent thermoelectric properties of the title sample.



Figure S16. The temperature-dependent κ_{lat} of the Cu_{0.0029}Pb(Se_{0.8}Te_{0.2})_{0.95} samples from Fig. S15. Two independently synthesized samples were investigated. The samples were tested twice under the same condition.

6. References

- G. Tan, S. Hao, S. Cai, T. P. Bailey, Z. Luo, I. Hadar, C. Uher, V. P. Dravid, C. Wolverton and M. G. Kanatzidis, *J. Am. Chem. Soc.*, 2019, 141, 4480-4486.
- 2. M. Jonson and G. D. Mahan, *Phys. Rev. B*, 1980, **21**, 4223-4229.
- B. Ge, H. Lee, C. Zhou, W. Lu, J. Hu, J. Yang, S.-P. Cho, G. Qiao, Z. Shi and I. Chung, *Nano Energy*, 2022, 94, 106941.
- 4. M. K. Miller and K. F. Russell, *Ultramicroscopy*, 2007, **107**, 761-766.
- C. Zhou, Y. Yu, Y.-L. Lee, B. Ge, W. Lu, O. Cojocaru-Mirédin, J. Im, S.-P. Cho, M. Wuttig, Z. Shi and I. Chung, *J. Am. Chem. Soc.*, 2020, 142, 15172-15186.
- C. Zhou, Y. Yu, X. Zhang, Y. Cheng, J. Xu, Y. K. Lee, B. Yoo, O. Cojocaru-Mirédin, G. Liu, S.-P. Cho, M. Wuttig, T. Hyeon and I. Chung, *Adv. Funct. Mater.*, 2019, **30**, 1908405.
- Q. Zhang, B. Liao, Y. Lan, K. Lukas, W. Liu, K. Esfarjani, C. Opeil, D. Broido, G. Chen and Z. Ren, *Proc. Natl. Acad. Sci. U. S. A.*, 2013, **110**, 13261-13266.
- C. Zhou, Y. Yu, Y. K. Lee, O. Cojocaru-Mirédin, B. Yoo, S. P. Cho, J. Im, M. Wuttig, T. Hyeon and I. Chung, *J. Am. Chem. Soc.*, 2018, 140, 15535-15545.
- B. Ge, Z. Shi, C. Zhou, J. Hu, G. Liu, H. Xia, J. Xu and G. Qiao, J. Alloys Compd., 2019, 809, 151717.
- C. Zhou, Y. K. Lee, J. Cha, B. Yoo, S.-P. Cho, T. Hyeon and I. Chung, *J. Am. Chem. Soc.*, 2018, 140, 9282-9290.
- Y. Xiao, H. Wu, W. Li, M. Yin, Y. Pei, Y. Zhang, L. Fu, Y. Chen, S. J. Pennycook, L. Huang, J. He and L.-D. Zhao, *J. Am. Chem. Soc.*, 2017, **139**, 18732-18738.
- 12. K. Hoang, S. D. Mahanti and M. G. Kanatzidis, Phys. Rev. B, 2010, 81, 15106.
- 13. S.-H. Wei, Comput. Mater. Sci., 2004, 30, 337-348.
- 14. Z. Xiao, Y. Zhou, H. Hosono and T. Kamiya, *Phys. Chem. Chem. Phys.*, 2015, 17, 18900-18903.
- 15. Y.-R. Luo, Comprehensive Handbook of Chemical Bond Energies, CRC press, 2007.
- B. Ge, H. Lee, L. Huang, C. Zhou, Z. Wei, B. Cai, S.-P. Cho, J.-F. Li, G. Qiao, X. Qin, Z. Shi and I. Chung, *Adv. Sci.*, 2022, 9, 2203782.
- 17. P. E. Blöchl, *Phys. Rev. B*, 1994, **50**, 17953-17979.
- 18. G. Kresse and J. Furthmüller, *Phys. Rev. B*, 1996, **54**, 11169.
- 19. G. Kresse and J. Hafner, J. Phys.: Condens. Matter, 1994, 6, 8245.
- J. P. Perdew, A. Ruzsinszky, G. I. Csonka, O. A. Vydrov, G. E. Scuseria, L. A. Constantin, X. Zhou and K. Burke, *Phys. Rev. Lett.*, 2008, 100, 136406.
- 21. A. D. Becke and E. R. Johnson, *The Journal of chemical physics*, 2006, 124.
- Y. Xiao, D. Wang, Y. Zhang, C. Chen, S. Zhang, K. Wang, G. Wang, S. J. Pennycook, G. J. Snyder, H. Wu and L.-D. Zhao, *J. Am. Chem. Soc.*, 2020, 142, 4051-4060.
- 23. G. Tan, L.-D. Zhao and M. G. Kanatzidis, Chem. Rev., 2016, 116, 12123-12149.
- 24. Z. Chen, B. Ge, W. Li, S. Lin, J. Shen, Y. Chang, R. Hanus, G. J. Snyder and Y. Pei, *Nat. Commun.*, 2017, **8**, 13828.
- Y. Lee, S. H. Lo, C. Chen, H. Sun, D. Y. Chung, T. C. Chasapis, C. Uher, V. P. Dravid and M. G. Kanatzidis, *Nat. Commun.*, 2014, 5, 3640.
- Z.-Z. Luo, S. Hao, X. Zhang, X. Hua, S. Cai, G. Tan, T. P. Bailey, R. Ma, C. Uher, C. Wolverton,
 V. P. Dravid, Q. Yan and M. G. Kanatzidis, *Energy Environ. Sci.*, 2018, 11, 3220-3230.

- 27. H. Wang, A. D. LaLonde, Y. Pei and G. J. Snyder, *Adv. Funct. Mater.*, 2013, 23, 1586-1596.
- L. You, Y. Liu, X. Li, P. Nan, B. Ge, Y. Jiang, P. Luo, S. Pan, Y. Pei, W. Zhang, G. J. Snyder, J. Yang, J. Zhang and J. Luo, *Energy Environ. Sci.*, 2018, 11, 1848-1858.
- X. Qian, H. Wu, D. Wang, Y. Zhang, J. Wang, G. Wang, L. Zheng, S. J. Pennycook and L.-D. Zhao, *Energy Environ. Sci.*, 2019, 12, 1969-1978.
- X. Qian, H. Wu, D. Wang, Y. Zhang, S. J. Pennycook, X. Gao, L. Zheng and L.-D. Zhao, *Mater. Today Phys.*, 2019, 9, 100102.