REVIEW ARTICLE OPEN

Computational strategies for design and discovery of nanostructured thermoelectrics

Shiqiang Hao¹, Vinayak P. Dravid¹, Mercouri G. Kanatzidis² and Christopher Wolverton¹

The contribution of theoretical calculations and predictions in the development of advanced high-performance thermoelectrics has been increasingly significant and has successfully guided experiments to understand as well as achieve record-breaking results. In this review, recent developments in high-performance nanostructured bulk thermoelectric materials are discussed from the viewpoint of theoretical calculations. An effective emerging strategy for boosting thermoelectric performance involves minimizing electron scattering while maximizing heat-carrying phonon scattering on many length scales. We present several important strategies and key examples that highlight the contributions of first-principles-based calculations in revealing the intricate but tractable relationships for this synergistic optimization of thermoelectric performance. The integrated optimization approach results in a fourfold design strategy for improved materials: (1) a significant reduction of the lattice thermal conductivity through multiscale hierarchical architecturing, (2) a large enhancement of the Seebeck coefficient through intramatrix electronic band convergence engineering, (3) control of the carrier mobility through band alignment between the host and second phases, and (4) design of intrinsically low-thermal-conductivity materials by maximizing vibrational anharmonicity and acoustic-mode Gruneisen parameters. These combined effects serve to enhance the power factor while reducing the lattice thermal conductivity. This review provides an improved understanding of how theory is impacting the current state of this field and helps to guide the future search for high-performance thermoelectric materials.

npj Computational Materials (2019)5:58; <https://doi.org/10.1038/s41524-019-0197-9>

INTRODUCTION

Although the unprecedented economic and societal growth in the world today can be attributed to the supply of traditional fossil fuels, the dramatic increase of fossil fuel combustion will inevitably lead to need for much higher efficiencies in how this energy is utilized. There is thus a growing demand for minimizing lost energy as well as for clean and renewable alternative energy sources. With over 65% of the energy released from nonrenewable sources lost as waste heat, thermoelectric technology can play a critical role in the energy landscape by enabling the direct conversion of heat into electricity.¹ The prospect of widespread solid-state thermoelectric devices with good reliability and scalability has thus attracted worldwide interest in waste heat recovery and solar heat utilization.

The ideal energy conversion efficiency of a thermoelectric system in power generation models can be expressed as

$$\eta = \frac{T_H - T_C}{T_H} \left[\frac{\sqrt{1 + ZT_{\text{avg}}} - 1}{\sqrt{1 + ZT_{\text{avg}}} + T_C/T_H} \right]. \quad (1)$$

Here, $T_H - T_C/T_H$ is the Carnot efficiency; T_H and T_C are the temperatures of the hot and cold ends, respectively; and $(ZT)_{\text{avg}}$ is the average temperature ZT value.² The efficiency is plotted as a function of T_H in Fig. 1a by fixing $T_C = 300$ K and assuming a series of ZT_{avg} values. The trend of the curves indicates that increasing the efficiency requires both high ZT values and a large temperature difference across the materials. Although the Carnot efficiency depends on external conditions, to increase η , we must

optimize the intrinsic figure of merit ZT , which is defined as

$$ZT = \frac{S^2 \sigma T}{\kappa_e + \kappa_L}. \quad (2)$$

In this expression, S , σ , κ_e , and κ_L are the Seebeck coefficient, electrical conductivity, and electric and lattice thermal conductivities, respectively.³ Therefore, to obtain a high value of ZT , both σ and S must be maximized, whereas κ_e and κ_L must be minimized. The well-known interdependence among these physical properties makes it challenging to develop strategies to improve the average ZT of a material.^{2,4–7}

After the first observation of the Seebeck thermoelectric phenomena in 1821 and the definition of the ZT equation by Altenkirch in 1911,⁶ it took several decades to develop first-generation thermoelectric devices. From a historical viewpoint, the development of thermoelectric materials has included the development of conventional semiconductors and complex and low-dimensional materials. Representative materials in these categories include group III–V and IV–IV compounds (e.g., InSb and SiGe), group IV and V chalcogenides (e.g., PbTe, Bi₂Te₃, Sb₂Te₃),⁸ complex skutterudites,^{9–11} clathrates,^{12,13} half-Heusler alloys,¹⁴ low-dimensional quantum wells,¹⁵ quantum dots,¹⁶ and nanowires.¹⁷ Notably, the phonon glass and electron crystal (PGEC)¹⁸ concept was first applied to complex skutterudites (CoSb₃) and clathrates (Sr₈Ga₁₆Ge₃₀ or Sr₄Eu₄Ga₁₆Ge₃₀). The PGEC concept suggests an idealized situation in which phonon transport occurs in the material as it would in an amorphous

¹Department of Materials Science and Engineering, Northwestern University, Evanston, IL 60208, USA and ²Department of Chemistry, Northwestern University, Evanston, IL 60208, USA

Correspondence: Christopher Wolverton (c-wolverton@northwestern.edu)

Received: 12 February 2019 Accepted: 26 April 2019

Published online: 14 May 2019

Fig. 1 **a** Thermoelectric efficiency as a function of the hot temperature with a fixed low temperature $T_C = 300$ K and fixed ZT_{avg} values. It is worth mentioning that the efficiency range of 20–30% is a threshold band to replace fossil fuel for that level of energy gain. **b** ZT performance for several representative materials as a function of temperature. The color bars at approximately 1, 1.5, and 2 represent the first-, second-, and third-generation thermoelectric achievements

glassy structure with a high degree of phonon scattering, whereas electron transport occurs as it would in a perfectly crystalline structure with minimum electron scattering. In this manner, a single material can exhibit a low lattice thermal conductivity and high power factor and thus achieve high ZT performance.¹⁹ The complex skutterudites and clathrates have cage-like open structures with heavy atoms placed into the interstitial cages to reduce the lattice thermal conductivity. These materials still maintain regular crystal structures^{19,20} and exhibit good electrical properties; therefore, good thermoelectric properties can be achieved.

The experimental breakthroughs for second-generation thermoelectric materials with ZT of approximately 1.5 were achieved by significantly decreasing the lattice thermal conductivity.^{2,4,7} Among the wide variety of research approaches applied, one emerged that involves the use of nanoscale precipitates and compositional inhomogeneities to dramatically suppress the lattice thermal conductivity.^{2,4,21,22} These second-generation materials could potentially produce power generation devices with conversion efficiencies of 11–15%.²³ The third generation of bulk thermoelectrics has been under development recently, and these materials exhibit high ZT values near or above 2 depending on the temperature T , and the consequent predicted device conversion efficiency is potentially increased to approximately 15–20%.²³ A representative third-generation material is spark-plasma-sintered PbTe–SrTe (4 mol%) doped with 2% Na, which exhibited a ZT value of approximately 2.2 at 915 K, as shown in Fig. 1b. Recently, an even higher ZT of 2.5 was achieved in the

same system PbTe with more heavy alloyed solubility of SrTe (8 mol%) realized by a nonequilibrium processing.²⁴ This outstanding ZT performance stems from the integration of many cutting-edge ZT enhancement approaches (which we detail below), namely, the enhancement of the Seebeck coefficient through valence band convergence,^{25,26} retention of the carrier mobility through minimization of the band energy offset between the matrix and precipitates,^{27–30} and reduction of the (lattice) thermal conductivity through all-length-scale phonon scattering via hierarchical architecturing from atomic-scale lattice disorder and nanoscale endotaxial precipitates to mesoscale grain boundaries and interfaces.³¹ Another record-setting-ZT material SnSe (ZT = 2.6 at 923 K) has been reported with an ultralow thermal conductivity induced by strong anharmonic and anisotropic bonding in the layered structure.³² In this system, the concept of PGEC was also elegantly reflected. In the SnSe orthorhombic sample, the nature of an “electron crystal” was secured by the high carrier mobility and power factor along the b -direction of the single crystal, whereas the “phonon glass” character was guaranteed by the anharmonicity of the atomic layered structure.^{32,33}

The wide scope of thermoelectric materials research^{20,23,34–39} covers theoretical investigations, material synthesis and characterization, and device assembly; in this review, we focus on the use of first-principles-based strategies to design, discover and optimize nanostructured thermoelectrics. We organize the discussion into four distinct strategies to enhance the thermoelectric performance of nanostructured bulk materials posed in Fig. 2.

Fig. 2 Potential strategies to improve thermoelectric performance. Strategy A: Formation of nanoscale precipitates to create phonon scattering centers to reduce the lattice thermal conductivity. Strategy B: Band alignment between matrix and second-phase candidates to retain a high carrier mobility. Strategy C: Band structure engineering of alloyed host materials to minimize the energy difference between light and heavy carrier bands to enhance Seebeck coefficients and power factors. Strategy D: Design of vibrational anharmonicity by maximizing the frequency differences at different volumes to find intrinsically low-thermal-conductivity materials. In Strategies B and C, the strategies can be implemented on either the valence band or conduction band, respectively, for p-type and n-type carriers

These four aspects cover recent computational strategies to improve the figure of merit from different angles:

Strategy A: Calculation of phase diagrams allows the prediction of compositions and temperatures where two-phase nanostructures or precipitates form. These two-phase morphologies induce the creation of phonon scattering centers and result in reduced lattice thermal conductivity.

Strategy B: The introduction of nanoscale precipitates entangles the thermal and electrical conductivity. By calculating and minimizing the band offset ΔE between the host matrix and precipitate, we can predict second-phase candidates that will retain high carrier mobility.

Strategy C: When nanoscale precipitates are introduced, there is still some solubility of the solute atoms in the matrix phase, and the resulting solid solutions can have distinct electronic structure from the pure host matrix. Band structure calculations of these dilute solid solutions allows one to search for solutes that minimize the energy difference between light and heavy carrier bands to achieve higher Seebeck coefficient and power factor.

Strategy D: In addition to the above strategies, we search for intrinsically low-thermal-conductivity materials by maximizing the acoustic-mode Grüneisen parameters (e.g., the phonon frequency differences at different volumes) that lead to large vibrational anharmonicity.

In the following sections, we review progress on these four topics, admittedly focusing primarily on work using first-principles calculations from our own groups. These calculations not only provide reasonable explanations for experimental observations and improve our understanding of material behavior but also provide rational design strategies for further development of high-performance thermoelectric materials.

STRATEGY A: REDUCTION OF LATTICE THERMAL CONDUCTIVITY THROUGH MULTISCALE HIERARCHICAL STRUCTURING

The thermal conductivity of thermoelectric materials can be decomposed into two principle components: the electrical thermal conductivity, which is related to thermal conduction by carriers (holes or electrons), and the lattice thermal conductivity, which is related to thermal conduction by phonons induced by lattice vibrations. Here, we mainly focus on the latter contribution.

Lattice thermal conductivity theory

The lattice contribution to thermal conductivity is related to microscopic vibrational dynamics as follows:^{40,41}

$$\kappa_L = \sum_q \sum_{s=1}^{3N} c_{q,s} v_{q,s}^2 \tau_{q,s}; c_{q,s} = \frac{k_B}{V} \frac{x^2 e^4}{(e^x - 1)^2}; x = \frac{\hbar \omega_{q,s}}{k_B T}, \quad (3)$$

where the sum is over all wave vectors q and $3N$ polarization indices s (N is the number of atoms in the primitive cell); $v_{q,s}$ is the group velocity; $\tau_{q,s}$ is the relaxation time associated with each mode; $c_{q,s}$ is the mode contribution to the heat capacity; $\omega_{q,s}$ is the frequency of the mode; k_B is Boltzmann's constant; $\hbar$ is Planck's constant; V is the volume; and T is the temperature. By integrating all the mode heat capacities, the lattice thermal conductivity can be written as

$$\kappa_L = \frac{1}{3} C_v \langle v \Lambda \rangle, \quad (4)$$

where C_v is the bulk volumetric isochoric heat capacity, the brackets indicate the average over all modes, and Λ is the phonon mean free path (MFP).

It is clear from Eq. (4) that the lattice thermal conductivity depends on C_v and the phonon MFP. In a solid material, acoustic phonons with a spectrum of wavelengths and MFPs govern most of the heat transport, and each phonon contributes to the total

thermal conductivity. During the heat transport, short- and medium-wavelength phonons are strongly scattered by point defects and nanostructures, whereas the long-wavelength phonons are more strongly affected by larger strains and boundaries. More scattering during heat transport results in a lower thermal conductivity. To achieve high thermoelectric performance by reducing the lattice thermal conductivity, a practical strategy is thus to introduce a wide range of point defects, solid solutions, nanostructures, grain boundaries, and strains into a single sample to induce as much scattering as possible.^{23,35} Utilizing multiple length scale defects for phonon scattering (from atomic point defects to meso-structures) can reduce the lattice thermal conductivity even down to the amorphous limit.³¹ To separate the contributions to lattice thermal conductivity by different length scale defects, one can use models calibrated by empirical input. For example, the MFP of phonon scattering by atomic-, nano-, and mesoscale structures has been determined.^{42,43} It was found that the most significant contribution about >50% of the thermal conductivity is dominated by the phonon modes with an MFP range of 5–100 nm, which can be attributed to scattering by nanoscale precipitates.⁴⁴ The contributions by phonon modes with an MFP of <5 nm, attributed to atomic-scale point defects, are much smaller, only about 25% of the lattice thermal conductivity. Finally, approximately 25% of the lattice thermal conductivity is contributed by phonon modes with MFPs of 0.1–1.0 μ m, which is attributed to scattering by the mesoscale grain structures.⁴⁴ Therefore, the introduction of multiscale structures in a single system to scatter a wide spectrum of heat-carrying phonons to reduce the lattice thermal conductivity should be a primary strategy for future improved thermoelectrics.

Examples

Many experimental results have provided evidence of the reduction of the lattice thermal conductivity by multiscale scattering.²⁹ From theoretical calculation point of view, direct DFT-based calculations can be used to determine the relative stability and hence the composition temperature ranges under which one should form two-phase nanostructures. Here, we present some examples of point defect solubilities and phase stabilities determined using first-principles calculations to demonstrate the existence of different-scale scattering centers, which are useful for clarifying experimental observations of reduced lattice thermal conductivity.

The first example involves calculation of point defects energies and Na solubilities for Na-doped PbQ (Q = Te, Se, S) using DFT, to help improve understanding of high-performance p-type lead chalcogenides.⁴⁵ Among these systems, Na is experimentally observed to have the highest solubility limit (~2 mol%) in PbS and the lowest solubility limit (~0.5 mol%) in PbTe.⁴⁵ These results are consistent with DFT calculations, which show that Na defects have the lowest and highest formation energies in PbS and PbTe, respectively.⁴⁵ Therefore, Na-doped PbQ samples, doped beyond these solubility limits, in fact contain a combination of point defects (solid solution) and nanoscale architectures. Therefore, in addition to providing charge carriers (holes) for PbQ, both the point defects (solid-solution formation) and nanoscale precipitates induced by Na doping reduce the lattice thermal conductivity by scattering heat-carrying phonons. These results help explain the reports of high thermoelectric performance in p-type PbQ materials and represent an example of computational studies of defects introduced into these materials to decrease thermal conductivity.

Another successful example of DFT calculations supporting experimental observation involves the morphology control of nanoparticles in the Na-doped PbTe–PbS system by tuning the ratio of PbS/Na.⁴⁶ The use of Na and other dopants separately and in combination may open new pathways for nanoparticle size and

morphology control. The morphology of crystalline precipitates in a solid-state matrix is known to be governed by complex but tractable energetic considerations driven largely by volume-strain-energy minimization and the anisotropy of interfacial energies. DFT and semi-classical calculations have shown that the (100) coherent interfacial energy between PbS and PbTe depends strongly on the presence of Na addition. With the addition of Na at the PbS side, the (100) coherent interfacial energy between PbS and PbTe decreases. On the contrary, the energy increases with the addition of Na at the PbTe side of the interface. These DFT calculated interfacial energy changes of PbTe/PbS interfaces with or without Na explain the significant change in PbS precipitate morphology found in these materials. Using analytical scanning/transmission electron microscopy and atom probe tomography, it was unambiguously demonstrated that Na partitions to the precipitates and segregates at the matrix/precipitate interfaces, inducing morphological anisotropy of the PbS precipitates, and validating the conclusion from DFT. This approach represents a new strategy using a method of partitioning a ternary addition to control the nanostructure size and morphology. The resulting nanostructure morphology not only reduces the lattice thermal conductivity, but as we will show below, these alloying additions can also stimulate multiband conduction and further enhance the electric conduction and thus power factor.⁴⁷

In addition to their use in evaluating the defect formation energies and particle segregation energies to control the solubility and morphology, respectively, DFT calculations have also been applied to construct phase diagrams, from which we can understand the fundamental phase behavior and hence driving force for precipitation of a minor phase as a nanostructure.^{48,49} Below we present an example of the 2% Na-doped PbTe–PbSe–PbS system, for which the thermoelectric properties have been observed to be superior to those of 2% Na-doped PbTe–PbSe and PbTe–PbS, with a ZT of ~2.0 achieved at 800 K. This good thermoelectric performance partially originates from the significant reduction of the lattice thermal conductivity, which is attributed to alloy scattering and point defects. The very low total thermal conductivity of 1.1 W/m·K at 300 K of the $x = 0.07$ composition is essentially attributed to phonon scattering from solid-solution defects rather than the assistance of endotaxial nanostructures.

To better understand the solubility behavior of these systems, Doak and colleagues⁴⁸ calculated phase diagrams of the pseudoternary $(\text{PbTe})_{1-x-y}(\text{PbSe})_x(\text{PbS})_y$ system using DFT mixing energies and regular solution models. These authors computed isothermal sections at 300, 600, and 900 K, shown in Fig. 3.⁴⁸ It is interesting to see there is a three-phase equilibrium between the PbTe-, PbSe-, and PbS-rich below the pseudobinary minimum

miscibility gap temperatures in the $(\text{PbTe})_{1-x-y}(\text{PbSe})_x(\text{PbS})_y$ system. As the temperature increases above the maximum miscibility gap temperature of $(\text{PbSe})_{1-x}(\text{PbS})_x$ (275 K), the three-phase region disappears due to a formation of PbSe and PbS solid solutions. For the other two combinations of $(\text{PbTe})_{1-x}(\text{PbSe})_x$ and $(\text{PbTe})_{1-x}(\text{PbS})_x$, each of them exhibits a miscibility gap between a PbTe-rich phase and a $(\text{PbSe})_{1-x}(\text{PbS})_x$ -rich phase. As the temperature increases above the miscibility gap temperature of $(\text{PbTe})_{1-x}(\text{PbSe})_x$ (630 K), the majority of ternary composition space becomes a two-phase region of $(\text{PbTe})_{1-x}(\text{PbS})_x$ with a minority of three-phase solid solution $(\text{PbTe})_{1-x-y}(\text{PbSe})_x(\text{PbS})_y$ (Fig. 3c). Using DFT to untangle this complex phase behavior is useful, since the computed phase diagram can be used to determine the stable phase of $(\text{PbTe})_{1-x-y}(\text{PbSe})_x(\text{PbS})_y$ above room temperature should be PbSe–PbS-rich phases in a PbTe-rich matrix.⁴⁸

The calculated phase diagrams suggest that many of these ternary compositions will form a two-phase mixture of solid solution matrix and precipitate nanostructures. However, in this case, the PbS precipitates were found to be large enough that one would not expect the lattice thermal conductivity to be significantly reduced by nanostructuring. But, the thermal conductivity in this case is nevertheless reduced by phonon scattering due to the solid solution. Also, the 2% p-type Na-doped $(\text{PbTe})_{1-2x}(\text{PbSe})_x(\text{PbS})_x$ system exhibits an increased power factor due to modification of the electronic structure, as we detail in Strategy B below. This increased power factor, combined with the very low total thermal conductivity induced by the solid solution yields a material with good thermoelectric performance.

STRATEGY B: RETENTION OF HIGH CARRIER MOBILITY THROUGH HOST/PRECIPIRATE BAND ALIGNMENT

The discussion in the previous section primarily focused on strategies to reduce the lattice thermal conductivity through the creation of multiscale phonon scattering centers. In all these cases, however, the power factor is actually reduced relative to that of the single-phase host material because of the additions of these multiscale centers that often have the potential to scatter the carriers. Therefore, care has to be taken in implementing the strategy to avoid this scenario to achieve further ZT improvements. A strategy targeting the control and minimization of the band offsets between two phases can be realized in bulk systems. If the conduction band minimum of the matrix is close in energy to that of the second phase, then electron transmission through the system should be more facile. Similarly, hole transport should also be facile if the two valence band maxima are close. Therefore, another generic operating concept for high-ZT thermoelectrics

Fig. 3 Isothermal sections of pseudoternary phase diagram of the $(\text{PbTe})_{1-x-y}(\text{PbSe})_x(\text{PbS})_y$ at **a** 300 K, **b** 600 K, and **c** 900 K.⁴⁸ These phase diagrams were computed from a combination of DFT mixing energies and regular solution models. The single-phase boundaries and tie-lines are shown in black and green, respectively. Some alloys at specific compositions of $(\text{PbTe})_{0.90}(\text{PbS})_{0.05}(\text{PbSe})_{0.05}$, $(\text{PbTe})_{0.86}(\text{PbS})_{0.07}(\text{PbSe})_{0.07}$, and $(\text{PbTe})_{0.76}(\text{PbS})_{0.12}(\text{PbSe})_{0.12}$, are respectively plotted as solid black, red, and blue circles. For each of these compositions, the stable equilibrium corresponds to a two-phase equilibrium, and the matrix and precipitate compositions are indicated by open circles connected by tie-lines of the same color as the alloy composition. Reproduced with permission from ref. ⁴⁸ copyright (ACS, 2014)

other than the creation of multiscale phonon scattering centers has emerged: a small energy difference in the relevant valence or conduction bands between the host and second phases ensures relatively fast electron or hole mobilities.

Calculation methods

Bulk calculations alone are insufficient to provide band alignments because they contain no absolute reference for the electrostatic potential.⁵⁰ To calculate band alignments, the band structures of the two materials must be aligned on a common energy scale. The common energy can be the universal hydrogen transition energy, the vacuum energy level, or the electrostatic potential across the interface between the two materials.⁵¹ The universal hydrogen transition level approach has been reported to be able to predict the electrical activity of hydrogen in any host material once some basic information about the band structure of that host is known.⁵² Briefly, DFT calculations within the general gradient approximation are used to determine the key quantities of the formation energy of interstitial H in the host and the electronic transition level. The formation energy of interstitial H in charge state q (where $q = +1, 0$, and -1) can be determined by placing H in a volume of the host material, $E^f(H^q) = E_{\text{tot}}(H^q) - E_{\text{tot}}(\text{bulk}) - \frac{1}{2}E_{\text{tot}}(H_2) + qE_F$, where $E_{\text{tot}}(H^q)$ is the total energy of H with q charge in this structure, $E_{\text{tot}}(\text{bulk})$ is the total energy of the pure host material, $E_{\text{tot}}(H_2)$ is given by an H_2 molecule at $T = 0$, and E_F is the Fermi level or the electron chemical potential. The Fermi-level position labeled as ϵ ($+/-$), where the positive and negative charge states are equal in energy, can be identified. Using this approach, the band energies of the materials are thus aligned with the universal hydrogen transition level.

The vacuum level or the ionization potential is another common energy that can be used to align the valence and conduction bands of two materials. For this process, two separate calculations are needed: (i) a bulk calculation to determine the bulk band structure relative to the average electrostatic potential and (ii) a slab calculation to determine the difference between the average of the electrostatic potential in the bulk and in vacuum. Ideally, the slabs should be thick enough to allow the electron density in the center of the slab to be identical to the bulk electron density. Generally, the two methods should give the same band alignment results for a pair of materials. We have used both the H transition level and vacuum level methods to align PbS and CdS band structures. The valence band maximum difference between PbS and CdS is 0.13 eV using the universal H method, which is in good agreement with the difference of 0.21 eV obtained using the vacuum level method with eight-layer-thick (001) slab calculations.

Simple band alignment

The generality of the concept of band alignment between the host and second phase is evident in the example of PbS system with addition of the second phases of MS ($M = \text{Cd, Zn, Ca, Sr}$).^{28,53} By adding different NaCl-type metal sulfides MS ($M = \text{Cd, Zn, Ca, Sr}$) as second phases, the carrier mobility in PbS host are adjusted significantly, due to the differences of alignment between the energy bands of the host and second phases. Carrier mobility is typically reduced by host/precipitate interfaces, but as the (valence or conduction) bands become aligned across this interface, the smaller the degradation of mobility. The energy difference between the host PbS valence band maximum and those of the metal sulfides are 0.13, 0.16, 0.53, and 0.63 eV for CdS, ZnS, CaS, and SrS, respectively. These energy differences suggest that the hole mobility in PbS with the above four separated second-phase additions should decrease. This point has been proven by experimental observations, where the hole mobilities at 923 K were approximately 37, 28, 25, and 22 cm^2/Vs , respectively.^{28,53} As a potential

thermoelectric material, PbS was abandoned in the past as not promising, but the second-phase band alignment approach gave the highest ZT value of 1.3 at 923 K for p-type $\text{Pb}_{0.975}\text{Na}_{0.025}\text{S}$ –3% CdS over a 160% improvement.²⁸

Band alignment using compositionally alloyed nanostructures

The PbSe system is another interesting example for which the enhanced thermoelectric performance can be partly attributed to the large carrier mobility induced by the host/precipitate band alignment. In this case, the band energy offsets between the PbSe host and second phases can be reduced using compositionally alloyed $\text{CdS}_{1-x}\text{Se}_x/\text{ZnS}_{1-x}\text{Se}_x$ nanostructures.²⁹ A series of experiments have been performed in the PbSe host for the second-phase addition of CdSe/ZnSe and CdS/ZnS. A very small difference in the carrier mobility in PbSe was observed with the addition of 1% CdSe, ZnSe, CdS, or ZnS. However, upon increasing the second-phase fraction to 4%, the carrier mobility at 300 K remained almost constant for the CdS and ZnS additions but decreased for the CdSe and ZnSe additions. As previously mentioned, the variations in carrier mobility are thought to be associated with valence band offsets between the host PbSe matrix and the nanostructured second-phase precipitates. Therefore, the DFT calculations of band alignment relative to PbSe were applied to try to explain the above experimental carrier mobility observations. Surprisingly, the valence band energy differences relative to PbSe were 0.06, 0.26, 0.13, and 0.30 eV for CdSe, CdS, ZnSe, and ZnS,²⁹ respectively, as shown in Fig. 4. The band offsets between perfectly ordered, stoichiometric phases were clearly insufficient to explain the small changes in the carrier mobilities for PbSe–(CdS/ZnS).

To obtain further insight into the carrier mobilities, we used DFT together with cluster expansion and Monte Carlo methods to investigate the quaternary phase diagram of (Pb,Cd)(S,Se) and the corresponding phase diagrams of (Pb,Cd)S, (Pb,Cd)Se, Cd(S,Se), and Pb(S,Se). Figure 5 clearly reveals that in the 0 K quaternary phase diagram, the tie line connects PbSe–CdS rather than PbS–CdSe, implying that the formation energy of PbSe + CdS is more favorable than that of PbS + CdSe. For the 200 K quaternary phase diagram, the single-phase points in the 0 K case grew into small single-phase regions because of the small amount of off-stoichiometry solid solutions. The tie lines in the 0 K case all grew into two-phase regions, which are shaded in yellow. For example, the diagonal two-phase region $\text{PbSe}_{1-x}\text{S}_x + \text{CdS}_{1-x}\text{Se}_x$ grew from PbSe + CdS at 0 K. In addition, the white triangle areas are the three-phase regions, which are surrounded by two-phase regions. It is interesting to see the quaternary phase diagram at 300 K, where the two-phase region connecting $\text{PbS}_{1-x}\text{Se}_x$ and $\text{PbSe}_{1-x}\text{S}_x$ grew into a large single phase of solid-solution Pb(S,Se). Based on the quaternary phase diagram, with the addition of up to 4% CdS into PbSe, the CdS in the host PbSe will induce the coexistence of the two phases $\text{PbSe}_{1-x}\text{S}_x + \text{CdS}_{1-x}\text{Se}_x$ at 300 K,

Fig. 4 Band alignment of PbSe with rock salt type CdS, CdSe, $\text{CdSe}_{0.75}\text{S}_{0.25}$, $\text{CdS}_{0.9}\text{Se}_{0.1}$, ZnS, and ZnSe

Fig. 5 Quaternary phase diagrams of (Pb,Cd)(S,Se) at **a** 0 K, **b** 200 K, and **e** 300 K. Binary phase diagram of **c** Cd(S,Se), **d** (Pb,Cd)S, **f** (Pb,Cd)Se, and **g** Pb(S,Se). All the two-phase regions are shaded in yellow

which can be expressed as a chemical reaction of $\text{PbSe} + \text{CdS} \rightarrow \text{PbSe}_{1-x}\text{S}_x + \text{CdS}_{1-x}\text{Se}_x$. These calculation results support the high-resolution energy-dispersive X-ray spectroscopy observation of these nanoscale precipitates.²⁹ In addition, the band alignments of $\text{CdS}_{0.9}\text{Se}_{0.1}$ and $\text{CdSe}_{0.75}\text{S}_{0.25}$ are much closer to PbSe than CdS and CdSe. We call these compositionally alloyed nanostructures. The valence-band energy levels for $\text{CdS}_{1-x}\text{Se}_x$ are thus intermediate between those of CdS and CdSe. Therefore, the very small experimental carrier mobility difference with 1% addition of CdSe or CdS can be understood based on the 0.06-eV band offset of CdSe and the intermediate valence band energy of $\text{CdS}_{1-x}\text{Se}_x$, which is very close to that of PbSe. Upon increasing the addition of CdSe and CdS to 4%, strong scattering of holes across the CdSe/PbSe interfaces is expected, whereas CdS is expected to remain in the form of $\text{CdS}_{1-x}\text{Se}_x$ with weak hole scattering.

In summary, in this section we have shown that by tailoring the alignment of electronic bands of the compositionally alloyed nanostructures relative to the host matrix, we can use this as design tool to tune desirable thermoelectric properties, specifically electronic mobility. Computational screening of band alignment

can be used to select second-phase nanostructures with the host matrix with aligned band energies. Together with the large reductions of the lattice thermal conductivity induced by the embedded nanostructures (Strategy A), the band-offset engineering (Strategy B) provides a powerful design strategy for advanced thermoelectric systems.

STRATEGY C: ENHANCEMENT OF SEEBECK COEFFICIENT AND POWER FACTOR THROUGH BAND STRUCTURE ENGINEERING

The aforementioned strategies to enhance the thermoelectric performance involved reducing the lattice thermal conductivity through multiscale hierarchical architectures and retaining the carrier mobility through band alignment. There is another performance-enhancing mechanism that involves modifying the electronic structure of the matrix itself, which can be guided by theory.^{25,26} In this section, we discuss the use of band structure engineering to further increase the power factor and thermoelectric performance by alloying to control the band gap and heavy/light hole splitting.

Fig. 6 Schematic diagram of the electronic band structure of SnTe and $\text{Sn}_{1-x}\text{Cd}_x\text{Te}$.⁵⁶ The energy difference between light-hole valence band (VB_L) and heavy-hole valence band (VB_H) are plotted. Reproduced with permission from ref. ⁵⁶ copyright (ACS, 2014)

We use rock-salt structure PbTe as an example to illustrate the mechanism of this band engineering effect. In the typical band structure of the rock-salt structure, the first valence band is located at the L point; because the effective mass of the L point is relatively low, the band is called a light hole band. The second valence band maximum is located along the Σ direction from Γ to K and is called a heavy hole band because of its relatively large effective mass. The energy difference between the light and heavy band for PbTe is 0.15 eV. Because the energy difference is relatively large, the carriers from the second band are not usually involved in carrier transport. In other words, the second heavy hole band does not contribute to the Seebeck coefficient or electrical conductivity. However, with increasing temperature, the energy difference between the two bands decreases, and thus, the second band begins to contribute to carrier transport. This decrease of the energy difference is generally called band convergence. Depending on the system effective mass and band difference, the Seebeck coefficient and electrical conductivity may be enhanced and reduced, respectively, because of the heavy effective masses of the second band.⁵⁴ The overall performance is determined by the competing effects on the Seebeck coefficient and electrical conductivity. Some examples have shown that the second heavy band involvement usually enhances the ZT performance at certain carrier concentrations.⁵⁵ In addition to being affected by temperature, the band convergence can also be controlled by using suitable dopants.

Another example of taking advantage of valence band engineering effects is alloying SnTe with Cd atoms resulting in a ZT value of ~ 0.96 at 823 K in p-type of $\text{SnCd}_{0.03}\text{Te}$ samples, a 60% improvement over that of the Cd-free sample.⁵⁶ A detailed comparison of the electronic band structure shows that the valence band energy difference between the light-hole and heavy-hole is significantly decreased. Specifically, it decreases from ~ 0.35 eV in pristine SnTe to ~ 0.12 eV with 3 mol% Cd doping. As shown in Fig. 6, the light-hole valence bands decrease and the heavy-hole valence band slightly increases with increasing Cd fraction, which induces the light- and heavy-hole band energy difference smaller. The band energy difference decrease directly enhances the density of state effective mass and thus increases Seebeck coefficients and contributes to improve power factors. Beside the single Cd doping, another example of SnTe shows a similar strong improvement of Seebeck coefficient due to Mg-doping⁵⁷ and Ge-doping⁵⁸ induced band convergence effect.⁵⁶

Based on a single dopant in the SnTe system, a further investigation of In/Cd codoping with CdS nanostructuring revealed a significant enhancement of the thermoelectric performance of p-type SnTe over a broad temperature plateau with a peak ZT value of ~ 1.4 at 923 K.⁵⁹ In this example, In and Cd respectively play a role to enhance Seebeck coefficients at low temperature and mid- to high-temperature range. At low temperature, In doping introduces resonant energy levels inside the valence bands. While at mid- to high-temperature range, Cd

doping leads to light- and heavy-hole band convergence for a high Seebeck coefficient. As supported by first-principles band structure calculations, the combination of the two dopants in SnTe yields enhancements of the Seebeck coefficient and power factor over a wide temperature range because of the synergy of the resonance levels and valence band convergence. Beyond the above electronic band structure modifications, all scale hierarchical structures can be formed in the codoped samples, which induces effective phonon scattering and strong reductions in lattice thermal conductivities. Therefore, the overall performance of SnTe with an average ZT of ~ 0.8 over 300–923 K makes it an attractive p-type material for thermoelectric power generation. Moreover, another example of Ag and In codoped SnTe system also shows a significant power factor enhancement because of a similar synergistic effect of resonance level and valence band convergence.⁶⁰

The band convergence effect is not only observed in the Cd-doped SnTe system; MgTe inclusion in PbTe⁵⁵ and the use Hg doping in SnTe⁶¹ bring the two valence bands (L and Σ) closer in energy by lowering both energies, which contributes to enhancing the Seebeck coefficient. Moreover, these dopants also increase the band gap of the host materials, which suppresses the bipolar thermal conductivity at high temperature and results in ubiquitous nanostructuring, thereby reducing the lattice thermal conductivity. The integration of these effects in a single material pushes ZT to a very high level, such as 1.35 at 910 K in $\text{Sn}_{0.98}\text{Bi}_{0.02}\text{Te}-3\%\text{HgTe}$,⁶¹ 1.9 at 773 K for Bi-doped $\text{Ge}_{0.87}\text{Pb}_{0.13}\text{Te}$,⁶² and even 2.0 at 823 K for Mg-doped PbTe.⁵⁵

STRATEGY D: SEARCH FOR INTRINSICALLY LOW-THERMAL-CONDUCTIVITY MATERIALS

Calculation methods

Based on Eq. (3), there are two main categories of atomistic simulation methods to calculate the lattice thermal conductivity: molecular dynamics methods and lattice dynamics methods. For the molecular dynamics methods in an equilibrium state, the system has an average of zero heat flux over a long time range with a constant average temperature. However, an instantaneous heat flux is not zero at each instant of time due to the instantaneous temperature fluctuations. The well-known Green-Kubo method,⁶³ which is based on the general fluctuation-dissipation theorem,⁶⁴ relates the lattice thermal conductivity of the system to the time required for such fluctuations to dissipate:

$$\kappa_{ij} = \frac{V}{k_B T} \int_0^\infty \langle q_i(0) q_j(t) \rangle dt. \quad (5)$$

Here, a lattice thermal conductivity tensor component κ_{ij} (i and $j = x, y, \text{ or } z$) is related to an integral of an average of the product of an instantaneous i direction heat flux $q_i(0)$ with an instantaneous j direction heat flux $q_j(t)$ over a simulation time range. Note that the infinite time limit is actually equal to the relaxation time within the duration of the simulation since the integral would be zero beyond the relaxation time.

Importantly, similar to many simulation studies, the limited simulation cell size tractable with molecular dynamics methods often leads to finite size effects.^{65,66} The direct relationship between the lattice thermal conductivity and phonon MFP is clear from Eq. (4). Therefore, in calculations of the lattice thermal conductivity, to accommodate the multiscale phonon scattering events that often occur in thermoelectric materials, a much larger simulation cell length is needed, which makes direct lattice thermal conductivity calculations using molecular dynamics simulations very difficult.

In lattice dynamics calculations, the potential energy of a system is expressed as a Taylor series expansion of atomic

Fig. 7 DFT-calculated phonon (a) and Gruneisen (b) dispersions.³² In (a), TA, TA', and LA (labeled as red, green, and blue) are respectively transverse acoustic phonon scattering branches and longitudinal acoustic phonon scattering branch. In (b), corresponding Gruneisen dispersions for TA, TA', and LA are also labeled as red, green, and blue dots. The inset values in (b) are the average Gruneisen parameters along the *a*, *b* and *c* axes. Reproduced with permission from ref.³² copyright (Nature, 2014)

displacements.⁶⁷ Based on the potential energy expression, within the quasi-harmonic approximation, the elements of the force constant matrix can be determined either by the finite displacement method^{68,69} or from perturbation theory.⁷⁰ By accounting for the masses of the system, the vibrational frequencies and wave vectors can be determined by diagonalization of the dynamical matrix, which allows both $c_{q,s}$ and $v_{q,s}$ in Eq. (3) to be determined. To calculate the lattice thermal conductivity, the relaxation time $\tau_{q,s}$ is also needed. To evaluate the relaxation time, a simple phenomenological approach can be used by including contributions of atomic-scale point defects, dislocations, boundaries, displacement layers, nanoscale precipitates, and the corresponding phonon–phonon interactions. Correlated to phonon scattering from above microstructures, the relaxation time can be expressed as⁷¹: $\tau_c^{-1} = \tau_U^{-1} + \tau_N^{-1} + \tau_D^{-1} + \tau_{NP}^{-1} + \tau_B^{-1} + \tau_S^{-1} + \tau_{PD}^{-1} + \tau_{DL}^{-1}$, where τ_U , τ_N , τ_D , τ_{NP} , τ_B , τ_S , τ_{PD} , and τ_{DL} are the relaxation times corresponding to scattering from Umklapp processes,⁷² normal processes,⁷³ point defects,⁷⁴ nanoparticles,⁷⁵ boundaries,⁷⁶ dislocations,⁷⁷ strains,⁷⁶ and displacement layers,⁷⁸ respectively.

Examples

The above phenomenological assessment can quantitatively evaluate the individual contributions of each type of

microstructures on the scattering of phonons at specific frequencies. The significant advantages of this phenomenological approach are that it can provide not only qualitative guiding principles regarding the different length scale contributions, but also quantitative extent of corresponding microstructure effects on phonon scattering. If we consider pure single crystals,^{19,20,79–82} many contributions to the relaxation time such as defects, boundaries, nanoparticles, and strains can be neglected, and we can focus solely on the normal phonon scattering and Umklapp phonon–phonon scattering based on the Debye–Callaway model.^{20,72,80,81,83,84} A very good example that uses the above model to calculate the lattice contribution is orthorhombic SnSe, where the ultrahigh ZT performance was clarified based on the origin of the intrinsically low-thermal conductivity. To understand the low lattice thermal conductivity of SnSe, first-principles DFT phonon calculations were performed within the quasi-harmonic approximation for the phonon and Gruneisen dispersions.^{32,85} It is known that the Gruneisen parameters characterizing the relationship between the phonon frequency and crystal volume change reflect the strength of the lattice anharmonicity. On the basis of the phonon dispersions along high symmetrical lines as plotted in Fig. 7, the Gruneisen dispersions of SnSe are calculated and exhibit anomalously high values suggesting very strong crystal anharmonicity. The strong lattice anharmonicity originated from the distorted SnSe polyhedra and a zig-zag accordion-like atomic structure of slabs in the *b*–*c* plane. Moreover, due to the van der Waals gap in SnSe along the *a* direction, the weaker bonding between the slabs strongly suppress the phonon transport inducing very low lattice thermal conductivity.^{32,86}

SUMMARY

We have described the use of four typical computational strategies to enhance the thermoelectric performance of nanostructured bulk materials. Thus far, the extraordinary thermoelectric performance of several bulk thermoelectric materials has been demonstrated with a high ZT > 2. All of these high-ZT materials elegantly reflect the PGEC concept. In particular, many of the enhanced figures of merit were achieved using a combination of minimizing electron scattering and maximizing all-length-scale heat-carrying phonon scattering using nanostructuring methods.^{87–89} The nanostructuring methods integrate many new concepts of invoking multiscale phonon scattering, including atomic-scale alloying, endotaxial nanostructuring, and mesoscale grain-boundary control, with band alignment and convergence engineering methods in a synergistic manner. This integrated methodology is also the most plausible approach to increase ZT to the next threshold of ZT = 3.

In the pursuit of higher ZT, first-principles calculations are critical to providing theory explanations,⁹⁰ material selections,^{91,92} and even ZT predictions.^{93,94} However, it remains difficult to quantitatively and accurately evaluate the thermoelectric performance of a bulk system with multiscale second phases. One reason for this difficulty is that the multiscale phonon scattering contributions to the lattice thermal conductivity may require multiscale simulation methodology, which is beyond the scope of first-principles calculations. Another reason for the difficulty is that carrier transport in a host with multiscale second phases remains unavailable, even though the semi-classical Boltzmann transport theory can be used to calculate the thermoelectric properties for pure crystals. To overcome the difficulties of the multiscale problems, one may first consider interface or grain-boundary configurations in nanocomposite materials including grain size, shape and distributions. With the known nanocomposite structure, it is interesting and necessary to investigate how the interfaces affect carrier and phonon transport including electrical conductivity and phonon relaxation time evaluations. A direct and relative easy computational strategy might be using Monte Carlo

technique, which analyzes the complicated phenomenon in terms of elementary processes in a simple and accurate way. By taking into account DFT-based parameters for interface effects on charge and phonon transport in host matrix with precipitates, we will be able to evaluate and design overall thermoelectric performance of complicate nanocomposite materials. However, as demonstrated in this review, advanced thermoelectric properties can be achieved with a sound and logical scientific basis with the aid of improved first-principles understanding of both the atomic and band structure of materials. We hope the theoretical estimations will provide further impetus to continue the search for higher thermoelectric performance.

ACKNOWLEDGEMENTS

The authors acknowledge support by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC0014520. We acknowledge the use of the supercomputing resource facilities (Quest) at Northwestern University.

AUTHOR CONTRIBUTIONS

S.H. and C.W. conceived the idea. All authors contributed to the discussion of the structure and the writing of the manuscript.

ADDITIONAL INFORMATION

Competing interests: The authors declare no competing interests.

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REFERENCES

- Bell, L. E. Cooling, heating, generating power, and recovering waste heat with thermoelectric systems. *Science* **321**, 1457 (2008).
- Sootsman, J. R., Chung, D. Y. & Kanatzidis, M. G. New and old concepts in thermoelectric materials. *Angew. Chem. Int. Ed.* **48**, 8616–8639 (2009).
- Shakouri, A. Recent developments in semiconductor thermoelectric physics and materials. *Annu. Rev. Mater. Res.* **41**, 399 (2011).
- Kanatzidis, M. G. Nanostructured thermoelectrics: the new paradigm? *Chem. Mater.* **22**, 648–659 (2010).
- Vineis, C. J., Shakouri, A., Majumdar, A. & Kanatzidis, M. G. Nanostructured thermoelectrics: big efficiency gains from small features. *Adv. Mater.* **22**, 3970–3980 (2010).
- Shakouri, A. Thermoelectric phenomena, materials, and applications. *Annu. Rev. Mater. Res.* **41**, 433–448 (2011).
- Snyder, G. J. & Toberer, E. S. Complex thermoelectric materials. *Nat. Mater.* **7**, 105–114 (2008).
- Wood, C. Materials for thermoelectric energy conversion. *Rep. Prog. Phys.* **51**, 459 (1988).
- Slack, G. A. & Tsoukala, V. Some properties of semiconducting IrSb₃. *J. Appl. Phys.* **76**, 1665 (1994).
- Nolas, G. S., Morelli, D. T. & Tritt, T. M. Skutterudites: a phonon-glass-electron crystal approach to advanced thermoelectric energy conversion applications. *Annu. Rev. Mater. Sci.* **29**, 89 (1999).
- Sales, B. C., Mandrus, D. & Williams, R. K. Filled Skutterudite antimonides: a new class of thermoelectric. *Mater. Sci.* **272**, 1325 (1996).
- Cohn, J. L., Nolas, G. S., Fessatidis, V., Metcalf, T. H. & Slack, G. A. Glasslike heat conduction in high-mobility crystalline semiconductors. *Phys. Rev. Lett.* **82**, 779 (1999).
- Guloy, A. M. et al. A guest-free germanium clathrate. *Nature* **443**, 320 (2006).
- Uher, C., Yang, J., Hu, S., Morelli, D. T. & Meisner, G. P. Transport properties of pure and doped MnSn (M = Zr, Hf). *Phys. Rev. B* **59**, 8615 (1999).
- Ohta, H. et al. Giant thermoelectric Seebeck coefficient of a two-dimensional electron gas in SrTiO₃. *Nat. Mater.* **6**, 129 (2007).
- Kim, W. et al. Thermal conductivity reduction and thermoelectric figure of merit increase by embedding nanoparticles in crystalline semiconductors. *Phys. Rev. Lett.* **96**, 045901 (2006).
- Boukai, A. I. Silicon nanowires as efficient thermoelectric materials. *Nature* **451**, 168–171 (2008).
- Slack, G. A. *CRC Handbook of Thermoelectrics*, Vol. 407 (CRC Press, Boca Raton, FL, 1995).
- He, J. et al. Ultralow thermal conductivity in full Heusler semiconductors. *Phys. Rev. Lett.* **117**, 046602 (2016).
- Lin, H. et al. Concerted rattling in CsAg₅Te₃ leading to ultralow thermal conductivity and high thermoelectric performance. *Angew. Chem. Int. Ed.* **55**, 11431 (2016).
- Liu, W. S., Yan, X., Chen, G. & Ren, Z. Recent advances in thermoelectric nanocomposites. *Nano Energy* **1**, 42–56 (2012).
- Pichanusakorn, P. & Bandaru, P. Nanostructured thermoelectrics. *Mater. Sci. Eng.* **67**, 19–63 (2010).
- Zhao, L. D., Dravid, V. P. & Kanatzidis, M. G. The panoscopic approach to high performance thermoelectrics. *Energy Environ. Sci.* **7**, 251 (2014).
- Tan, G. et al. Non-equilibrium processing leads to record high thermoelectric figure of merit in PbTe-SrTe. *Nat. Commun.* **7**, 12167 (2016).
- Heinrich, H., Lischka, K., Sitter, H. & Kriechbaum, M. Experimental determination of symmetry of second valence-band maxima in PbTe. *Phys. Rev. Lett.* **35**, 1107 (1975).
- Sitter, H., Lischka, K. & Heinrich, H. Structure of the second valence band in PbTe. *Phys. Rev. B: Solid State* **16**, 680 (1977).
- Biswas, K. et al. Strained endotaxial nanostructures with high thermoelectric figure of merit. *Nat. Chem.* **3**, 160 (2011).
- Zhao, L. D. et al. Raising the thermoelectric performance of p-type PbS with endotaxial nanostructuring and valence-band offset engineering using CdS and ZnS. *J. Am. Chem. Soc.* **134**, 16327 (2012).
- Zhao, L. D. et al. High thermoelectric performance via hierarchical compositionally alloyed nanostructures. *J. Am. Chem. Soc.* **135**, 7364 (2013).
- Samanta, M. & Biswas, K. Low thermal conductivity and high thermoelectric performance in (GeTe)_{1–2x}(GeSe)_x(GeS)_x: competition between solid solution and phase separation. *J. Am. Chem. Soc.* **139**, 9382 (2017).
- Biswas, K. et al. High-performance bulk thermoelectrics with all-scale hierarchical architectures. *Nature* **489**, 414 (2012).
- Zhao, L. D. et al. Ultralow thermal conductivity and high thermoelectric figure of merit in SnSe crystals. *Nature* **508**, 373 (2014).
- Cheng Chang et al. 3D charge and 2D phonon transports leading to high out-of-plane ZT in n-type SnSe crystals. *Science* **360**, 778 (2018).
- Liu, W., Yan, X., Chen, G. & Ren, Z. Recent advances in thermoelectric nanocomposites. *Nano Energy* **1**, 42–56 (2012).
- He, J., Kanatzidis, M. G. & Dravid, V. P. High performance bulk thermoelectrics via a panoscopic approach. *Mater. Today* **16**, 166–176 (2013).
- Hao, S., Dravid, V. P., Kanatzidis, M. G. & Wolverton, C. Research update: prediction of high figure of merit plateau in SnS and solid solution of (Pb_{0.5}Sn)_{0.5}. *APL Mater.* **4**, 104505 (2016).
- Hao, S. et al. Theoretical prediction and experimental confirmation of unusual ternary ordered semiconductor compounds in Sr-Pb-S system. *J. Am. Chem. Soc.* **136**, 1628–1635 (2014).
- Zhao, J. et al. Semiconducting pavonites CdM₂Bi₄Se₈ (M = Sn and Pb) and their thermoelectric properties. *Chem. Mater.* **29**, 8494 (2017).
- Hao, S. et al. Design strategy for high performance thermoelectric materials: the prediction of electron doped KZrCuSe₃. *Chem. Mater.* **31**, 3018–3024 (2019).
- Ziman, J. M. *Electrons and Phonons* (Oxford University Press, Oxford, UK, 1960).
- Srivastava, G. P. *The Physics of Phonons* (Taylor & Francis Group, New York, NY, 1990).
- Qiu, B., Bao, H., Zhang, G. Q., Wu, Y. & Ruan, X. L. Molecular dynamics simulations of lattice thermal conductivity and spectral phonon mean free path of PbTe: Bulk and nanostructures. *Comput. Mater. Sci.* **53**, 278–285 (2012).
- Tian, Z., Esfarjani, K., Shiomi, J., Henry, A. S. & Chen, G. On the importance of optical phonons to thermal conductivity in nanostructures. *Appl. Phys. Lett.* **99**, 053122 (2011).
- Lan, Y., Minnich, A. J., Chen, G. & Ren, Z. Enhancement of thermoelectric figure-of-merit by a bulk nanostructuring approach. *Adv. Funct. Mater.* **20**, 357–376 (2010).
- He, J. et al. Role of sodium doping in lead chalcogenide thermoelectrics. *J. Am. Chem. Soc.* **135**, 4624–4627 (2013).
- He, J. et al. Morphology control of nanostructures: Na-doped PbTe-PbS system. *Nano Lett.* **12**, 5979–5984 (2012).
- Girard, S. N. et al. High performance Na-doped PbTe-PbS thermoelectric materials: electronic density of states modification and shape-controlled nanostructures. *J. Am. Chem. Soc.* **133**, 16588 (2011).
- Korkosz, R. J. et al. High ZT in p-type (PbTe)_{1–2x}(PbSe)_x(PbS)_x thermoelectric materials. *J. Am. Chem. Soc.* **136**, 3225–3237 (2014).
- Doak, J. W. & Wolverton, C. Coherent and incoherent phase stabilities of thermoelectric rocksalt IV–VI semiconductor alloys. *Phys. Rev. B* **86**, 144202 (2012).
- Van, C. G., de Walle & Neugebauer, J. First-principles calculations for defects and impurities: applications to III-nitrides. *J. Appl. Phys.* **95**, 3851 (2004).

51. Van de Walle, C. G. Electronic materials theory: interfaces and defects. *J. Vac. Sci. Technol. A* **21**, S182 (2003).
52. Van de Walle, C. G. & Neugebauer, J. Universal alignment of hydrogen levels in semiconductors, insulators and solutions. *Nature* **423**, 626–628 (2003).
53. Zhao, L. D. et al. Raising the thermoelectric performance of p-type PbS with endotaxial nanostructuring and valence-band offset engineering using CdS and ZnS. *J. Am. Chem. Soc.* **134**, 7902–7912 (2012).
54. Wang, H., LaLonde, A. D., Pei, Y. & Snyder, G. J. The criteria for beneficial disorder in thermoelectric solid solutions. *Adv. Funct. Mater.* **23**, 1586–1596 (2013).
55. Zhao, L. D. et al. All-scale hierarchical thermoelectrics: MgTe in PbTe facilitates valence band convergence and suppresses bipolar thermal transport for high performance. *Energy Environ. Sci.* **6**, 3346–3355 (2013).
56. Tan, G. et al. High thermoelectric performance of p-type SnTe via a synergistic band engineering and nanostructuring approach. *J. Am. Chem. Soc.* **136**, 7006–7017 (2014).
57. Banik, A., Shenoy, U. S., Anand, S., Waghmare, U. V. & Biswas, K. Mg alloying in SnTe facilitates valence band convergence and optimizes thermoelectric properties. *Chem. Mater.* **27**, 581 (2015).
58. Banik, A. et al. Engineering ferroelectric instability to achieve ultralow thermal conductivity and high thermoelectric performance in Sn_{1-x}GexTe. *Energy Environ. Sci.* **12**, 589 (2019).
59. Tan, G. et al. Codoping in SnTe: enhancement of thermoelectric performance through synergy of resonance levels and band convergence. *J. Am. Chem. Soc.* **137**, 5100–5112 (2015).
60. Banik, A., Shenoy, U. S., Saha, S., Waghmare, U. V. & Biswas, K. High power factor and enhanced thermoelectric performance of SnTe-AgInTe₂: synergistic effect of resonance level and valence band convergence. *J. Am. Chem. Soc.* **138**, 13068 (2016).
61. Tan, G. et al. Extraordinary role of Hg in enhancing the thermoelectric performance of p-type SnTe. *Energy Environ. Sci.* **8**, 267 (2015).
62. Wu, D. et al. Origin of the high performance in GeTe-based thermoelectric materials upon Bi₂Te₃ dDoping. *J. Am. Chem. Soc.* **136**, 11412–11419 (2014).
63. Green, M. S. Markoff random processes and the statistical mechanics of time-dependent phenomena. Irreversible processes in fluids. *J. Chem. Phys.* **22**, 398–413 (1954).
64. Kubo, R. The fluctuation-dissipation theorem. *Rep. Prog. Phys.* **29**, 255–284 (1966).
65. Volz, S. G. & Chen, G. Molecular-dynamics simulation of thermal conductivity of silicon crystals. *Phys. Rev. B* **61**, 2651–2656 (2000).
66. Sun, L. & Murthy, J. Domain size effects in molecular dynamics simulation of phonon transport in silicon. *Appl. Phys. Lett.* **89**, 171919 (2006).
67. Maradudin, A. A., Montroll, E. W. & Weiss, G. H. *Theory of Lattice Dynamics in the Harmonic Approximation* (Academic Press, New York, NY, 1963).
68. Kresse, G., Furthmüller, J. & Hafner, J. Ab initio force constant approach to phonon dispersion relations of diamond and graphite. *Europhys. Lett.* **32**, 729–734 (1995).
69. Alfé, D. PHON: A program to calculate phonons using the small displacement method. *Comput. Phys. Commun.* **180**, 2622–2633 (2009).
70. Gonze, X. & Lee, C. Dynamical matrices, Born effective charges, dielectric permittivity tensors, and interatomic force constants from density-functional perturbation theory. *Phys. Rev. B* **55**, 10355–10368 (1997).
71. Callaway, J. & Vonbaeyer, H. C. Effect of point imperfections on lattice thermal conductivity. *Phys. Rev.* **120**, 1149 (1960).
72. Morelli, D. T., Heremans, J. P. & Slack, G. A. Estimation of the isotope effect on the lattice thermal conductivity of group IV and group III–V semiconductors. *Phys. Rev. B* **66**, 195304 (2002).
73. Steigmeier, E. F. & Abeles, B. Scattering of phonons by electrons in germanium-silicon alloys. *Phys. Rev. A* **136**, 1149 (1964).
74. Walker, C. T. & Pohl, R. O. Phonon scattering by point defects. *Phys. Rev.* **131**, 1433 (1963).
75. Kim, W. & Majumdar, A. Phonon scattering cross section of polydispersed spherical nanoparticles. *J. Appl. Phys.* **99**, 2188251 (2006).
76. Carruthers, P. Theory of thermal conductivity of solids at low temperatures. *Rev. Mod. Phys.* **33**, 92 (1961).
77. Zou, J., Kottchetkov, D., Balandin, A. A., Florescu, D. I. & Pollak, F. H. Thermal conductivity of GaN films: effects of impurities and dislocations. *J. Appl. Phys.* **92**, 2534–2539 (2002).
78. Klemens, P. G. Some scattering problems in conduction theory. *Can. J. Phys.* **35**, 441 (1957).
79. Morelli, D. T., Jovic, V. & Heremans, J. P. Intrinsically minimal thermal conductivity in cubic I-V-VI₂ semiconductors. *Phys. Rev. Lett.* **101**, 035901 (2008).
80. Zhang, Y. et al. First-principles description of anomalously low lattice thermal conductivity in thermoelectric Cu-Sb-Se ternary semiconductors. *Phys. Rev. B* **85**, 054306 (2012).
81. Tan, G., Hao, S., Zhao, J., Wolverton, C. & Kanatzidis, M. G. High thermoelectric performance in electron-doped AgBi₃S₅ with ultralow thermal conductivity. *J. Am. Chem. Soc.* **139**, 6467 (2017).
82. He, J. et al. Bi₂PdO₄: a promising thermoelectric oxide with high power factor and low lattice thermal conductivity. *Chem. Mater.* **29**, 2529 (2017).
83. Asen-Palmer, M. et al. Thermal conductivity of germanium crystals with different isotopic compositions. *Phys. Rev. B* **56**, 9431 (1997).
84. Hao, S., Shi, F., Dravid, V. P., Kanatzidis, M. G. & Wolverton, C. Computational prediction of high thermoelectric performance in hole doped layered GeSe. *Chem. Mater.* **28**, 3218 (2016).
85. Zhao, L. D. et al. Ultra-high power factor and thermoelectric performance in hole doped SnSe. *Science* **351**, 141 (2016).
86. Clarke, D. T. Materials selection guidelines for low thermal conductivity thermal barrier coatings. *Surf. Coat. Technol.* **163–164**, 67–74 (2003).
87. Ohta, M. et al. Enhancement of thermoelectric figure of merit by the insertion of MgTe nanostructures in p-type PbTe doped with Na₂Te. *Adv. Energy Mater.* **2**, 1117–1123 (2009).
88. Pei, Y. et al. Stabilizing the optimal carrier concentration for high thermoelectric efficiency. *Adv. Mater.* **23**, 5674–5678 (2011).
89. Pei, Y., Heinz, N. A., LaLonde, A. & Snyder, G. J. Combination of large nanostructures and complex band structure for high performance thermoelectric lead telluride. *Energy Environ. Sci.* **4**, 3640–3645 (2011).
90. Kutorasinski, K., Wiendlocha, B., Kaprzyk, S. & Tobola, J. Electronic structure and thermoelectric properties of n- and p-type SnSe from first-principles calculations. *Phys. Rev. B* **91**, 205201 (2015).
91. Opahle, I., Parma, A., McEniry, E. J., Drautz, R. & Madsen, G. K. H. High-throughput study of the structural stability and thermoelectric properties of transition metal silicides. *New J. Phys.* **15**, 105010 (2013).
92. Curtarolo, S. et al. The high-throughput highway to computational materials design. *Nat. Mater.* **12**, 191–201 (2013).
93. Madsen, G. K. H. & Singh, D. J. BoltzTraP. A code for calculating band-structure dependent quantities. *Comp. Phys. Commun.* **175**, 67 (2006).
94. Pizzi, G., Volja, D., Kozinsky, B., Fornari, M. & Marzari, N. BoltzWann: a code for the evaluation of thermoelectric and electronic transport properties with a maximally-localized Wannier functions basis. *Comp. Phys. Commun.* **185**, 422 (2014).

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