Makrials Views www.MaterialsViews.com

Harnessing Topological Band Effects in Bismuth Telluride Selenide for Large Enhancements in Thermoelectric Properties through Isovalent Doping

Devender, Pascal Gehring, Andrew Gaul, Alexander Hoyer, Kristina Vaklinova, Rutvik J. Mehta, Marko Burghard, Theodorian Borca-Tasciuc, David J. Singh, Klaus Kern, and Ganpati Ramanath*

Realizing high thermoelectric figure-of-merit, ZT, materials is an exacting challenge because it simultaneously requires a high Seebeck coefficient α and a high electrical conductivity σ , while these properties are unfavorably coupled.^[1-7] Here, we show that 0.2-2 at% sulfur doping of Bi₂Te₂Se nanoplates result in up to 200% higher α and 400% higher σ . Additionally, bulk nanostructured pellets fabricated from nanoplates with sub-at% sulfur-doping exhibit 20%–80% increases in α and σ . Such simultaneous increases in α and σ at high charge carrier concentrations are unusual, and indicate substantial changes in the electronic band structure. Analyses of nanocrystal properties using parabolic and nonparabolic band models reveal an \approx 500% increase in the effective density of states effective mass m_{DOS}^* with sulfur doping. First principles calculations suggest that the large electronic structure changes are underpinned by the extreme sensitivity^[8] of the inverted conduction band features in Bi₂Te₂Se to spin-orbit splitting, which can be modified by chemical doping. This band topology-doping nexus resolves the conundrum of simultaneous increases in α and σ despite contrarian correlations with m^*_{DOS} . Our findings open up a completely new pathway for accessing higher ZT in topologicalinsulator-based pnictogen chalcogenides, and conceivably other

Dr. Devender, A. Gaul, Dr. R. J. Mehta, Prof. G. Ramanath Department of Materials Science and Engineering Rensselaer Polytechnic Institute Troy, NY 12180, USA E-mail: ramanath@rpi.edu Dr. P. Gehring, A. Hoyer, K. Vaklinova, Dr. M. Burghard, Prof. K. Kern Max Planck Institute for Solid State Research Heisenbergstrasse 1, D-70569 Stuttgart, Germany Prof. T. Borca-Tasciuc Department of Mechanical Aerospace and Nuclear Engineering Rensselaer Polytechnic Institute Troy, NY 12180, USA Prof. D. J. Singh Department of Physics and Astronomy University of Missouri Columbia, MO 65211-7010, USA Prof. K. Kern Institut de Physique de la Matière Condensée Ecole Polytechnique Fédérale de Lausanne 1015 Lausanne, Switzerland

DOI: 10.1002/adma.201601256

such systems, for transformative applications in solid-state thermoelectric refrigeration and power generation.

Achieving the revolutionary potential of thermoelectric materials for solid-state refrigeration requires bulk materials with a higher figure-of-merit ZT than the state-of-the-art $ZT \approx 1$ near room temperature.^[1-4] Tetradymite pnictogen chalcogenides, i.e., groups V and VI compounds of the type V₂VI₃, exhibit a high $ZT = \alpha^2 \sigma T/\kappa$) at room temperature because their complex crystal structure with heavy elements enable a low thermal conductivity κ , while the low bandgap and degenerate electronic bands are conducive^[5-7] for a high power factor $\alpha^2 \sigma$. Importantly, these compounds are topological insulators^[8] where the complex electronic structure arising from spin-orbit induced band inversion, and topologically protected metallic surface states,^[9,10] provide opportunities to achieve high α and high σ . The ZT can be further improved by nanostructuring, which decreases κ via increased phonon scattering at grain boundaries. For small enough grain sizes, this ZT increase is partially offset by the concomitant charge carrier mobility decrease^[11,12] that lowers σ . Thus, there is a great deal of interest in devising strategies to simultaneously increase α and σ by tuning the electronic band structure via subatomic-percent doping^[1,2] and compositional control to realize high ZT.^[13,14]

A variety of impurity additions (e.g., Sn, Pb, and Cu)^[13–15] to pnictogen chalcogenides have been investigated. The highest *ZT* values have been obtained so far by pnictogen and/or chalcogen self-alloying. We recently showed that subatomic-percent sulfur doping can produce up to 250% *ZT* increases^[1] in nano-structured V_2VI_3 compounds. We also showed^[2] that such enhancements are related to sulfur-induced alterations in the antisite defect chemistry, and hence the charge carrier concentrations, but the underlying connections with changes in the electronic structure are yet to be revealed and understood.

Here, we report that dilute sulfur additions can cause simultaneous multifold increases in α and σ in n-type Bi₂Te₂Se nanocrystals as well as bulk nanostructured pellets fabricated by sintering the nanocrystals. Thermoelectric transport measurements, and Mott and Boltzmann transport modeling indicate that these unusual property enhancements arise from large electronic band structure changes indicated by multifold increases in the density of states effective mass m_{Dos}^* . First principles calculations suggest that such profound changes are induced by small doping levels due to the extreme sensitivity of topological insulator band structure features to small changes in the spin-orbit coupling, which can be manipulated by



www.MaterialsViews.com



Figure 1. a) An optical micrograph of an Au-contacted Bi₂Te₂Se nanoplate. T_1-T_2 denotes the temperature gradient obtained using a heating current I_{H} , B is the magnetic field, while V_1 and V_2 are voltages measured to obtain σ , n, and α in van der Pauw, Hall, and Seebeck experiments, respectively. b) Electron density n plotted as a function of N_s in the Bi₂Te₂Se nanoplates. Experimentally measured c) σ and d) α from the Bi₂Te₂Se nanoplates, plotted as a function of n for 50 K \leq $T \leq$ 250 K for $N_s = 0$ (squares), $N_s = 0.2$ at% (circles), $N_s = 1$ at% (triangles), and $N_s = 2$ at% (diamonds). Solid curves denote nonparabolic band Boltzmann transport model calculations of σ and α using different density of states effective mass m_{DOS}^* values. Dashed lines denote isotherms only to guide the eye. Unless error bars are shown, experimental uncertainties are less than the symbol size.

doping. The observed doping-induced simultaneous increases in α and σ at high majority carrier concentrations is unusual, and completely different from that seen in the bipolar charge carrier transport regime,^[6,7] and distinct from resonant state effects suggested^[15,16] for IV-VI compounds. Our findings suggest a new pathway for obtaining higher *ZT* in nanomaterials of topological insulator-based pnictogen chalcogenides and conceivably other such systems, to enable new thermoelectric materials for transformative applications.

Hexagonal Bi₂Te₂Se nanoplates with 0.1-10 µm edge lengths and \approx 7–20 nm thicknesses were grown from vapor phase fluxes on oxidized Si(001) wafers by heating pnictogen chalcogenide sources.^[17,18] The nanoplates were then sulfur doped by immersing the substrates in millimolar solutions of thioglycolic acid. Raman spectroscopy showed that the sulfur concentration $N_{\rm S}$ (see Figure S1, Supporting Information) was in the 0.2 $\leq N_{\rm S} \leq$ 2 at% range, while Auger electron spectroscopy confirmed the stoichiometry of the Bi₂Te₂Se nanoplates to be within ±1%. Au contact patterns (**Figure 1**a) were created on the nanoplates by e-beam lithography for measurements in an Oxford Instruments cryostat with a variable temperature insert that can access the 1.4 K $\leq T \leq$ 300 K temperature range.

We find that the Bi₂Te₂Se nanoplates exhibit monotonic increases in both α and σ with increasing $N_{\rm S}$ (see Figure 1). Hall measurements of the nanocrystals at 50 K $\leq T \leq$ 300 K show that the electron concentration *n* monotonically increases with $N_{\rm S}$ (see Figure 1b). This electron density *n* is more than tenfold greater than $n = 3 \times 10^{19}$ cm⁻³ seen in undoped Bi₂Te₂Se nanoplates^[6–8] where $p \approx 10^{15}$ cm⁻³ (see Figure S2, Supporting Information) due to the point defect chemistry.^[5] Thus, all our Bi₂Te₂Se nanoplates are extrinsic n-type semiconductors that are far away from the bipolar charge carrier transport regime for all sulfur concentrations investigated, including $N_{\rm S} = 0$.

Increasing $N_{\rm S}$ increases *n*, which is manifest as an increase in σ (Figure 1c). For a given N_S, however, σ decreases with increasing temperature, as in a metal, suggesting that the nanoplates are degenerately doped semiconductors wherein the Fermi level $E_{\rm F}$ is placed in the conduction band. The Seebeck coefficient α also increases with *n*, contrary to the usual trend for an extrinsic semiconductor far from the bipolar charge conduction (Figure 1d). The highest values of $\sigma = 1.2 \times 10^5 \ \Omega^{-1} \ m^{-1}$ and $\alpha = -130 \ \mu V \ K^{-1}$ were obtained for the highest sulfur level $N_{\rm S} = 2$ at% investigated, suggesting that further enhancements in the properties may be possible at higher doping levels. Our nanoplates showing high σ indicate high crystal quality. Furthermore, sulfur doping resulted in well-defined Raman peak shifts without changes in the peak width (Figure S1a, Supporting Information), indicating that the observed changes in α and σ , are attributable to sulfur doping.

The electron mobility μ_n decreases with increasing temperature as well as with increasing $N_{\rm S}$ (Figure 2a), as expected,^[5,6] consistent with increased phonon scattering and impurity scattering, respectively. We find that $\mu_n = 150-200 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for $n < 10^{20} \text{ cm}^{-3}$ and decreases to $\mu_n \approx 50-80 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ with increasing *n*. The metal-like conductivity behavior observed at any given sulfur doping level $N_{\rm S}$ is consistent with, and

(a) 200 λ 0.4 μ_n (cm² V⁻¹ s⁻¹) 160 N_s (at.%) 0.0 120 0.5 80 40 N_s (at.%) (b) 0.8 2.0 $m_{\rm Dos}^*$ / $m_{\rm e}$ 0.6 1.0 0.4 0.2 0.0 0.0 250 50 200 300 150 100 Temperature (K)

Figure 2. a) Electron mobility μ_n , and b) the effective density of states effective mass m_{DOS}^* plotted as a function of temperature, for Bi₂Te₂Se nanoplates with different sulfur concentrations N_S . The bold lines are curve fits to the equation $\mu_n \propto T^{\lambda-2}$. We obtained m_{DOS}^* by fitting the experimentally measured α values to the single-parabolic-band Mott equation. The dashed lines connecting the data points are only to guide the eye. Unless error bars are shown, experimental uncertainties are less than the symbol size.

attributable to, the μ_n decrease with increasing temperature. Since extrinsic scattering from local and extended defects would decrease μ_n , the high σ obtained indicates the high quality of our nanocrystals. Fitting our data to $\mu_n \propto T^{\lambda-2}$, we obtain $0.4 \leq \lambda \leq 0.6$, which indicate acoustic phonon scattering of electrons^[19,20] for $0 \leq N_S \leq 2$ at%.

Although the actual band structure of Bi₂Te₂Se is highly nonparabolic, we start our analysis with parabolic band models to capture the overall trends. We extract the effective charge carrier effective mass m_{DOS}^* (see Figure 2b) by fitting the measured properties with the single parabolic band Mott equation^[15,16] $\alpha = \frac{8\pi^2}{3} \frac{k_B^2 T}{eh^2} m_{DOS}^* \left\{ \frac{\pi}{3n} \right\}^{2/3}$, and $\sigma = ne\mu_n$, where *e* is the electron charge, and *h* and k_B the Planck and Boltzmann constants, and *T* the absolute temperature. Within this model, we find that dilute sulfur additions yield up to a 500% increase in m_{DOS}^* at E_F , pointing to a very substantial change in the electronic band structure. The high carrier density implies increase in the electronic density of states near E_F .

We further computed α and σ using Boltzmann transport equations with a nonparabolic density of states description used for narrow bandgap V₂VI₃ semiconductors.^[8,21–23] The properties computed by this method using $E_{\rm g} = 0.30$ eV and



 $m_{\text{DOS}}^* = 0.15m_{\text{e}}$ for undoped Bi₂Te₂Se, and $E_{\text{g}} = 0.14$ eV and $m_{\text{DOS}}^* = 0.18m_{\text{e}}$ for undoped Bi₂Te₃, are in excellent agreement with experimental measurements reported for single crystals of these materials (see Figures S2 and S3, Supporting Information). Thus, our model is a valid means of describing sulfurdoping-induced α and σ increase in our Bi₂Te₂Se nanocrystals in terms of m_{DOS}^* and charge carrier concentrations.

Our simulations of σ and α (bold lines in Figure 1c,d) for different electron density regimes n associated with different parts of the band structure specified by m_{DOS}^* mimic the experimentally observed trends. In particular, our calculations using the experimentally measured n show that for each doping level the Bi2Te2Se nanoplates exhibit the Pisarenko trend of increasing α and decreasing σ as a function of temperature that can be described by a characteristic m_{DOS}^* value. More importantly, we also find that the experimentally observed sulfurdoping-induced simultaneous increases in α and σ can be obtained by invoking multifold increases in m_{pos}^* in the model. Thus, both parabolic and nonparabolic band models indicate that a sizeable m_{pos}^* increase is needed to explain the multifold increases in α and σ observed in our experiments, again pointing to large band structure changes induced by dilute sulfur additions.

We hypothesize that the sulfur-induced simultaneous increases in α and σ arise from profound changes in the inverted conduction band underpinning the topological insulating behavior in Bi2Te2Se. Recent theoretical work^[8] presaged that the high sensitivity of the chalcogen-derived conduction band inversion features and the Fermi surface anisotropy and corrugation in this material to spin-orbit coupling offers opportunities for simultaneous increases in α and σ . Thus, it is reasonable to expect that sulfur doping would significantly impact the inverted band structure, and hence, α and σ . This inference is strongly supported by our experimental results on sulfurdoped n-type Bi₂Te₂Se showing that α increases with electron concentration for $n \approx 3 \times 10^{19}$ to 2×10^{20} cm⁻³, opposite to the usual trend. Also, undoped Bi2Te2Se nanocrystals show α < 30 µV K⁻¹, which is multifold lower than our measured values for S-doped Bi2Te2Se nanocrystals, underscoring the key role of sulfur doping.

The large effect of sulfur doping can be explained in terms of the extreme sensitivity of the inverted band structure in Bi2Te2Se to small spin-orbit coupling^[8] changes induced by sulfur doping. Adding sulfur, a lighter chalcogen than Se and Te, is expected to lower the spin-orbit coupling.^[24-26] In order to qualitatively capture the consequent effect on the band structure, we calculated the electronic density of states following the method of Shi et al.^[8] (see Figure S4, Supporting Information). We simulated sulfur doping by decreasing the spin-orbit coupling in our calculations by artificially increasing the speed of light by ≈2.25%. Our results (see Figure 3) show a large bandgap decrease of 25% (≈0.06 eV) and the increased conduction band density of states. These changes arising from the significantly altered relative positions of the band structure near the Γ and Z points (Figure S4, Supporting Information) correlate with the simultaneous increase in α and σ (see Figure 3) from the Mott equation described above, and are qualitatively consistent with Shi et al.^[8] Changes seen in the valence band density of states suggest that α and σ may be sensitive to sulfur



www.MaterialsViews.com



Figure 3. Relative density of states g(E) for Bi₂Te₂Se computed by first principles calculations to capture the large sulfur doping effect via alterations in spin orbit coupling (SOC). The curves were obtained for two SOC strengths of 1.00 and 0.95, representing undoped and sulfur-doped Bi₂Te₂Se, respectively. The 5% decrease in SOC results in a 25% decrease in bandgap, and large alterations in g(E) near the conduction and valence band edges E_C and E_V .

doping in p-Bi₂Te₂Se as well. Although our calculations do not attempt to quantitatively reproduce our experimental data or directly confirm topological insulator behavior in sulfur-doped Bi₂Te₂Se, they do confirm a very strong sensitivity of the topological band structure features to small reductions in the spin orbit strength that might be expected from sulfur substitution of chalcogen sites. Similar effects could be conceivably achieved in other topological insulator-based thermoelectrics via suitable iso- or heterovalent doping.

We also considered the possible roles of sulfur-induced strain effects and resonance states. Our calculations with a 0.3 at% uniform volume compression had little effect on α and σ at 300 K, ruling out strain effects. This conclusion is supported by the invariance of the Bi₂Te₂Se lattice parameters with sulfur doping (see the table in Supporting Information). Dopant-induced resonance in the conduction band (as suggested for Tl-doped PbTe)^[15,16] is also a possibility. However, we note that such resonances in ordinary materials increase α but decrease $\sigma^{[19]}$ due to increased scattering phase space and decreased band velocities, contrary to our experimental results showing increases in α and σ . Although the lack of additional Raman peaks (Figure S1, Supporting Information) in sulfurdoped nanoplates suggest random sulfur occupancy of the chalcogen sites in the lattice. We note that our theoretical calculations invoke the sulfur-induced change in spin-orbit coupling, and do not presume dopant site occupancy.

Since thermoelectric cooling applications depend on bulk materials with a high *ZT*, we investigated the transmutability of the above doping-induced effect of simultaneous increases in α and σ in nanocrystals, to bulk nanostructured Bi₂Te₂Se pellets. We prepared Bi₂Te₂Se pellets from gram-quantities sulfurdoped nanocrystals synthesized by a microwave-stimulated

chemical approach^[1] in which thioglycolic acid used in the synthesis is the source of sulfur doping. Pellets created by compacting and sintering yielded no observable texture, consistent with our results obtained on pellets of other pnictogen chalcogenides.^[1] We chose this method because the vapor phase growth approach does not yield gram quantities of nanocrystals needed to fabricate pellets. X-ray diffraction confirmed the rhombohedral structure, and spectroscopic analyses verified the Bi₂Te₂Se stoichiometry to be within ±1%. However, the highest $N_{\rm S}$ in the wet-chemically synthesized nanoplates and their pellets was tenfold lower than that in the thioglycolic-acid-treated nanocrystals grown from vapor phase fluxes.

We find that Bi₂Te₂Se nanostructured pellets also exhibit monotonic and simultaneous increases in α and σ with sulfur doping (**Figure 4**a). This trend is, again, unusual because it is at high electron concentrations (10^{19} cm⁻³ $\leq n \leq 10^{20}$ cm⁻³), far from the bipolar charge carrier transport regime. We note that the measured $|\alpha|$ values for both our nanocrystals and our bulk pellets are slightly higher than that reported^[6,7] for stoichiometric Bi₂Te₂Se. The nearly identical lattice parameters in pristine and sulfur-doped Bi₂Te₂Se nanocrystals and pellets (see the table in Supporting Information) indicate that the enhanced properties are not due to lattice strain, but likely a manifestation of sulfur-induced electronic structure changes as seen in individual nanoplates. The highest $\sigma = 10^5 \Omega^{-1} m^{-1}$ and $\alpha = -95 \ \mu V \ K^{-1}$ at 950 ppm sulfur,



Figure 4. a) Electrical conductivity σ (circles), Seebeck coefficient α (squares), and the total (triangles), and lattice (diamonds) thermal conductivities (κ and κ_L) of nanostructured Bi₂Te₂Se pellets measured at room temperature. b) The increase in *ZT* plotted as a function of sulfur concentration N_S . The connecting lines are only to guide the eye.



yielding a room temperature ZT = 0.55, tantamount to a >40% increase (Figure 4b).

The highest α and σ values seen in the pellets are about 30% lower than that in Bi2Te2Se nanocrystals probably due to the factor-of-ten lower sulfur levels in the pellets than that seen in the nanocrystals grown from vapor phase fluxes followed by sulfur treatment. While nanograin boundary scattering effects^[27] in the pellets could also be a factor, our results show that the α and σ increases are determined predominantly by the sulfur level. In contrast, $\kappa_{\rm I}$ and the average nanograin size in the pellets are insensitive to the sulfur level, indicating that thermal transport is determined by phonon scattering at nanograin boundaries.^[1] Thus, we are persuaded to infer that the α and σ increases seen in bulk nanostructured Bi₂Te₂Se pellets are primarily underpinned by sulfur-induced alterations in the topological band structure, as seen in individual nanocrystals, and not dominated by surface and nanograin boundary effects. We note that κ the thermal conductivity does increase slightly with sulfur doping from ≈ 0.45 to ≈ 0.55 W m⁻¹ K^{-1} due to an increase in the electronic component κ_{e} .

In summary, our study demonstrates that sulfur doping results in simultaneous multifold increases in α and σ in n-type Bi₂Te₂Se nanocrystals as well as bulk nanostructured pellets. Boltzmann transport models indicate that such unusual behavior is due to profound changes in the electronic band structure as indicated by doping-induced multifold increases in the effective density of states effective mass m_{DOS}^* . Firstprinciples calculations suggest that the large electronic structure changes are attributable to the extreme sensitivity of the inverted conduction band features to small spin-orbit splitting changes induced by sulfur doping. Thus, mild chemical doping offers a means to access subtle features of the topological insulator band structure that promote simultaneous increases in α and σ . Our findings are attractive for untangling the unfavorable coupling between α and σ in topological insulator-based pnictogen chalcogenides, and conceivably other such systems (e.g., $Bi_2Te_{3-x}Se_x$, where Se content is optimized^[39]) to realize higher ZT thermoelectrics for transformative applications.

Experimental Section

Individual Nanocrystals: Bi2Te2Se nanoplates were grown on a 300-nm-thick thermal SiO₂ on Si(001) substrates from vapor fluxes obtained by heating Bi_2Te_3 and Bi_2Se_3 powders at 582 °C in a tube furnace with a 80 sccm Ar flow.^[17,18] Sulfur doping was realized by treating the nanoplates with 5500 \times 10⁻³ M thioglycolic acid (TGA), followed by a 200 °C anneal for 30 min. The sulfur content $N_{\rm S}$ in the nanoplates was determined by modeling E_g^2 and the A_{1g}^2 Raman mode shifts (Figure S1a,b, Supporting Information) into relative contributions of ${\rm Bi}_2{\rm S}_3$ and ${\rm Bi}_2{\rm Te}_2{\rm Se}$ phases. The stoichiometry was determined from relative intensities of Bi MNN, Te MNN, Se LMM, and S KLL Auger peaks using a PHI 700 instrument at 5-10 keV with a 5 µm diameter 5-50 nA electron beam. We determined σ , μ , and n of the undoped and sulfur-doped Bi2Te2Se nanoplates using van der Pauw and Hall techniques in an Oxford cryostat using Au-contacted nanoplates created by e-beam lithography. The Seebeck coefficient α was determined by generating a temperature gradient across the nanoplate with a high AC current in the 5 mA $\leq I_{\rm H} \leq$ 10 mA range at a frequency *f* (see Figure 1a) and measuring the thermovoltage at $2f^{[28]}$ Au resistors patterned at the nanoplate ends were used to determine the nanoplate temperature via the resistance-temperature relationship that was mapped separately at low temperatures using low currents and all our measurements were carried out on test devices fabricated with identical geometry, dimensions and spacings of resistors and contacts.^[38]

Nanostructured Pellets: Bi₂Te₂Se pellets were prepared by sintering nanocrystals synthesized by a wet-chemical process involving microwave heating of molecularly ligated chalcogen and pnictogen complexes with TGA in a polyol solvent.^[1] TGA allows shape- and size-control and provides sulfur doping. The nanoplate powders were cleaned with acetone and dried, cold-compacted in a hydraulic press, and sintered in a 10⁻⁶ Torr vacuum at 350 °C for 2 h. X-ray absorption spectroscopy (XAS) was carried out at NSLS I in Brookhaven with 2–15 keV incident X-ray beams and a fluorescence PIPS detector. The S K α , Bi $L\alpha_3$, and Te $L\alpha_2$ peak intensities^[29] and photoelectron cross sections were used to determine N_5 . Wavelength dispersive X-ray spectroscopy (WDX) was carried out in a SX-100 instrument to verify N_5 values obtained by XAS. Spectra from standards, and pyrite FeS₂, facilitated quantification.

We measured σ , μ_n , and *n* from the pellets using linear four-probe, van der Pauw, and Hall techniques, respectively. Both α and κ were determined using a computer-interfaced setup that measures the Seebeck voltage at different temperature gradients.^[1] We extracted κ from the pellet resistance R_S by measuring temperature gradients across the pellet for different heat fluxes. We used a parallel resistance model $\frac{1}{R_T} = \frac{1}{R_S} + \frac{1}{R_c}$ to determine R_S from the total measured resistance R_T by accounting for R_C denotes parasitic conduction and radiation losses. We determined R_C by measuring pellets of epoxy and commercial bismuth telluride with known κ for different pellet thicknesses. The measurement uncertainties are $< \pm 1\%$ (van der Pauw) and $\approx \pm 3\%$ (linear four-probe) for σ , $< \pm 1\%$ for α and $\approx \pm 5\%$ for κ , which were identical to our earlier work.^[1]

Boltzmann Modeling of Properties, and First Principles Calculations: We modeled σ and α using^[30,31,23] $\sigma = -\frac{e^2}{3}\int \sigma(E) dE = -\frac{e^2}{3}\int g(E)\tau(E)\nu(E)^2 \left(\frac{\partial f(E_{\rm F},E)}{\partial E}\right) dE$, and $\alpha = \frac{e}{3T}\frac{\int (E-E_{\rm F})\sigma(E)dE}{\sigma}$, where $\sigma(E)$ is the density of states, $\sigma(E)$ the charge scattering relaxation

where g(E) is the density-of-states, $\tau(E)$ the charge scattering relaxation time from Matthiessen's rule, ν (*E*) the carrier band velocity, and $f(E_{\rm F},E)$ the Fermi-Dirac distribution. Literature values^[30–32] of σ , α , *n*, and *p* for Bi₂Te₂Se and Bi₂Te₃ single-crystals were used to obtain model parameters, e.g., phonon and defect scattering potentials, charge carrier effective masses, and bandgap $E_{\rm g}$. We chose self-consistent inertial and DOS effective masses^[32] to capture crystalline anisotropy in σ , and isotropy in α .^[5] We determined $E_{\rm F}$ from the Kane model of nonparabolic band structure^[30,35] and accounted for antisite defects using the Brooks-Herring model.^[36] The large changes in the electron density at low temperature are possibly driven by large corrugations in the bandstructure and antisite defect formation.^[23,30,31]

First principles calculations were carried out following the approach outlined by Shi et al.,^[8] using the general potential linearized augmented planewave method as implemented in the WIEN2k code and the modified Becke-Johnson potential of Tran and Blaha.^[37] All our calculations were carried out with spin-orbit coupling. We simulated decreased spin-orbit coupling by increasing the speed of light in the code only in the spin-orbit part of the calculation.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

The authors gratefully acknowledge funding from National Science Foundation grants ECCS 1002280 and CMMI 1100933, and the Friedrich Wilhelm Bessel Award from the Alexander von Humboldt foundation. Work at the University of Missouri was supported by the Department



www.MaterialsViews.com

of Energy, Office of Science, Basic Energy Sciences through S 3 TEC an Energy Frontier Research Center under award #DE-SC0001299/DE-FG02-09ER46577.

Received: March 4, 2016 Published online: May 11, 2016

- R. J. Mehta, Y. L. Zhang, C. Karthik, B. Singh, R. W. Siegel, T. Borca-Tasciuc, G. Ramanath, *Nat. Mater.* 2012, *11*, 233.
- [2] R. J. Mehta, Y. L. Zhang, H. Zhu, D. S. Parker, M. Belley, D. J. Singh, R. Ramprasad, T. Borca-Tasciuc, G. Ramanath, *Nano Lett.* **2012**, *12*, 4523.
- [3] R. J. Mehta, G. Ramanath, Am. Ceram. Soc. Bull. 2012, 91, 28.
- [4] G. J. Snyder, E. S. Toberer, Nat. Mater. 2008, 7, 105.
- [5] D. M. Rowe, CRC Handbook of Thermoelectrics, 1st ed., CRC Press, Boca Raton, FL, USA 1995.
- [6] D. M. Rowe, Thermoelectrics Handbook: Macro to Nano, 1st ed., CRC Press, Boca Raton, FL, USA 2006.
- [7] G. S. Nolas, J. Sharp, H. J. Goldsmid, *Thermoelectrics: Basic Principles and New Materials Developments*, 1st ed., Springer, Dallas, TX, USA 2001.
- [8] H. Shi, D. Parker, M. H. Du, D. J. Singh, Phys. Rev. Appl. 2015, 3, 014004.
- [9] D. Kim, P. Syers, N. P. Butch, J. Paglione, M. S. Fuhrer, Nano. Lett. 2014, 14, 1701.
- [10] B. Hamdou, Adv. Energy Mater. 2015, 5, 1500280.
- [11] C. J. Vineis, A. Shakouri, A. Majumdar, M. G. Kanatzidis, Adv. Mater. 2010, 22, 3970.
- [12] M. G. Kanatzidis, Chem. Mater. 2010, 22, 648.
- [13] J. Baxter, Z. Bian, G. Chen, D. Danielson, M.S. Dresselhaus, A.G. Fedorov, T. S. Fisher, C. W. Jones, E. Maginn, U. Kortshagen, A. Manthiram, A. Nozik, D.R. Rolison, T. Sands, L. Shi, D. Sholl, Y. Wu, *Energy Environ. Sci.* **2009**, *2*, 559.
- [14] R. J. Mehta, C. Karthik, B. Singh, R. Teki, T. Borca-Tasciuc, G. Ramanath, ACS Nano 2010, 4, 5055.
- [15] G. J. Snyder, E. S. Toberer, Nat. Mater. 2008, 7, 105.

- [16] J. P. Heremans, V. Jovovic, E. S. Toberer, A. Saramat, K. Kurosaki, A. Charoenphakdee, S. Yamanaka, G. J. Snyder, *Science* **2008**, *321*, 554.
- [17] P. Gehring, B. F. Gao, M. Burghard, K. Kern, Nano Lett. 2012, 12, 5137.
- [18] P. Gehring, B. F. Gao, M. Burghard, K. Kern, Appl. Phys. Lett. 2012, 100, 0212402.
- [19] A. H. Wilson, The Theory of Metals, Cambridge University Press, Oxford, UK 1953.
- [20] M. Cutler, J. F. Leavy, R. L. Fitzpatrick, Phys. Rev. 1963, 133, A1143.
- [21] Z. Fisk, H. R. Ott, T. M. Rice, J. L. Smith, Nature 1986, 320, 124.
- [22] J. Horak, Z. Stary, J. Votinsky, Phil. Mag. B 2006, 69, 31.
- [23] H. Morkoc, Handbook of Nitride Semiconductors and Devices, Electronic and Optical Processes in Nitrides, 1st ed., Wiley, Hoboken, NJ, USA 2009.
- [24] S.-Y. Xu, Y. Xia, L. A. Wray, S. Jia, F. Meier, J. H. Dil, J. Osterwalder, B. Slomski, A. Bansil, H. Lin, R. J. Cava, M. Z. Hasan, *Science*. 2011, *332*, 560.
- [25] M. Neupane, Phys. Rev. B 2012, 85, 235406.
- [26] P. Gehring, H.M. Benia, Y. Weng, R. Dinnebier, C. R. Ast, M. Burghard, K. Kern, *Nano Lett.* **2013**, *13*, 1179.
- [27] P. Puneet, R. Podila, M. Karakaya, S. Zu, J. He, T. M. Tritt, M. S. Dresselhaus, A. M. Rao, *Sci. Rep.* **2013**, *3*, 3213.
- [28] X. Lin, J. Yin, J. Zhou, Q. Wang, W. Guo, Appl. Phys. Lett. 2012, 100, 183108.
- [29] S. Calvin, E. E. Carpenter, B. Ravel, V.G. Harris, Phys. Rev. B 2002, 66, 223305.
- [30] B. L. Huang, M. Kaviany, Phys. Rev. B 2008, 77, 12.
- [31] H.-W. Jeon, H-P. Ha, D.-B. Hyun, J.-D. Shim, J. Phys. Chem. Sol. 1990, 52, 579.
- [32] A. Jacquot, N. Farag, M. Jaegle, M. Bobeth, J. Schmidt, D. Ebling, H. Böttner, J. Electron. Mater. 2010, 39, 1861.
- [33] M. Stordeur, M. Stolzer, H. Sobotta, V. Riede, Phys. Stat. Sol. B 2006, 150, 165.
- [34] M. Situmorang, H. J. Goldsmid, Phys. Stat. Sol. B 2006, 134, K83.
- [35] W. Szymanksla, T. Dietl, J. Phys. Chem. Sol. 2002, 39, 1025.
- [36] A. Hashibon, C. Elsasser, Phys. Rev. B 2011, 84, 144117.
- [37] F. Tran, P. Blaha, Phys. Rev. Lett. 2009, 102, 226401.
- [38] A. Soni, Z. Yanguan, Y. Ligen, M. K. K. Aik, M. S. Dresselhaus, Q. Xiong, Nano Lett. 2012, 12, 1203.
- [39] Y. M. Zuev, W. Chang, P. Kim, Phys. Rev. Lett. 2009, 102, 096807.