Pressure-induced insulator-to-metal transitions for enhancing thermoelectric power factor in bismuth telluride-based alloys†

Andrew Gaul,a Qing Peng,*b David J. Singh,c Ganpati Ramanathd and Theodorian Borca-Tasciuexactb

First-principles calculations revealing insulator-to-metal transitions in Bi₂Te₃ and Bi₂Te₂Se, at 9 GPa and 12.5 GPa, respectively, match with prior experiments. Our electronic band structure calculations and accompanying Boltzmann transport calculations of thermoelectric properties for Bi₂₋ₓSbxTe₂₋ₓSeₓ alloys explain and predict large power factor changes induced by pressure. Complex band degeneracy changes preceding insulator-to-metal transitions significantly alter the density of states near the Fermi level, and foster the disentangling of the unfavorable coupling between Seebeck coefficient and electrical conductivity. Our findings on pressure-induced changes in thermoelectric power factor provide insights for designing VₓIₓ-based high-performance thermoelectric materials through strategies such as alloying, high-pressure processing, and strain engineering.

I. Introduction

Achieving thermoelectric materials with high figure of merit ZT = $\frac{\alpha^2}{\kappa}T$ requires the simultaneous realization of a high Seebeck coefficient $\alpha$, high electrical conductivity $\sigma$, and a low thermal conductivity $\kappa$. These properties are, however, usually coupled unfavorably. Disentangling the unfavorable coupling requires the manipulation of the crystal structure, the electronic and phononic band structures, and the nanoscale grain structure.1 Trydimite pnictogen-chalcogenides of the type VₓVIₓ are low bandgap semiconductors with degenerate, non-parabolic band structures that are conducive for a high power factor $\alpha^2/\kappa$.2 For example, bulk Bi₂Te₃ single-crystals exhibit $ZT = 0.87$,3 and bulk nanostructured Biₓ₋₄Sbx₋₄Teₓ₋₄ has shown $ZT = 1.8$4. Realizing materials with $ZT > 3$ is desirable for advanced applications in solid-state refrigeration and power harvesting from waste heat.5–7

Although nanostructuring drastically decreases $\kappa$, the concomitant decrease in $\alpha^2/\kappa$ is a barrier to realizing high ZT nanostructured materials. Our recent works8,9 have shown that reaping simultaneous increases in $\alpha$ and $\sigma$ through dilute doping could be a means to address this challenge. In particular, we demonstrated that 0.2 to 2 at% sulfur doping can yield up to 2-fold increase in $\alpha$, and up to 4-fold increase in $\sigma$ in n-Bi₂Te₂Se. This unusual behavior is due to multifold increases in the carrier density-of-states effective mass $m\ast D\ast$, underpinned by band topology effects that strongly influence the near-edge electronic structure and bandgap. Experimentally observed pressure-induced power factor increases in p-Bi₂₋ₓSbxTeₓ alloys10 have also been attributed to electronic topological transitions.10,11 Thus, there is interest in further understanding the nexus between pressure, band topology and thermoelectric power factor to obtain high ZT materials.

Here, our first principles calculations show insulator-to-metal transitions in Bi₂Te₃,12,13 and Bi₂Te₂Se14 in agreement with prior experiments. We find that the complex changes in band topology and degeneracy, occurring immediately prior to these transitions, explain the $\alpha^2/\kappa$ increase in p-BiSbTe₃ alloys10 and n-Bi₂Te₂Se15 and presage increased $\alpha^2/\kappa$ in n-Bi₂Te₃. This behavior is contrary to $\alpha^2/\kappa$ decreases in p-Bi₂Te₃,10 undermined by band-degeneracy-decreasing topological transitions,16 and in p-SbxTe₁₋ₓ arising from anti-site-defect-induced degenerate hole concentrations that preclude high $\alpha$.18 We also find that pressure-induced band structure changes increase band degeneracy in the p-BiSbTe₃ alloy, contrary to previous reports of negligible change under hydrostatic pressure.19 Our results underscore the
correlation between high $x^2\sigma$ and the existence of multiple degenerate electronic bands creating a high density-of-states near the Fermi level pinned near the band edge. Our findings should provide insights for realizing high $2T$ pnictogen chalcogenide thermoelectrics through a combination of alloying, high pressure processing and/or strain engineering.

II. First-principles computational methods

We carried out density functional theory (DFT) using the Vienna *ab initio* simulation package (VASP v5.3.5)\textsuperscript{20,21} with projector-augmented wave pseudopotentials. We used a revised exchange-correlation functional of Perdew, Burke, and Ernzerhof (PBEsol)\textsuperscript{22} to favor solids and surfaces instead of free atoms, over a wide range of electron density gradients within the generalized gradient approximation (GGA).\textsuperscript{22} This functional accurately yields lattice parameters and bond distances. We carried out ionic relaxations starting from experimental atomic positions until the atomic forces were $< 0.1$ eV nm$^{-1}$.

Self-consistent field calculations were carried out using a $\Gamma$-centered, $12 \times 12 \times 12$ $k$ point grid, spanning the first Brillouin zone of the primitive rhombohedral unit cell (Fig. 1). We set the plane wave energy cutoff to 300 eV for all the compounds studied. Relaxations were concluded when the ground state energy difference between subsequent calculation steps became $< 10^{-5}$ eV. After calculating the charge density, we determined the electronic density-of-states (DOS) using the linear tetrahedron method on calculating the charge density, we determined the electronic structure of pnictogen chalcogenides.\textsuperscript{9} All pressures in the simulation cells converged with $< 0.1$ GPa fluctuations.

III. Pressure effects on the crystal structure and elastic properties

The structure of $V_2VI_3$ alloys, specified by the $R3m$ space group, can be described in terms of quintuple stacks of $VI_{6c}$-$VI_{6c}$-$VI_{3a}$-$VI_{6c}$ layers (Fig. 1). In Bi$_2$Sb$_2$Te$_3$ and Bi$_2$Te$_2$Se, Bi and Sb atoms occupy 6c sites ($\pm v$, $\pm v$, $\pm v$). In Bi$_2$Sb$_2$Te$_3$, Te occupies both 3a ($0, 0, 0$) and 6c ($\pm u$, $\pm u$, $\pm u$) sites. In Bi$_2$Te$_2$Se, Se occupies 3a sites and Te occupies 6c sites. The calculated lattice parameters agree well with reported experimental values,\textsuperscript{23,24} see Table 1. Although this experimental data is unavailable for BiSbTe$_3$, the accuracy of our calculations for this alloy is ensured by the bounds set by our calculations for Bi$_2$Te$_3$ and Sb$_2$Te$_3$. All calculated parameters are well within 2% of experiment, in most cases within 1%.

The bulk moduli of Bi$_2$Te$_3$, Bi$_2$Te$_2$Se, and Sb$_2$Te$_3$ calculated by two different methods (see Table 2) agree well with previously reported experimental values.\textsuperscript{12,25–28} The higher than usual $B_0'$ values indicate high bonding anharmonicity, consistent with low thermal conductivity.\textsuperscript{29} In the first method, we used DFT to determine the zero-pressure bulk modulus $B_0$ by setting tight convergence criteria, namely, $< 0.01$ eV nm$^{-1}$ for ionic forces and $< 10^{-8}$ eV for the electronic energy step difference, followed by averaging the directional moduli. In the second method, we also determined $B_0$ by fitting $P-V$ curves generated from the calculated unit cell volumes at different pressures with the third-order Birch–Murnaghan isothermal equation of state, $P(V) = \frac{3B_0}{2} \left( \frac{V_0}{V} \right)^{7/3} - \frac{5}{2} \left( \frac{V_0}{V} \right)^{5/3} \left\{ 1 + \frac{3}{4} \left( B_0' - 4 \right) \left( \frac{V_0}{V} \right)^{2/3} - 1 \right\}$, where the zero-pressure unit cell volume $V_0$ and the pressure derivative of the bulk modulus $B_0'$ at zero pressure were fitting parameters.

Fig. 2 shows our calculated $P-V$ curves for Bi$_2$Te$_3$, Bi$_2$Te$_2$Se, and Sb$_2$Te$_3$ compared with experimentally reported data.\textsuperscript{26,30–33}

![Fig. 1](image-url) (a) Schematic sketches of a primitive rhombohedral unit cell (left) and expanded cell (right) showing layering along [0001] in Bi$_2$Sb$_2$Te$_3$ and Bi$_2$Te$_2$Se. (b) First Brillouin zone of $V_2VI_3$ compounds specified by the $R3m$ space group. The number of equivalent Brillouin zone locations is denoted by degeneracy, $g$: $g = 1$ for $\Gamma$, $g = 2$ for $Z$, and $g = 6$ for all other labeled points.
IV. Pressure effects on electronic structure and thermoelectric properties

A. Band behavior near insulator-metal transitions

Our calculated zero-pressure bandgaps for Bi$_2$Te$_3$ and Bi$_2$Te$_2$Se are 10–30% lower than that reported by experimental studies. For example, for Bi$_2$Te$_3$, our calculations presage a bandgap $E_G = 110$ meV, while experiments yield $130 \leq E_G \leq 160$ meV. For Bi$_2$Te$_2$Se, our calculations indicate $E_G = 265$ meV, while experiments show $E_G \sim 300$ meV. Such a difference in $E_G$ is consistent with other DFT studies, and arises because the GGA functional does not accurately capture the discontinuous energy change associated with electron transfer. This deviation is particularly large for Sb$_2$Te$_3$; our calculations show $E_G = 100$ meV, which is 65% lower than the experimental $E_G = 280$ meV. However, our values are similar to those reported in other DFT studies. Hence, we only consider band trends in Sb-containing compounds, and do not make bandgap predictions.

Band structure calculations reveal insulator-to-metal transition pressures to be $P_{\text{IMT}} = 9.0$ GPa for Bi$_2$Te$_3$, and $P_{\text{IMT}} = 12.5$ GPa for Bi$_2$Te$_2$Se. Our results for Bi$_2$Te$_3$ agree well with reports based on optical and electrical measurements showing

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**Table 1** Theoretical structural parameters of Bi$_2$Te$_3$, Sb$_2$Te$_3$, and Bi$_2$Te$_2$Se obtained with DFT. The values are within 2% of those obtained by experiment.

<table>
<thead>
<tr>
<th></th>
<th>Bi$_2$Te$_3$</th>
<th>BiSbTe$_3$</th>
<th>Sb$_2$Te$_3$</th>
<th>Bi$_2$Te$_2$Se</th>
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<tr>
<td>Density (g cm$^{-3}$)</td>
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<td>7.88</td>
<td>7.26</td>
<td>6.51</td>
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<td>—</td>
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</tr>
<tr>
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<td>0.3999</td>
<td>—</td>
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<td>$\alpha_1$ (nm)</td>
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<td>0.4390</td>
<td>0.4337</td>
<td>0.4264</td>
</tr>
<tr>
<td>$\alpha_2$ (nm)</td>
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<td>1.0331</td>
<td>1.0447</td>
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<tr>
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<tr>
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<td>1.0420</td>
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<tr>
<td>$\delta$ (nm)</td>
<td>0.4383</td>
<td>0.4390</td>
<td>0.4337</td>
<td>0.4264</td>
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**Table 2** Bulk moduli values of Bi$_2$Te$_3$, Sb$_2$Te$_3$, and Bi$_2$Te$_2$Se obtained with first principles theoretical calculations, and by fitting PV data with the Birch–Murnaghan equation of state (E.O.S.).

<table>
<thead>
<tr>
<th></th>
<th>Experimental $B_0$ (GPa)</th>
<th>Theoretical $B_0$ (GPa)</th>
<th>E.O.S. $B_0$ (GPa)</th>
<th>E.O.S. $B''_0$ (GPa)</th>
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<tr>
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<td>37.7</td>
<td>6.4</td>
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<td>37.8</td>
<td>6.5</td>
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<tr>
<td>Bi$_2$Te$_2$Se</td>
<td>30.2, f</td>
<td>39.0</td>
<td>31.6</td>
<td>8.6</td>
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</tbody>
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Experiments have captured multiple pressure-induced structural phase transitions in all three materials, the first of which are observed between $\sim 7.5$–9 GPa for Bi$_2$Te$_3$, $\sim 10$–13 GPa for Bi$_2$Te$_2$Se, and $\sim 7$–11 GPa for Sb$_2$Te$_3$. Since periodic boundary conditions do not allow us to access phase changes, we only consider the $R\bar{3}m$ phase. By this approach, however, we are able to capture the insulator-to-metal transitions right before the structural transitions to the $C2/m$ phase.

Our DFT calculations also capture changes in bonding and lattice parameters. Pressure-induced bonding changes are most manifest across adjacent Te$_{6c}$–Te$_{6c}$ layers which have the longest and hence, the weakest, bonds (Fig. 3a and b). Pressure-effects on the $\sim 20\%$ longer in-plane bonds between any two identical elements with equivalent Wyckoff positions are less significant. We observe a 0.5% increase in the rhombohedral angle $\theta_R$ with initial increases in pressure (Fig. 3c and d), followed by a $\theta_R$ decrease at higher pressures near the insulator-to-metal transitions, i.e., at $\sim 7$ GPa for Bi$_2$Te$_3$ and Sb$_2$Te$_3$, and at $\sim 12$ GPa for Bi$_2$Te$_2$Se. The $\theta_R$ decrease is consistent with experimentally reported out-of-plane compression along [0001] in Bi$_2$Te$_3$, Bi$_2$Te$_2$Se, and Sb$_2$Te$_3$, while the subsequent $\theta_R$ decrease corresponds to in-plane compression along [1010], which becomes stronger immediately before the structural phase transition (Fig. 4). The smooth changes in the lattice parameters, bond lengths, and density shown in Fig. 3 and 4 are not unexpected because our calculations cannot detect crystal structure changes. The normalized lattice parameter and bonding changes in Sb$_2$Te$_3$ are nearly identical (within $\lesssim 1\%$) to those in Bi$_2$Te$_3$, and hence, are not shown separately.

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![Fig. 2](image-url) Pressure–volume relationships obtained by our DFT calculations (filled symbols) plotted together with the Birch–Murnaghan model fits (lines) and experimentally measured values (unfilled symbols) for Bi$_2$Te$_3$, Bi$_2$Te$_2$Se, and Sb$_2$Te$_3$. For both Bi$_2$Te$_3$ and Bi$_2$Te$_2$Se, our calculated insulator-to-metal transition (IMT) pressures lie close to the structural phase transition pressure ranges.
This experimental variation is not unexpected because our calculations show a negligible change in this pressure range. Although the $P_{\text{IMT}}$ for Bi$_2$Te$_2$Se has not been experimentally measured, extrapolating optical reflectivity results suggests that $P_{\text{IMT}} \approx 10$ GPa, which is consistent with the prognosis based on our calculations.

The pressure-induced band structure changes at, and between, different momenta are captured in Fig. 5. In particular, including spin orbit coupling in our calculations reveals that the conduction band minimum (CBM) for Bi$_2$Te$_3$ is between the high symmetry $Z$ and $F$ points, and the valence band maximum (VBM) is between the off-symmetry “a” point and the $\Gamma$ point (see Fig. 1b). The secondary CBMs are along $\Gamma-Z$ and $Z-a$ with two- and six-fold degeneracy respectively. The secondary VBMs are along $L-Z$, $Z-a$, and $Z-F$, all with six-fold degeneracy ($g = 6$). In Bi$_2$Te$_2$Se, the CBM is along $\Gamma-Z$ while the VBM is along $Z-F$. The secondary CBMs are along $Z-F$, $Z-a$, and $L-Z$ and secondary VBMs are along $Z-a$, $L-Z$, and $a-\Gamma$. The primary CBM has a lower degeneracy of $g = 2$, while all the rest of the extrema have $g = 6$. In both Bi$_2$Te$_3$ and Bi$_2$Te$_2$Se, the insulator-to-metal transitions occur when the $L$ point CBM crosses into the $a-\Gamma$ VBM. Finally, in Sb$_2$Te$_3$, we find that the CBM and VBM are located along $\Gamma-Z$ and $a-\Gamma$ with band degeneracies of $g = 2$ and $g = 6$, respectively. The secondary CBMs are located along $Z-F$ and $Z-a$, while the secondary VBMs are located along $L-Z$, $Z-a$, and $Z-F$, all with a degeneracy of $g = 6$.

Energy band shifts and the activation of additional bands along different momenta (Fig. 5) correlate with the pressure-induced increases in DOS near the conduction band edges in Bi$_2$Te$_3$ and Bi$_2$Te$_2$Se (Fig. 6). This effect can be described in terms of an increase in the density-of-states effective mass $m_{\text{DOS}}^* = (g^2 m_x m_y m_z)^{1/3}$, where $m_x$, $m_y$ and $m_z$ are the carrier effective masses along the Cartesian directions. Although complex energy surfaces cannot be simply described in terms of individual ellipsoids especially at high $g$, this description in terms of $m_{\text{DOS}}^*$ qualitatively captures contributions from multiple bands with large anisotropy.
High charge carrier effective mass and high degeneracy are conducive for high $\alpha$ for a given carrier concentration, but typically yields low carrier mobility and low $\sigma$. High DOS near $E_F$ fosters a high $\alpha$ that scales with $m_{DOS}^*$ in the two-parabolic-band limit, as described by the Mott expression $\alpha = \frac{8\pi^2k_B^2}{3\hbar^2}m_{DOS}^* T \left( \frac{\pi}{3n} \right)^2$. In contrast, $\sigma$ is governed by the inertial effective mass, $m_{I}^*$ and $m_{DOS}^*$ due to anisotropic band extrema (e.g., away from the zone center where, $m_x > m_z$) in $V_2VI_3$ compounds offers a means to decouple the inverse correlation between $\alpha$ and $\sigma$. The anisotropy manifests as multifold lower carrier mobilities in certain directions (e.g., mobility along [10\%10] is five-fold higher than that along [0001] in Bi$_2$Te$_3$), effectively implying that $m_{I}^*$ can be significantly lower than $m_{DOS}^*$. Thus, tapping into high $m_{DOS}^*$ and low $m_{I}^*$ is an attractive and viable strategy to achieve a high power factor $\alpha^2\sigma$ in $V_2VI_3$ compounds. More generally, $\alpha$ and $\sigma$ are governed by different integrals over the electronic states near $E_F$, which can be exploited to obtain simultaneously high $\alpha$ and $\sigma$ in certain materials with highly non-parabolic band structures.

B. Emerging thermoelectric transport trends

Despite the high degeneracy and non-parabolic band structure of Bi$_2$Te$_3$ (Fig. 5a), an experimentally-observed $\sim 65\%$ power factor drop occurs at 5 GPa, likely due to the following factors. Stoichiometric Bi$_2$Te$_3$ forms with p-type Bi$_{\text{Te}}$ antisite defects, causing valence-band-structure-dominated carrier transport. Lower $\alpha$ correlates with a lower $m_{DOS}^*$ arising from the break in quasi-degeneracy of the VBM between 2–4 GPa (Fig. 5a), caused by the divergence of the $Z-a$ and $Z-F$ bands from the $a-G$ and $L-Z$ bands. This topological transition has been experimentally observed. The pressure-induced bandgap decrease promotes bipolar charge carrier transport, which also diminishes $\alpha$. Altogether, $\alpha$ drops to $\sim 25 \mu$V K$^{-1}$ at 5 GPa in p-Bi$_2$Te$_3$. For n-Bi$_2$Te$_3$, the Mott formulation predicts a higher $\alpha$ at higher pressures due to an increase in the conduction band DOS (Fig. 6a), but bipolar transport counteracts this effect, at least partially. Experimentally, n-Bi$_2$Te$_3$ with $n \leq 10^{19}$ cm$^{-3}$ can show $|\alpha| > 100 \mu$V K$^{-1}$ up to 6.5 GPa, and a modest $\sim 30\%$ increase in power factor is achieved in the range of 2–6 GPa.

The Sb$_2$Te$_3$ band structure behaves differently under pressure than that of Bi$_2$Te$_3$. As in Bi$_2$Te$_3$, the VBM is along $a-G$, and...
at 0 pressure there are already three quasi-degenerate secondary VBMs along $L-Z$, $Z-a$, and $Z-F$. However, all extrema are brought closer to the band edge with an increase in pressure (Fig. 5d). Although there are no bands suppressed as in Bi$_2$Te$_3$, the quasi-degeneracy is still broken because all valence bands move towards the edge at different rates. Thus, the DOS is not initially increased with pressure (Fig. 6d), and the power factor is experimentally observed to decrease with increasing pressure.

Sb$_2$Te$_3$ has a better potential for high power factor under pressure than Bi$_2$Te$_3$, since the primary and secondary VBM move in parallel, and it has a higher zero-pressure bandgap of ~280 meV, which is large enough to withstand pressure-induced reductions and still be able to prevent bipolar conduction. Favorable band edge topologies are not easy to employ because of facile Sb$_{Te}$ antisite defect formation that creates degenerate hole concentrations of $10^{20}$–$10^{21}$ cm$^{-3}$, leading to low $\alpha$. Nevertheless, sub-atomic percent S doping has been shown to suppress Sb$_{Te}$ antisite formation, presaging $ZT = 2.48$. Pressure-induced effect could serve as an additional knob to realize high power factor in Sb$_2$Te$_3$-based alloys.

Alloying Sb$_2$Te$_3$ with Bi completely changes the pressure effect on $x^2\sigma$, which can be explained through a band structure balancing paradigm. Our calculations yield similar electronic structures with multiple degenerate, non-parabolic band edges for Bi$_2$Te$_3$ and Sb$_2$Te$_3$ (Fig. 5a and d). However, our calculations on BiSbTe$_3$ to approximate a Bi$_{0.6}$Sb$_{1.4}$Te$_3$ alloy without the use of a supercell show that, pressure initially increases the VBM quasi-degeneracy (Fig. 5b) and thus increases the valence band DOS near $E_F$ (Fig. 6b), which is a behavior not seen in p-Bi$_2$Te$_3$ or p-Sb$_2$Te$_3$. The band behavior is more balanced such that all four valence bands move in unison towards the valence edge. The p-Bi$_{0.6}$Sb$_{1.4}$Te$_3$ composition yields an average bandgap of $E_G = 200$ meV, which is large enough to prevent bipolar conduction, even when decreased to 150 meV at 4 GPa (see Section V). The hole concentration of ~$2 \times 10^{19}$ to ~$6 \times 10^{19}$ cm$^{-3}$ indicates that Bi alloying allows defect control for carrier density optimization for targeting high $x^2\sigma$ by harnessing favorable band edge topology.

The resultant complex shapes of the additional bands prognosticate higher $\sigma$ due to the cumulative effect of carrier transport through multiple channels (or band extrema (i)), described by
the addition of new bands does not change as drastically as \( \sigma \), because \( x \) is inversely proportional to \( \sigma \) only within a single band, and not to the system total. This exact \( \sigma \) and \( x \) behavior has been observed in p-Bi\(_{0.6}\)Sb\(_{1.4}\)Te\(_3\) under pressure, where a twelve-fold increase in \( \sigma \) is accompanied by only a 20% decrease in \( x \). For example, at 4 GPa, \( x^2\sigma = 34.5 \text{ mW m}^{-1} \text{ K}^{-2} \), which is eight-fold higher than the zero-pressure 4.3 mW m\(^{-1} \) K\(^{-2} \) value, which is close to the largest reported single crystal alloy in-plane ([10\( \bar{1}0 \)]) value of 4.8 mW m\(^{-1} \) K\(^{-2} \). These alloys typically have zero-pressure \( \kappa = 1.3-1.6 \text{ W m}^{-1} \text{ K}^{-1} \), and \( \kappa \) has been shown to only increase two-fold at 4 GPa in BiSbTe\(_3\),\(^\text{51} \) presaging ZT > 3 at this pressure.

The pressure-induced \( x^2\sigma \) increases in n-Bi\(_2\)Te\(_3\) and p-BiSbTe\(_3\) alloys suggest that similar results should be achievable in Bi\(_2\)Te\(_2\)Se where, Te\(_a\) antisite defects create an n-type behavior.\(^\text{9,52} \) Indeed, the Bi\(_2\)Te\(_2\)Se conduction band DOS with pressure (Fig. 6c), similar to that seen in n-Bi\(_2\)Te\(_3\),\(^\text{9,52} \) at 5 GPa, our calculated Bi\(_2\)Te\(_2\)Se bandgap is halved from \( E_\text{g} = 265 \text{ meV} \) to 130 meV, which is high enough to inhibit bipolar charge carrier transport. While \( g = 2 \) for the primary \( \Gamma-Z \) CBM, the secondary \( Z-F \) CBM (\( g = 6 \)) becomes the primary CBM at 1 GPa, leading to the tripling of the CBM band degeneracy. Between 3–7 GPa, three more six-fold degenerate CBMs are activated along \( L-Z, Z-a, \) and \( \Gamma-Z \) (Fig. 5c). The presence of five bands with 2- to 6-fold degeneracy within \( \sim 2k_\text{B}T \) of the optimum 300 K bandgap (150 meV) provide stable enhancements in \( x^2\sigma \) up to 8 GPa.

V. Boltzmann thermoelectric transport calculations

A. BoltzTraP computational methods

We calculated \( x \) and \( \sigma \) directly from our first principles band structure results with Boltzmann transport equations, using BoltzTraP code.\(^\text{14} \) The band structure data for these calculations were obtained by additional self-consistent DFT calculations using a 36 \( \times \) 36 \( \times \) 36 \( \Gamma \)-centered \( k \)-point grid, symmetrized to 4237 \( k \)-points in the first Brillouin zone. This mesh was interpolated in BoltzTraP onto a mesh 5 times as dense, and no fixed doping levels were used in any calculations. We used scissors operations to revise the bandgaps of all systems (Fig. 7). Bi\(_2\)Te\(_3\) and Bi\(_2\)Te\(_2\)Se were normalized to their experimental 0 GPa values, since the DFT calculations produced <30% error in zero-pressure bandgaps, and predicted reasonable insulator-to-metal transition pressures. However, since DFT produced >60% error in zero-pressure bandgap values, we linearly scaled the data for Sb\(_2\)Te\(_3\) and BiSbTe\(_3\) to agree with the experimental zero-pressure values.

We used a constant scattering relaxation time \( \tau = 2.5 \times 10^{-14} \text{ s} \), which is within \( \sim 20\% \) of \( \tau \) for all our systems at 0 GPa.\(^\text{37,39,53,54} \) The experimental studies previously discussed\(^\text{10,15} \) show pressure-induced carrier concentration increases as well as increases in carrier mobility, which cannot be accounted for purely by measured decreases in \( m_\text{DOS} \), implying an increase in \( \tau \) with pressure. Thus our calculations set a lower limit on pressure-induced enhancements in \( x^2\sigma \).

B. Predictions of thermoelectric properties

Our calculations show that \( x^2\sigma \) increases with pressure for p-Bi\(_2\)Te\(_3\), n-Bi\(_2\)Te\(_2\)Se, and p-BiSbTe\(_3\) for charge carrier concentrations in the \( 10^{18-10} \text{ cm}^{-3} \) range (Fig. 8). In contrast, \( x^2\sigma \) decreases for p-Bi\(_2\)Te\(_3\) and p-Sb\(_2\)Te\(_3\) in the same range (Fig. 8). For \( n < 10^{19} \text{ cm}^{-3} \), n-Bi\(_2\)Te\(_3\) and n-Bi\(_2\)Te\(_2\)Se, \( x^2\sigma \) exhibits a minima and maxima, respectively, at \( \sim 5 \text{ GPa} \), whereas both materials show almost monotonic increases in \( x^2\sigma \) with pressure for \( n > 10^{19} \text{ cm}^{-3} \). In BiSbTe\(_3\), \( x^2\sigma \) increases and plateaus with pressure for \( p < 10^{19} \text{ cm}^{-3} \), but increases and peaks at \( \sim 3 \text{ GPa} \) before decreasing again for \( p > 10^{19} \text{ cm}^{-3} \). These results indicate that the contributions of new bands at higher carrier concentrations promote high \( x^2\sigma \), and explain the experimental results that show the best \( x^2\sigma \) enhancements occurring at carrier concentrations in the \( 2-6 \times 10^{19} \text{ cm}^{-3} \) range.\(^\text{10,46} \) Our calculated trends match the experimentally measured \( x^2\sigma \) decrease in n-Bi\(_2\)Te\(_3\) at \( n \leq 10^{19} \text{ cm}^{-3} \),\(^\text{14} \) and experimental measurements of \( x^2\sigma \) at higher carrier concentrations are needed to verify our prognosis of high power factor increases obtained at \( \sim 4 \text{ GPa} \).

Our above results collectively show that complex band topology near \( E_\text{F} \) created by many highly-degenerate bands is an essential ingredient in obtaining higher-than-bulk power factor in thermoelectric materials. This is most clearly seen in Fig. 9, where the power factor of all the materials we have studied is plotted at a constant carrier concentration as a function of pressure. The n-type systems showing the most prominent favorable pressure-induced band structure alterations also exhibit
the largest power factor enhancements; greater than two-fold increase can be achieved by adjusting band structure at a fixed carrier concentration. These findings indicate that band structure engineering through manipulation of lattice strain (i.e., pressure) is a potent means to optimize any system to realize high thermoelectric figure of merit materials.

VI. Summary

Our first-principles calculations reveal pressure-induced changes in the lattice parameters, bulk moduli, and insulator-to-metal transitions, in Bi$_{2-x}$Sb$_x$Te$_3$ and Bi$_2$Te$_3$Se that are in agreement with experiments. The resultant changes in the thermoelectric power factors in all Bi$_{2-x}$Sb$_x$Te$_3$$_3$Se$_2$ systems are explained based upon changes in the bandgap and the electronic band topology. In particular, we prognosticate large pressure-induced power factor increases in n-Bi$_2$Te$_3$ at ~ 4 GPa. Thus, lattice strain is an attractive knob to favorably modify the electronic band structure topology to realize high thermoelectric power factors without significantly increasing the thermal conductivity, leading to higher $ZT$. Combining strain-induced band structure engineering together with other methods such as theoretically-guided doping$^8$ could hold the keys to creating the next generation of high-efficiency thermoelectric materials.

![Fig. 8](image-url) Calculated power factors $\sigma^2$ from BoltzTraP for (a) p- and n-Bi$_2$Te$_3$, (b) p- and n-Bi$_2$Te$_2$Se, (c) p-BiSbTe$_3$, and (d) p-Sb$_2$Te$_3$, for different pressures (indicated in GPa next to curves). The chemical potential $\mu = 0$ meV at the bandgap centers. The slight changes or even reversals of power factor trends correlate with experimentally observed variations.$^{46}$

![Fig. 9](image-url) Pressure-induced changes in power factor for n-Bi$_2$Te$_3$ ($n \sim 3 \times 10^{19}$ cm$^{-3}$), n-Bi$_2$Te$_2$Se ($n \sim 3 \times 10^{19}$ cm$^{-3}$), p-Bi$_2$Te$_3$Se ($p \sim 2 \times 10^{19}$ cm$^{-3}$), p-BiSbTe$_3$ ($p \sim 2 \times 10^{19}$ cm$^{-3}$), p-Sb$_2$Te$_3$ ($p \sim 3 \times 10^{19}$ cm$^{-3}$), and p-Bi$_2$Te$_3$ ($p \sim 2 \times 10^{19}$ cm$^{-3}$). For identical carrier concentrations at 300 K, the application of pressure significantly increases power factor for both n-Bi$_2$Te$_3$ and n-Bi$_2$Te$_2$Se, while degrading power factor in all p-type systems except p-BiSbTe$_3$, matching experimental findings.
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