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Theoretical limits of thermoelectric figure of merit in n-type TiO_2 polymorphs

Dylan Bayerl* and Emmanouil Kioupakis

¹*Department of Materials Science and Engineering,
University of Michigan, Ann Arbor, Michigan 48109, USA*

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We calculate the conduction band structures and n-type thermoelectric transport properties for the TiO_2 polymorphs rutile, anatase, and brookite from first principles within the constant-relaxation-time approximation. Although the Seebeck coefficient is nearly isotropic in all polymorphs, the power factor is anisotropic and takes its largest values along [100] in rutile and anatase, and along [010] for brookite. We also identify the free-carrier concentrations and temperatures that maximize the power factor. Our results for the theoretical upper bounds of the figure of merit at high temperature show that optimized rutile exhibits thermoelectric conversion efficiency that is superior to anatase and brookite and can reach values desirable for waste-heat recovery applications.

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Thermoelectric energy conversion offers a method to recover waste heat as electrical power from high-temperature industrial and transportation applications. Current research aims to identify thermoelectric materials that are both thermodynamically stable and thermoelectrically efficient at high temperatures. Titanium dioxides (TiO_2) are promising in this regard. Three naturally occurring polymorphs—rutile, anatase, and brookite—are stable in atmosphere at high temperatures (rutile melts near 2100 K¹ while anatase and brookite transform irreversibly to rutile above approximately 900 K and 1100 K, respectively^{2,3}). Furthermore, large n-type Seebeck coefficients have been measured from -360 to -700 $\mu\text{V/K}$ in rutile⁴⁻⁶ and from -240 to -500 $\mu\text{V/K}$ in anatase,⁷⁻¹¹ while power factors as high as 14 $\mu\text{W}/(\text{K}^2\text{cm})$ have been reported.¹² Despite these promising characteristics, the highest reported value of the dimensionless thermoelectric figure of merit $ZT = \sigma S^2 T / \kappa$ to date is 0.35 at 973 K in rutile,¹³ which is well below that of the current best thermoelectric materials.

Recent advances in understanding the behavior of excess charge carriers in TiO_2 and identifying new dopants show great promise for the development of TiO_2 -based thermoelectric devices. Calculations by Janotti *et al.*¹⁴ revealed the dual nature of excess carriers in TiO_2 , showing that delocalized carriers give rise to the high mobility measured experimentally and thus dominate transport. Other calculations indicate that the unintentional n-type conductivity reported in anatase and rutile TiO_2 stems from oxygen vacancies.¹⁵ However, impurity doping is needed to achieve the high free-electron concentrations required for thermoelectric applications. Pentavalent cation doping with Nb or Ta can achieve up to 8% cation substitution and produce free-carrier concentrations as high as $5 \times 10^{20} \text{ cm}^{-3}$ for anatase.¹⁶ High dopant concentrations increase the free-carrier concentration, electrical conductivity, and thermal conductivity while reducing the Seebeck coefficient,^{7,12} exemplifying the trade-off that makes increasing ZT challenging.

In this work, we use first-principles methods to calculate the band structure and thermoelectric transport properties of n-type rutile, anatase, and brookite TiO_2 . We analyze features in the band structure that affect electronic transport and we identify optimal temperatures and free-carrier concentrations to maximize the thermoelectric power factor of TiO_2 . We also compute the *electronic* ZT ($Z_e T$) to compare relative thermoelectric performance between polymorphs, and then estimate the maximum possible ZT ($Z_{\text{max}} T$) of rutile using electronic relaxation times extracted from literature. Our analysis establishes upper bounds on the thermoelectric figures of merit in these TiO_2 polymorphs and demonstrates that at least a twofold improvement over previously reported values is possible under optimal conditions.

Our computational methodology employs density functional theory (DFT) and many-body perturbation theory. We use DFT with the local density approximation and the plane-wave norm-conserving pseudopotential method¹⁷⁻¹⁹ with a semicore Ti pseudopotential including 3s and 3p orbitals in the valence. Subsequently, we apply quasiparticle corrections with the GW method^{20,21} using the generalized plasmon-pole model of Hybertsen and Louie,²² and the static-remainder²³ correction to converge the Coulomb-hole sum. The Ti semicore shell is excluded from the plasmon-pole sum rule to preclude nonphysical screening by core electrons.²⁴⁻²⁶ These parameters converge quasiparticle band gaps to within 0.1 eV. Quasiparticle corrections also modify the band dispersion and the relative energies of conduction band valleys, on which transport coefficients intimately depend. We therefore use quasiparticle band structures for calculating transport properties, improving on previous theoretical work that investigated only the rutile polymorph without quasiparticle corrections.²⁷ We interpolate the quasiparticle band structures with the maximally localized Wannier function (MLWF) method.^{28,29} Basis sets of 26 MLWFs for anatase and rutile and 104 MLWFs for brookite interpolate the band structures with a maximum error of 10 meV for states within 2 eV from the band edges. Transport coefficients (electrical conductivity σ , Seebeck coefficient S , and electronic thermal conductivity κ_e) are calculated using the Boltzmann transport formalism with an approach similar to the method developed independently by Pizzi *et al.*,³⁰ employing the rigid-band and constant-relaxation-time approximations. While full calculations of the relaxation time due to the various scattering mechanisms are needed to predict transport coefficients, they are computationally expensive and beyond the scope of the analysis we perform here. Carrier velocities are calculated using finite differences on dense meshes that converge transport coefficients to three significant digits. Structural parameters used in our calculations are taken from experimental measurements at room temperature and atmospheric pressure.^{31,32}

Our calculated band structures for the rutile, anatase, and brookite polymorphs of TiO_2 are in reasonable agreement with experiment and previous calculations. We calculate the indirect electronic band gap of rutile as 3.49 eV for the $\Gamma \rightarrow \text{R}$ transition, while the smallest direct gap is 3.56 eV at Γ . The fundamental band gap of anatase is also indirect, with 3.87 eV between $0.85 \text{ X} \rightarrow \Gamma$, whereas the smallest direct gap is 4.42 eV at Γ . We calculate that the fundamental gap of brookite is direct at Γ with a magnitude of 3.99 eV. These findings are compared to previously reported experimental and theoretical band gaps in Table I.

We calculated Seebeck coefficients for a range of free-carrier concentrations and temperatures from 300 K up to the phase-transformation temperatures. For this range of free-carrier concentrations, the Fermi level at 300 K spans an energy range from at most 0.16 eV below up to 0.23 eV above the conduction band minimum (Fig. 1). The presence of multiple conduction band valleys near the Fermi level increases the magnitude of the Seebeck coefficient. We therefore expect rutile (Fig. 1a) to have a larger Seebeck coefficient than anatase (Fig. 1b) and brookite (Fig. 1c). Indeed, at all corresponding temperatures and free-carrier concentrations, the Seebeck coefficient of rutile (Fig.

65 2a,b) is larger than those of both anatase (Fig. 2c,d) and brookite (Fig. 2e,f). The Seebeck coefficient of anatase is
 66 the smallest of the three polymorphs, being 5% - 20% smaller than in brookite and 30% - 60% smaller than in rutile
 67 at corresponding temperatures and free-carrier concentrations. Additionally, we find that the Seebeck coefficient is
 68 isotropic to within 1% in all three polymorphs. Our calculated Seebeck coefficients are in reasonable agreement with
 69 available experimental data for rutile^{4,5} and anatase,^{10,11} as summarized in the insets of Figs. 2a,c.

70 We also evaluated the thermoelectric power factor (σS^2) in the constant-relaxation-time approximation to estimate
 71 optimal temperature and free-carrier concentrations for TiO₂-based thermoelectric devices. Specifically, we analyze the
 72 ratio $\sigma S^2/\tau$ to remove the dependence on the constant-relaxation-time parameter τ from our transport calculations.
 73 This necessity precludes direct comparison of the magnitude of $\sigma S^2/\tau$ between different TiO₂ polymorphs since carrier
 74 relaxation rates may vary between them, but it yields meaningful conclusions about optimizing thermoelectric energy
 75 conversion for each polymorph.

76 We first consider $\sigma S^2/\tau$ of each TiO₂ polymorph in different crystallographic directions at a fixed temperature of
 77 300 K (Fig. 3a,c,e). While $\sigma S^2/\tau$ of rutile is nearly isotropic (Fig. 3a), there is considerable anisotropy in anatase (Fig.
 78 3c) and brookite (Fig. 3e). Anisotropic $\sigma S^2/\tau$ implies that fully optimized bulk thermoelectric devices incorporating
 79 these materials must take the preferred transport directions into account. Ideally, such devices would be constructed
 80 from appropriately oriented single crystals. However, in the case of devices assembled from, e.g., sintered powders,
 81 rutile would sustain the least efficiency loss of the three polymorphs from the presence of randomly oriented grains.

82 Another key observation is that $\sigma S^2/\tau$ is maximized in these TiO₂ polymorphs at free-carrier concentrations in
 83 excess of 10^{20} cm^{-3} . However, the particular free-carrier concentration that maximizes $\sigma S^2/\tau$ depends on temperature,
 84 which we investigate in the preferred transport directions (Fig. 3b,d,f). In every case, $\sigma S^2/\tau$ increases with increasing
 85 temperature up to the phase transformation temperature of each polymorph. Furthermore, as temperature increases,
 86 higher free-carrier concentrations are required to maximize $\sigma S^2/\tau$. Of the three polymorphs, rutile requires the
 87 highest free-carrier concentrations to maximize $\sigma S^2/\tau$, from 10^{21} cm^{-3} at 300 K to $5 \times 10^{21} \text{ cm}^{-3}$ at 2000 K. Anatase
 88 and brookite require approximately an order of magnitude lower free-carrier concentrations to maximize $\sigma S^2/\tau$. At
 89 300 K, $\sigma S^2/\tau$ is maximized with 10^{20} cm^{-3} in anatase and $2 \times 10^{20} \text{ cm}^{-3}$ in brookite. Near the phase transformation
 90 temperatures, $5 \times 10^{20} \text{ cm}^{-3}$ yields the maximum $\sigma S^2/\tau$ in both anatase (at 900 K) and brookite (at 1100 K). Note
 91 that the experimentally measured power factor may show a maximum at lower free-carrier concentrations since the
 92 electronic relaxation time decreases with increasing temperature or free-carrier concentration.

93 Next, we calculate the quantity $Z_e T = \sigma S^2 T / \kappa_e$ for each TiO₂ polymorph in the preferred transport direction (Fig.
 94 4). $Z_e T$ is related to the thermoelectric figure of merit $ZT = \sigma S^2 T / (\kappa_e + \kappa_l) = Z_e T / (1 + \kappa_l / \kappa_e)$, and is often called
 95 the *electronic ZT*. ZT approaches $Z_e T$ in the limit where the lattice thermal conductivity κ_l is small compared to
 96 the electronic thermal conductivity κ_e . $Z_e T$ is thus useful for comparing relative thermoelectric performance of the
 97 various TiO₂ polymorphs. This comparison reveals that rutile has superior thermoelectric properties to anatase and
 98 brookite. At corresponding temperatures and free-carrier concentrations, $Z_e T$ is between approximately 2 to 10 times
 99 higher in rutile (Fig. 4a,d) than in anatase (Fig. 4b,e) or brookite (Fig. 4c,f). The ratio of $Z_e T$ of rutile to the other
 100 polymorphs increases with increasing free-carrier concentration (Fig. 4a,b,c), but decreases slightly with increasing
 101 temperature (Fig. 4d,e,f).

102 Last, we estimate an upper bound for ZT ($Z_{\max} T$) in rutile—the most promising polymorph. We approach this by
 103 calculating κ_l in the amorphous limit, estimating the electronic relaxation time from conductivity measurements in
 104 the literature, and recalculating transport parameters based on this estimate. In the amorphous limit, short-range
 105 scattering dominates the lattice thermal conductivity, establishing a lower limit of $\kappa_l = C_v l v / 3 = k_b N l v / 2$, where
 106 C_v , l , v , and N are respectively the heat capacity, phonon mean free path, sound velocity, and atomic density.⁴² The
 107 parameters for rutile $l = 0.196 \text{ nm}$ (average nearest-neighbor distance), $v = 6850 \text{ m/s}$ (average sound velocity),⁴³ and
 108 $N = 9.6 \times 10^{22} \text{ cm}^{-3}$ yield $\kappa_l = 0.89 \text{ W m}^{-1} \text{ K}^{-1}$. This value of κ_l is comparable to experimental measurements of
 109 reduced rutile samples wherein abundant defect planes scatter phonons.⁴⁴ We then estimate the electronic relaxation
 110 time from conductivity measurements by Kitagawa *et al.*,⁴ which yield an average value of $\tau_{\text{exp}} = 2 \times 10^{-16} \text{ s}$ for
 111 free-carrier concentrations between 10^{20} cm^{-3} and $5 \times 10^{20} \text{ cm}^{-3}$ at 300 K.

112 The upper bound $Z_{\max} T$ for rutile derived from κ_l in the amorphous limit and the experimental relaxation time
 113 τ_{exp} is shown in Fig. 5a,b. $Z_{\max} T$ increases with both temperature and free-carrier concentration up to a maximum
 114 near $3 \times 10^{21} \text{ cm}^{-3}$. The maximum value of $Z_{\max} T$ of rutile is 0.93, reached near the melting temperature. This value
 115 is the highest achievable ZT among these TiO₂ polymorphs and implies energy conversion performance comparable to
 116 commercially available thermoelectric materials. Figure 5c shows the Lorenz number $\kappa_e / (\sigma T)$ of the three polymorphs,
 117 indicating the onset of non-parabolic band effects for free-carrier concentrations above 10^{20} cm^{-3} in rutile and 10^{19}
 118 cm^{-3} in anatase and brookite.

119 The large Seebeck coefficients in these three TiO₂ polymorphs and the behavior of $\sigma S^2/\tau$ and $Z_e T$ indicate that
 120 all are potentially suitable for thermoelectric energy conversion. The rutile polymorph is particularly well-suited for
 121 two reasons. First, the high thermodynamic stability of bulk rutile precludes phase transformation below the melting
 122 temperature near 2100 K, placing a high upper limit on the operating temperature. On the other hand, anatase and

brookite readily phase transform at approximately 960 K and 1160 K, respectively, limiting the operating temperature for thermoelectrics based on these polymorphs. Second, $Z_e T$ is larger in rutile than in anatase and brookite. This is primarily due to the greater number and multiplicity of conduction band valleys near the band edge in rutile. Furthermore, our calculation of $Z_{\max} T$ indicates that TiO_2 thermoelectric efficiency can be significantly enhanced by mitigating lattice thermal conductivity, optimizing free-carrier concentration, and operating at high temperature. For example, the record $ZT = 0.35$ in rutile at 973 K reported by Liu *et al*¹³ is comparable to our calculated value of $Z_{\max} T = 0.36$ at the same temperature, but is only a fraction of the maximum value $Z_{\max} T = 0.93$ at 2000 K. For these reasons, TiO_2 shows significant promise for high-temperature thermoelectric applications, and rutile-based thermoelectrics may offer the best thermal-energy conversion performance over the widest temperature range among these three TiO_2 polymorphs.

In conclusion, we calculated the quasiparticle band structure and n-type thermoelectric transport properties of the rutile, anatase, and brookite polymorphs of TiO_2 from first principles within the constant-relaxation-time approximation. We found that the Seebeck coefficients are large and isotropic in each polymorph, and have the largest magnitude in rutile. Analysis of $\sigma S^2/\tau$ as a proxy for the power factor shows that the power factor can be maximized with free-carrier concentrations between 10^{20} cm^{-3} and 10^{21} cm^{-3} in anatase and brookite, and above 10^{21} cm^{-3} in rutile. Our analysis indicates that the rutile polymorph has distinct advantages over anatase and brookite, having the largest values for the Seebeck coefficient and $Z_e T$, as well as the best thermal stability over the widest temperature range. Moreover, our calculation of $Z_{\max} T$ shows that ZT approaching unity is theoretically achievable in heavily doped rutile near the melting temperature. Our findings indicate that these common TiO_2 polymorphs are promising thermoelectric materials for waste-heat recovery at high temperatures.

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* bayerl@umich.edu

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FIGURES

FIG. 1. Conduction band structures of rutile (a), anatase (b), and brookite (c) TiO_2 . Shaded regions show the range of the Fermi level E_f for free-carrier concentrations between 10^{18} cm^{-3} and $5 \times 10^{20} \text{ cm}^{-3}$ at 300 K. The Fermi energy increases with carrier concentration and exceeds the conduction band minimum in all three polymorphs at $5 \times 10^{20} \text{ cm}^{-3}$ and 300 K. Brillouin zones are labeled following the convention of Ref. 41.

FIG. 2. Seebeck coefficients of n-type TiO_2 polymorphs as a function of free-carrier concentration (n) and temperature from 300 K up to the phase-transformation temperatures. The Seebeck coefficient of rutile (a,b) is significantly larger than those of anatase (c,d) and brookite (e,f) at corresponding temperatures and carrier concentrations. Experimental data measured near 300 K are summarized in the insets of (a) and (c).

FIG. 3. The power factor divided by the relaxation time ($\sigma S^2/\tau$) of n-type TiO_2 polymorphs as a function of the free-carrier concentration (n), crystallographic direction, and temperature. The ratio is nearly isotropic in rutile (a), but considerably anisotropic in anatase (c) and brookite (e). Above 300 K, the maximum value is achieved for a carrier density of 10^{20} cm^{-3} in anatase (d), $2 \times 10^{20} \text{ cm}^{-3}$ in brookite (f), and higher than 10^{21} cm^{-3} in rutile (b).

FIG. 4. The ratio of the power factor divided by electronic thermal conductivity ($\sigma S^2/\kappa_e$) of n-type TiO_2 polymorphs as a function of the free-carrier concentration (n) and temperature. Rutile (a,d) exhibits significantly larger values for this ratio than anatase (b,e) and brookite (c,f) at corresponding temperatures and free-carrier concentrations, and thus has potentially superior thermoelectric energy conversion efficiency.

FIG. 5. The calculated upper bound of ZT for rutile in the amorphous limit of thermal transport ($Z_{max}T$) as a function of temperature (a) and free-carrier concentration (b). The Lorenz number of rutile, anatase, and brookite polymorphs at 300 K in the preferred transport direction of each (c).

TABLES

TABLE I. Indirect (E_{gap}^i) and minimum direct (E_{gap}^d) band gaps of the rutile, anatase, and brookite TiO_2 polymorphs, along with the locations of the valence band maximum (VBM) and conduction band minimum (CBM), as determined by various approaches using the GW method and measured by experiment (*).

Rutile			
Source	VBM \rightarrow CBM	E_{gap}^i (eV)	E_{gap}^d (eV)
This work	$\Gamma \rightarrow \text{R}$	3.49	3.56
Ref. 33	$\Gamma \rightarrow \Gamma$	—	3.40
Ref. 34	$\Gamma \rightarrow \Gamma$	—	3.46
Ref. 35	$\Gamma \rightarrow \Gamma$	—	3.59
Ref. 36	$\Gamma \rightarrow \text{R}$	3.34	3.38
* Ref. 37	—	3.00	3.37
* Ref. 38	$\Gamma \rightarrow \Gamma$	—	3.00
* Ref. 39	—	3.03	—
Anatase			
Source	VBM \rightarrow CBM	E_{gap}^i (eV)	E_{gap}^d (eV)
This work	$0.85\text{X} \rightarrow \Gamma$	3.87	4.42
Ref. 33	$\text{X} \rightarrow \Gamma$	3.70	3.9
Ref. 34	$0.88\text{M} \rightarrow \Gamma$	3.73	3.8
Ref. 35	$\text{X} \rightarrow \Gamma$	3.83	4.29
Ref. 36	$0.88\text{X} \rightarrow \Gamma$	3.56	4.14
* Ref. 38	—	3.2	—
* Ref. 37	—	3.21	3.53
* Ref. 39	—	3.24	—
* Ref. 40	—	3.34	—
Brookite			
Source	VBM \rightarrow CBM	E_{gap}^i (eV)	E_{gap}^d (eV)
This work	$\Gamma \rightarrow \Gamma$	—	3.99
Ref. 34	$\Gamma \rightarrow \Gamma$	—	3.45
* Ref. 37	—	3.13	3.56
* Ref. 39	—	3.27	—
* Ref. 38	$\Gamma \rightarrow \Gamma$	—	3.4









