Y$_2$Te$_3$: A New $n$-type Thermoelectric Material

Michael Y. Toriyama, a, * Dean Cheikh, b Sabah K. Bux, b G. Jeffrey Snyder, a Prashun Gorai, a

Rare-earth chalcogenides $R_{e_{3-x}}Ch_4$ ($R_e = $ La, Pr, Nd, $Ch = $ S, Se, Te) have been extensively studied as high-temperature thermoelectric (TE) materials owing to their low lattice thermal conductivity ($\kappa$) and tunable electron carrier concentration via cation vacancies. In this work, we introduce Y$_2$Te$_3$, a rare-earth chalcogenide with a rock-salt-like vacancy-ordered structure, as a promising $n$-type TE material. We computationally evaluate the transport properties, optimized TE performance, and doping characteristics of Y$_2$Te$_3$. Combined with a low $\kappa$, multiple low-lying conduction band valleys yield a high $n$-type TE quality factor. We find that a maximum figure-of-merit $zT > 1.0$ can be achieved when Y$_2$Te$_3$ is optimally doped with electron concentrations $1 - 2 \times 10^{20}$ cm$^{-3}$. We use defect calculations to show that Y$_2$Te$_3$ is $n$-type dopable under Y-rich growth conditions, which suppresses the formation of acceptor-like cation vacancies. Furthermore, we propose that optimal $n$-type doping can be achieved with halogens (Cl, Br, I), with I being the most effective dopant. Our computational results as well as experimental results reported elsewhere motivate further optimization of Y$_2$Te$_3$ as an $n$-type TE material.

1 Introduction

The efficiency of a thermoelectric (TE) device largely depends on the dimensionless figure of merit $zT = S^2\sigma/\kappa$, where $S$ is the Seebeck coefficient, $\sigma$ is the electrical conductivity, $\kappa$ is the thermal conductivity, and $T$ is the temperature. A route to achieving higher $zT$ is through the reduction of $\kappa$. Since materials with low $\kappa$ are desired, many studies have been dedicated to discovering novel low-$\kappa$ materials for TE applications. Zhu et al. combined graph neural networks and random forest approaches to identify rare-earth chalcogenides as materials with low lattice thermal conductivity ($\kappa$), in agreement with known high-performing TE materials. La$_{3-x}$Te$_4$, which has been extensively studied for high-temperature TE applications, forms a defected Th$_3$P$_4$ structure type due to the valence imbalance of stoichiometric La$_3$Te$_4$. The high TE performance of La$_{3-x}$Te$_4$ partly stems from synergistic effects of light and heavy bands leading to overall advantageous electrical transport properties, as well as enhanced phonon scattering from La vacancies. Similar materials, such as Pr$_{3-x}$Te$_4$, Nd$_{3-x}$Te$_4$, and La$_{3-x}$Se$_4$, also exhibit low $\kappa$ and high TE performance, likely due to the high degree of phonon scattering from the cation vacancies. Inspired by this chemical space of materials, the valence-balanced Sc$_2$Te$_3$ was synthesized and found to have $\kappa < 2$ W/mK. The TE performance of rare-earth chalcogenide TE materials, it is, therefore, natural to ask if there are other potentially high-performing TE materials within this chemical space.

Zhu et al. identified Y$_2$Te$_3$ as a low-$\kappa$, material with promising TE performance in their preliminary investigations. The orthorhombic crystal structure of Y$_2$Te$_3$ (space group $Fddd$, Figure 1) can be understood as a rock-salt derived structure with ordered cation vacancies, which is isostuctural with the orthorhombic polymorph of Sc$_2$Te$_3$. The vacancy-ordered structures of Y$_2$Te$_3$ and Sc$_2$Te$_3$ are related to that of rhombohedral Sb$_2$Te$_3$, as evidenced by their phase transitions in phase-change memory alloys. Specifically, the structural relationship can be understood as a gathering of the ordered vacancies to form a van der Waals gaps in the rhombohedral Sb$_2$Te$_3$ structure, similar to the phase transition mechanism of Ge$_2$Sb$_2$Te$_5$. Therefore, it is not surprising that layered structures such as Sb$_2$Te$_3$ and Bi$_2$Te$_3$, which are derived from rock-salt-like structures, as well as Ge$_2$Sb$_2$Te$_5$, are well-known TE materials.

Besides the preliminary studies undertaken by Zhu et al., relatively little is known about the fundamental TE transport properties and doping characteristics of Y$_2$Te$_3$. The ordered vacancies in the Y$_2$Te$_3$ structure likely promotes point defect scattering of phonons and lattice softening, both of which contribute to the lowering of $\kappa$. The TE performance of Y$_2$Te$_3$ was found to be comparable to La$_{3-x}$Te$_4$ and Yb$_{14}$MnSb$_{11}$, reaching a $zT \sim 0.8$ at 900 K when doped/alloyed with Bi. In their study, Zhu et
Acknowledged the anomalous n-type doping with Bi$^{3+}$, which is instead expected to isoelectronically substitute Y$^{3+}$.\textsuperscript{10} As such, there are open questions about the transport properties and doping behavior of orthorhombic Y$_2$Te$_3$.

To answer some of these questions and to guide future experimental studies, we perform first-principles calculations to investigate the electronic structure, n-type transport properties, and doping behavior of Y$_2$Te$_3$. We find that there are multiple low-lying and dispersive conduction band (CB) valleys that contribute to high CB degeneracy with the possibility of further enhancement through band convergence. Electrical transport properties obtained by solving the Boltzmann transport equations reveal that electron mobility in Y$_2$Te$_3$ is limited by polar optical phonon scattering rather than acoustic deformation scattering, which is generally assumed to the dominant mechanism in TE materials. Combined with a low $\kappa_L$, we predict that a maximum n-type $z_T$ of 1.0–1.2 can be achieved at an optimal electron concentration of 2 × 10$^{20}$ cm$^{-3}$. Using first-principles calculations, we show that the optimal electron concentration can be achieved through halogen doping under Y-rich growth conditions.

## 2 Results and Discussion

### 2.1 Electronic Structure and Transport Properties

The calculated band structure of Y$_2$Te$_3$ along high-symmetry k-point paths\textsuperscript{33,34} is shown in Figure 2(a). The presence of Te$p$ states at the valence band edge (Figure S1) leads to a triply degenerate valence band maximum (VBM) at the $\Gamma$ point. On the other hand, the conduction band edge contains multiple low-lying valleys that are mainly composed of Y$d$ states. We find that the conduction band minimum (CBM) is located at the Y-point yielding an indirect band gap ($E_g$) of 1.78 eV. Additional band valleys exist at $\Gamma$ (+0.003 eV), between X and A (+0.115 eV), and at X (+0.180 eV). The corresponding Fermi surface of Y$_2$Te$_3$, calculated at an isosurface 0.15 eV above the CBM, is shown in Figure 2(b). The two carrier pockets at Y, along with pockets at $\Gamma$ and between X and A, together yield a CB degeneracy ($N_c$) of 4.

We compare the optimized TE performances of p-type and n-type Y$_2$Te$_3$ by assessing the material quality factor $\beta$, which is given by

$$\beta \propto \frac{\mu_0 m^*_{\text{DOS}}}{\kappa_L} \Gamma^{5/2}$$

(1)

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<th>$\mu_0$</th>
<th>$\kappa_L$</th>
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Table 1 Computed electronic structure parameters, transport and thermoelectric properties of p- and n-type Y$_2$Te$_3$. $N_V$ is the valence (p-type) and conduction (n-type) band degeneracy, $m^*_{\text{DOS}}$ is DOS effective mass, $\mu_0$ is the intrinsic carrier mobility (300 K), $\kappa_L$ is the lattice thermal conductivity (300 K), and $\beta/\beta_{\text{PbTe}}$ is the quality factor, normalized to that of PbTe.

Fig. 2 (a) Band structure of orthorhombic Y$_2$Te$_3$ calculated along special $k$-point paths of the Brillouin zone. Y$_2$Te$_3$ has an indirect band gap $E_g$ of 1.78 eV while the direct gap at $\Gamma$ is only 0.003 eV larger. There are additional low-lying conduction band valleys along X-A and at X, which are above the conduction band minimum (CBM) by 0.115 eV and 0.180 eV, respectively. (b) Fermi surface at 0.15 eV above the CBM. Two carrier pockets exist at Y as shown with two different colors.

where $\mu_0$ is the intrinsic carrier mobility, $m^*_{\text{DOS}}$ is the density-of-states effective mass, and $\kappa_L$ is the lattice thermal conductivity. We calculate $\mu_0$ and $\kappa_L$ at 300 K using parameterized semi-empirical models, where the model inputs are obtained from density functional theory (DFT) calculations. The details of these models and methods to calculate the input parameters are documented in Refs. 35 and 36. We estimate the room-temperature $\kappa_L$ in single crystals to be 2.96 W/mK, which is higher than the experimentally measured value of 1.9 W/mK (at 300 K)\textsuperscript{10} in polycrystalline samples where grain boundary scattering lowers $\kappa_L$. We also estimate the room-temperature electron and hole mobilities to be 62 and 20 cm$^2$/Vs, respectively (Table 1). The mobility computed with the semi-empirical model provides an estimate of the intrinsic phonon scattering-limited mobility and therefore should be treated as an upper limit. Additional sources of scattering such as ionized impurities in heavily-doped semiconductors will reduce the carrier mobility.\textsuperscript{37}

Larger $\beta$ values signify higher optimized TE performance. We find that Y$_2$Te$_3$ has a larger n-type $\beta$ of 1.2 (relative to PbTe) compared to p-type (Table 1). The larger $\beta_n$ of Y$_2$Te$_3$ is attributed
Thermoelectric transport properties of Y$_2$Te$_3$ calculated using Boltzmann transport theory, including the (a) electrical conductivity ($\sigma$), (b) Seebeck coefficient ($S$), and (c) figure-of-merit $zT$. The TE properties are plotted as functions of temperature and electron concentrations. Experimental $\sigma$ and $S$ of Bi-doped Y$_2$Te$_3$ ($Y_2Te_{2.7}Bi_{0.3}$) are shown as black markers.

Motivated by the predictions based on the quality factor, we perform detailed charge transport calculations within the Boltzmann transport formalism, as implemented in the AMSET package (see Computational Methods for details). A key advantage of AMSET is that it does not assume a constant relaxation time – an approximation that often leads to inaccurate predictions of charge transport properties. The electrical conductivity ($\sigma$) and Seebeck coefficient ($S$) of Y$_2$Te$_3$, which are calculated in the temperature range 300-1200 K and electron concentrations between $10^{18}$ - $10^{21}$ cm$^{-3}$, are presented in Figures 3(a) and 3(b), respectively. We compare our calculated $\sigma$ and $S$ with experimental values for Bi-doped Y$_2$Te$_3$ reported in Ref. 10. The measured $\sigma$ and $S$ for Y$_2$Te$_{2.7}Bi_{0.3}$ samples (denoted by circles in Figures 3a, 3b) lie between our calculated values at electron concentrations $>10^{19}$ cm$^{-3}$, suggesting that Bi-doping results in electron concentrations $>10^{19}$ cm$^{-3}$. However, $n$-type doping with Bi is non-intuitive because Bi is expected to isoelectronically substitute on the Y site. We performed detailed defect calculations to address this perplexity in Section 2.3.

We calculate $zT$ as a function of electron concentrations and temperatures (Figure 3c) from the computed charge transport properties and the experimental $\kappa_L$ reported in Ref. 10 for undoped, polycrystalline Y$_2$Te$_3$. We chose to use the experimental $\kappa_L$ values to allow direct comparison with experiments and also to provide a realistic prediction of $zT$. Since the experimental $\kappa_L$ values in Ref. 10 are reported at temperatures different from the ones we report in Figure 3c, we fit the temperature dependence assuming $\kappa_L$ is limited by Umklapp scattering: $\kappa_L = \frac{A}{T} + B$.
where $A$ and $B$ are fitted parameters.\textsuperscript{46} The experimentally measured $\kappa_s(T)$ is well captured by the $T^{-1}$ dependence. Consequently, we find that maximum $zT$ between 0.9 and 1.2 can be achieved at 900 – 1200 K, when $Y_2Te_3$ is optimally doped with $1.2 \times 10^{20}$ cm$^{-3}$ electron concentration (Figure 3c).

It is typically assumed that acoustic deformation potential scattering limits carrier mobility in thermoelectric materials.\textsuperscript{47–49} However, our detailed charge transport calculations reveal that both electron and hole mobility in $Y_2Te_3$ is limited by polar optical phonon scattering (Figures 4 and S2a). In fact, recent studies have revealed that carrier mobility in common semiconductors such as GaAs,\textsuperscript{50–52} CsPbBr$_3$,\textsuperscript{53} and SnSe\textsuperscript{54} is limited by polar optical phonon scattering as well.

The room-temperature electron (62 cm$^2$/Vs) and hole (20 cm$^2$/Vs) mobilities estimated with the semi-empirical models, reported in Table 1, are in close agreement with the mobilities (electron - 49 cm$^2$/Vs, holes - 22 cm$^2$/Vs) obtained from detailed Boltzmann transport calculations (Figures 4, S2a). Furthermore, the predicted maximum $zT$ of $n$-type $Y_2Te_3$ (~1.2, Figure 3c) is higher than $p$-type (~0.8, see Figure S2b). This trend is consistent with the larger $\beta_n$ compared to $\beta_p$ (Table 1). Accordingly, this study provides further validation of the fitted transport models\textsuperscript{35,36} used to predict high TE performance in e.g. binary compounds,\textsuperscript{55} oxides,\textsuperscript{56} and Zintl phases.\textsuperscript{57,58}

### 2.2 Native Point Defects in $Y_2Te_3$

To realize the predicted $n$-type TE performance of $Y_2Te_3$, it must be suitably doped with electrons and the free electron concentration must be tuned to optimize the performance. Whether a material can be optimally doped depends largely on the self-doping behavior of the native defects. The presence of high concentrations of acceptor-like defects will limit $n$-type doping due to the charge compensation by the holes created by the acceptor defects. Therefore, to probe whether $Y_2Te_3$ can be doped $n$-type, we calculate the formation energies of native defects using first-principles calculations. The details of the defect calculations are provided in the Methods section.

Defect formation energy ($\Delta E_{Dn}$) varies with the thermodynamic growth conditions (Eq. 3) of a material, which are determined by the chemical potentials of the constituent elements. In the case of $Y_2Te_3$, $\Delta E_{Dn}$ will depend on the chemical potentials of $Y$ ($\mu_Y$) and Te ($\mu_Te$). The elemental chemical potentials $\mu_i$ are commonly expressed relative to their chemical potentials at standard conditions such that $\mu_i = \mu_i^0 + \Delta \mu_i$, where $\Delta \mu_i$ quantifies the deviation from standard conditions. The allowable range of $\Delta \mu_i$ is dictated by the thermodynamic phase stability of the material in the grand potential phase diagram obtained through a convex hull analysis.

Figure 5 shows the convex hull formed by the stable competing phases in the binary Y-Te chemical space. The allowed range of $\Delta \mu_Y$ and $\Delta \mu_Te$, for the phase stability is set by the two-phase equilibrium of $Y_2Te_3$ with either YTe or YTe (Table S2). Here, the equilibrium between $Y_2Te_3$ and YTe is denoted as “most Y-poor” condition since $Y_2Te_3$ is stable under these thermodynamic conditions despite being compositionally Y-deficient. In a similar fashion, the two-phase equilibrium with YTe is denoted as the “most Y-rich” condition. Since the elemental chemical potentials are different under these two conditions, we present the corresponding native defect formation energies separately in Figures 6(a) and 6(b).

Under the most Y-poor condition (Figure 6a), $Y_2Te_3$ is an intrinsic semiconductor with the equilibrium Fermi energy ($E_{F, eq}$) pinned near mid-gap, yielding a net hole concentration of $1.1 \times 10^{16}$ cm$^{-3}$ at $T = 923$ K, which is the typical solid-state synthesis temperature. We find that $Y_2Te_3$ cannot be doped $n$-type under Y-poor conditions because the low formation energy of acceptor-like cation vacancies ($V_Y$) indicates that electrons generated by a donor dopant will be charge compensated by the holes produced by $V_Y$. Similarly, it will be difficult to dope $Y_2Te_3$ $p$-type under Y-poor conditions due to the low formation energy of the amphoteric anti-site defect $Te_Y$. At Fermi energies closer to the valence band, $Te_Y$ acts as a singly-charged donor defect such that holes introduced by an extrinsic $p$-type dopant will be charge compensated by the electrons from $Te_Y$. As a result, we predict that it will be difficult to dope $Y_2Te_3$ either $n$- or $p$-type under Y-poor conditions, and will remain an intrinsic semiconductor with low free carrier concentrations.

Our defects calculations suggest that it is possible to dope $Y_2Te_3$ $n$-type under Y-rich conditions (Figure 6b) since the formation of acceptor-like native defects ($V_Y$ and $Te_Y$) is suppressed i.e., acceptor defects have high formation energy. In fact, under Y-rich conditions $Y_2Te_3$ is found to be self-doped $n$-type with a free electron concentration of $1.0 \times 10^{20}$ cm$^{-3}$ at $T = 923$ K. The relatively high electron concentration is due to the low formation energy of donor-like cation interstitials ($Y_i$), which reside at the vacancy sites in the ordered-vacancy structure of $Y_2Te_3$ (Figure S3). In addition, the generated electrons are free conduction electrons and not localized at mid-gap states that require temperature activation. The mid-gap states associated with $V_Te$ are occupied when $E_{F, eq}$ is located at $\sim 1.5$ eV above the VBM.
Fig. 6 Formation energy (Δ$E_{\text{pr}}$) of native defects in Y$_2$Te$_3$ under the (a) most Y-poor and (b) most Y-rich conditions within the region of phase stability (Figure 5). The Fermi energy ($E_F$) is referenced to the valence band maximum (VBM) i.e., $E_F = 0$ at VBM. The conduction band minimum is labeled CBM. Formation energy of different defect types are plotted in different colors. Multiple lines of the same color represent defects at unique Wyckoff sites. The equilibrium Fermi energy ($E_{F,\text{eq}}$), shown as a dashed vertical line, is calculated at 923 K. Y$_2$Te$_3$ is insulating under the most Y-poor conditions, but n-type under the most Y-rich conditions due to the low formation energy of donor Y interstitials.

### 2.3 Dopants in Y$_2$Te$_3$

Typically, carrier concentrations on the order of $10^{19} - 10^{21}$ cm$^{-3}$ are needed to fully optimize the performance of most thermoelectric materials.$^{59-61}$ Therefore, we explore plausible extrinsic dopants to further enhance the electron concentration in n-type Y$_2$Te$_3$. We find that halogens (Cl, Br, I) can increase the electron concentration under the most Y-rich and halogen-poor conditions, when Y$_2$Te$_3$ is in three-phase equilibrium with YTe and YX$_3$ ($X = \text{Cl, Br, or I}$). As shown in Figure 7, halogens preferentially substitute on the Te site and create 1-electron shallow donor states. Halogen doping does not introduce mid-gap states, and the generated electrons are therefore available as freely conducting electrons. We predict that the maximum achievable free electron concentrations are $1.1 \times 10^{20}$ cm$^{-3}$ (Cl doping), $1.5 \times 10^{20}$ cm$^{-3}$ (Br doping), and $2.0 \times 10^{20}$ cm$^{-3}$ (I doping). The trend in the electron concentrations can be understood in terms of the halogen solubilities – the lower the formation energy of substitutional X$_{Te}$ defects, the higher is the solubility and concentration of generated electrons. An additional benefit of halogen doping is that the conduction band edge is composed of Y-$d$ states (Figure S1); accordingly, substitution on the Te site does not significantly perturb the conduction band dispersion, and electron mobility will not be severely affected by doping.

The substitution of halogen dopants on the chalcogenide site is a common n-type doping strategy in TE materials e.g., I doping of PbTe,$^{62}$ J-doping of Bi$_2$Te$_3,$$^{63}$ Br-doping of SnSe,$^{64}$ and halogen doping to realize n-type Bi$_2$Se$_3$. However, as the defect energetics (and, therefore, the carrier concentrations) are dependent on the thermodynamic equilibrium of the growth conditions,$^{65}$ we emphasize the need to dope Y$_2$Te$_3$ under Y-rich conditions. In practice, precise control of the thermodynamic equilibrium (set by the elemental chemical potentials) can be achieved through careful phase boundary mapping experiments,$^{56,67}$ wherein the competing phases of a material are detected as impurity phases to gauge the thermodynamic state of the material.

A range of carrier concentrations can be achieved by halogen doping of Y$_2$Te$_3$ depending on the thermodynamic equilibrium at different growth conditions (Table S3). For example, while the maximum electron concentration achieved by I doping is $2.0 \times 10^{20}$ cm$^{-3}$, it is also possible to have much lower electron concentration e.g., $9.2 \times 10^{19}$ cm$^{-3}$ when Y$_2$Te$_3$ is in equilibrium with YTe and YI. This is a direct consequence of two factors: (1) the fundamental dependence of the defect formation energy on the elemental chemical potentials, which are set by the thermodynamic conditions, and (2) charge compensation by acceptor-like defects at certain thermodynamic conditions where they are favorable. As a result, halogen doping of Y$_2$Te$_3$ will require careful consideration of the thermodynamic state to rationally optimize n-type doping.

Zhu et al. acknowledged the anomalous n-type doping with Bi$^{3+}$, which is expected to isoelectronically substitute Y$^{3+}$. We try to confirm with defect calculations whether Bi can indeed result in n-type character. We consider Bi substitution on Y and Te sites as well as the formation of Bi interstitials. Due to the similarity in their ionic radii, octahedrally-coordinated Bi$^{3+}$ (1.03 Å) is expected to preferentially substitute Y$^{3+}$ (0.9 Å) as opposed to Te$^{2-}$ (2.21 Å).$^{68}$ In principle, isovalent Bi substitution on Y should not generate electronic carriers. Bi is known to isovalently substitute Y in bixbyte Y$_2$O$_3$, which has similar octahedral coordination as in Y$_2$Te$_3$. However, we find that the defect energetics (Figure 8) are more nuanced than this simplified treatment.

Our results suggest that isovalent Bi substitution on the Y site (Bi$_{Y}$) is preferred under Y-poor/Bi-rich conditions (Figure 8a), which is the expected behavior for Bi doping. In this case, no
additional charge carriers (electrons or holes) are created, and the equilibrium Fermi energy ($E_{F, eq}$) is pinned in the gap such that $Y_2Te_3$ is insulating. Under Y-rich/Bi-poor conditions on the other hand, Bi substitution on Te ($Bi_{Te}$) becomes energetically favorable. The tendency of Bi to substitute on chalcogen sites is not uncommon; for instance, Bi/Te and Bi/Se anti-site defects are found in $Bi_2Te_3$ and $Bi_2Se_3$, respectively.71 Bi-doping on the Se site has been able to achieve n-type SnSe.72 Interestingly, in $Y_2Te_3$, $Bi_{Te}$ is an amphoteric defect i.e., it acts as a donor when $E_F$ is close to the VB and an acceptor when $E_F$ is close to the CB. Under Y-rich/Bi-poor conditions, the equilibrium $E_F$ is closer to the CB where $Bi_{Te}$ is an acceptor defect (Figure 8b). Due to the high formation energy of $Bi_{Te}$, the dopant does not generate compensating holes significantly, and we therefore predict negligible change in the free electron concentration.

Our results show that Bi doping still maintains the n-type character due to donor $Y_{se}$ in agreement with the n-type character of Bi-doped $Y_2Te_3$ observed experimentally.10 However, it is also observed experimentally that increasing the nominal Bi concentration reduces the n-type Seebeck coefficient and electrical resistivity, suggesting an increase in the electron concentration.10 This anomalous effect cannot be explained by a simple site substitution doping mechanism. The Bi-doped $Y_2Te_3$ samples by Zhu et al.10 were prepared with high (nominal) concentrations of Bi, which is beyond the dilute doping limit (typically < 1%). Therefore, one plausible explanation for the observed n-type character of Bi-doped $Y_2Te_3$ is that Bi substitution significantly alters the electronic dispersion of both the conduction and valence band edges through substitution on the Y and Te sites, respectively, as the CB and VB edges are primarily composed of Y-$d$ and Te-$p$ orbitals, respectively (Figure S1). In particular, the perturbation of the CB edge may induce convergence of the multiple low-lying valleys (Figure 2a). Secondly, Bi incorporation may form an alloy (rather than a material with dilute doping) with native defect energetics that are different from the undoped $Y_2Te_3$. Finally, unintentional doping may also lead to confusing results. For example, unintentional H incorporation is responsible for the persistent n-type character of wurtzite ZnO and prevent p-type doping.73,74 We therefore attribute the n-type character of Bi-doped $Y_2Te_3$ to either a change in the defect energetics combined with a change in the band edge dispersion or unintentional n-type doping not directly related to Bi.

2.4 Thermoelectric Figure-of-Merit

The calculated temperature-dependent figure-of-merit ($zT$) is shown in Figure 9 for undoped and I-doped $Y_2Te_3$. Undoped $Y_2Te_3$ grown under Y-poor conditions (Figure 6a) has a net electron concentration of $1.1 \times 10^{26}$ cm$^{-3}$, and the low carrier concentration yields $zT$ values < 0.1 across the entire temperature range of interest. I-doped $Y_2Te_3$ under Y-rich conditions on the other hand yields an optimal electron concentration of $2 \times 10^{20}$ cm$^{-3}$ (see Section 2.3) such that $zT > 1.0$ above 1000 K.

For comparison, we also plot the measured $zT$ of Bi-doped $Y_2Te_3$ ($Y_2Te_2.7Bi_{0.3}$) in Figure 9. Although not explicitly measured, we predict that the electron concentrations of the samples reported by Zhu et al. are between $10^{19}$ to $10^{20}$ cm$^{-3}$ as evidenced by the electrical conductivity (Figure 3a) and Seebeck coefficient (Figure 3b). However, the optimal electron concentration of $Y_2Te_3$ is $1.2 \times 10^{20}$ cm$^{-3}$ (Figure 3c), which means that Bi-doping is slightly suboptimal and results in a lower $zT$ than
I-doping (Figure 9).

Nonetheless, the high n-type TE performance of Bi-doped Y$_2$Te$_3$ cannot be ignored. Although our defect calculations do not directly explain the high electron concentrations of Bi-doped samples assuming a simple site substitution doping mechanism (see Section 2.3), Bi doping appears to be a feasible route to realizing high zT in Y$_2$Te$_3$. We recommend that future studies focus on optimizing electron concentration via halogen doping and clarify the anomalous Bi doping.

Fig. 8 Formation energy ($\Delta E_{\text{DF}}$) of point defects in Bi-doped Y$_2$Te$_3$ under (a) Y-poor (equilibrium with YTe$_2$, Bi$_2$Te$_3$), and (b) Y-rich conditions (equilibrium with YTe, Bi$_2$Te$_3$). $\Delta E_{\text{DF}}$ of native defects (Figure 6b) is shown for reference. The Fermi energy ($E_{\text{F,eq}}$) is referenced to the valence band maximum (VBM) i.e., $E_{\text{F,eq}} = 0$ at VBM. Formation energy of different defect types are plotted in different colors. Multiple lines of the same color represent defects at unique Wyckoff sites. The equilibrium Fermi energy ($E_{\text{F,eq}}$) is calculated at 923 K. Bi substitution on the Y site is preferred under Y-poor/Bi-rich conditions while substitution on the Te site under Y-rich/Bi-poor conditions.

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2.5 Oxidation Effects

Our results suggest that Y$_2$Te$_3$ is a promising n-type thermoelectric material that can be doped with halogens or Bi. However, based on the earlier works on rare-earth chalcogenides, we anticipate synthetic challenges in preparing phase-pure samples. Rare-earth chalcogenides are prone to oxidation and therefore, we computationally assessed the oxidation of Y$_2$Te$_3$. In the ternary Y-Te-O phase diagram (Figure S4), Y$_2$Te$_3$ shares a tie line with Y$_2$O$_3$ forming two three-phase regions where it is in equilibrium either with YTe and Y$_2$O$_3$ (Y-rich), or with YTe$_3$ and Y$_2$O$_3$ (Y-poor). We investigate if it is possible to suppress the formation of Y$_2$O$_3$ by tuning the oxygen partial pressure ($p_{O_2}$). The oxygen partial pressure is related to the O$_2$ chemical potential ($\Delta C_{O_2} = \Delta C_{O_0}$, where $\Delta C_{O_0}$ is the elemental oxygen chemical potential), as:

$$p_{O_2} = p_{O_2}^0 \exp \left[ \frac{\Delta C_{O_2} - C_p (T - T_0) + T \left[ S_0 + C_p \ln (T/T_0) \right]}{k_B T} \right]$$

where $C_p = 7/2$ k$_B$ is the constant-pressure heat capacity for a diatomic molecule assuming an ideal gas behavior, $S_0 = 205$ J mol$^{-1}$ K$^{-1}$, k$_B$ is the Boltzmann constant and $p_{O_2}^0$ is the partial pressure under standard conditions i.e., $p_{O_2}^0 = 1$ atm. In order to suppress the formation of Y$_2$O$_3$ at a given temperature ($T$), $p_{O_2}$ should be lower than the value fixed by the three-phase equilibrium regions. Our analysis shows that, at 1000 K, $p_{O_2}$ must be lower than at least 3.3 $\times$ 10$^{-13}$ atm (Y-poor condition) to prevent the formation of Y$_2$O$_3$. Such low oxygen partial pressure is currently not achievable even in ultra-high vacuum systems (10$^{-13}$ atm), suggesting oxidation of Y$_2$Te$_3$ is imminent. However, the above analysis assumes thermodynamic equilibrium, whereas oxidation is often kinetics and diffusion-limited. It is possible that surface oxidation will protect the bulk from further oxidation, as is observed in other chalcogenide-based thermoelectric materials e.g., SnSe$^{77,78}$ and Sc$_2$Te$_3$. Therefore, we recommend that future experimental studies of Y$_2$Te$_3$ pay close attention to the pres-
ence of oxide inclusions in the bulk, as reproducibility has proven difficult in oxidized rare-earth thermoelectric materials such as La$_{3-x}$Te$_4$.\textsuperscript{14,15}

3 Conclusions

We have computationally assessed the prospect of Y$_2$Te$_3$ as a n-type TE material. A high conduction band valley degeneracy contributes to the superior n-type electrical transport properties, which combined with the low lattice thermal conductivity, yields a high figure-of-merit $zT$ > 1.0 when Y$_2$Te$_3$ is optimally doped to electron concentrations of $1 - 2 \times 10^{20}$ cm$^{-3}$. Our defect calculations reveal that Y$_2$Te$_3$ is natively n-type under Y-rich growth conditions due to the facile formation of donor cation interstitials. The free electron concentration can be enhanced through halogen doping on the Te site, with I being the most effective dopant. We also clarify through defect calculations that the reported n-type character of Bi-doped Y$_2$Te$_3$ is not a direct consequence of electron generation from Bi substitution, and further studies are necessary to resolve the unusual experimental observation. We propose that halogens are “better” n-type dopants because they preferentially substitute on the Te site and likely do not perturb the conduction band edge, which is dominated by Y-d states.

CRediT Statement

Michael Toriyama: Conceptualization, Investigation, Data Curation, Writing (Original Draft), Writing (Editing). Dean Cheikh: Investigation, Data Curation, Writing (Editing). Sabah K. Bux: Writing (Editing), Supervision. G. Jeffrey Snyder: Investigation, Writing (Editing), Supervision. Prashun Gorai: Conceptualization, Investigation, Data Curation, Writing (Editing), Supervision, Project Administration.

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Conflicts of interest

There are no conflicts to declare.

Computational Methods

First-principles density functional theory (DFT) calculations were performed using the Vienna Ab initio Simulation Package (VASP).\textsuperscript{79,80} The generalized gradient approximation of Perdew-Burke-Ernzerhof (PBE) was used as the exchange correlation functional.\textsuperscript{81} The core and valence electrons were treated with the projector-augmented wave (PAW) method.\textsuperscript{82,83} A plane-wave energy cutoff of 340 eV was used, and a Hubbard on-site energy correction of $U = 3$ eV was applied to the Y-d orbitals.\textsuperscript{84,85}

The electronic structure of Y$_2$Te$_3$ was calculated from the charge density of the fully-relaxed structure using the tetrahedron method for k-point integration and a Γ-centered $8 \times 8 \times 4$ k-point mesh.\textsuperscript{56} It is well-known that the PBE functional underestimates the band gap of semiconductors and insulators, which directly affects the defect formation energy and resulting charge carrier concentrations. We address the band gap underestimation by shifting the band edge positions based on GW quasiparticle energy calculations.\textsuperscript{87} Due to the presence of Te, we also included band edge shifts due to relativistic spin-orbit coupling (SOC) effects.\textsuperscript{55} The two band edge shifts together result in valence (conduction) band shifts of -0.511 (+0.490) eV relative to the PBE band edges, yielding a band gap of 1.78 eV.

The charge transport properties of Y$_2$Te$_3$ were calculated with the Ab initio Scattering and Transport (AMSET) package.\textsuperscript{81} We found that the transport properties are converged with an interpolated k-point mesh of $33 \times 33 \times 33$. The scissor operator was applied to correct the band gap to 1.78 eV, which was calculated with the GW approximation and adjusted to include SOC effects. We considered acoustic deformation potential, polar optical phonon, and ionized impurity scattering in our transport calculations. The required material parameters were obtained from DFT calculations. Specifically, the elastic stiffness tensor was calculated using the finite difference method, and the static and high-frequency dielectric tensors were calculated using density functional perturbation theory (DFPT). The material parameters used to calculate the scattering rates are summarized in the Supplementary Information. The electrical transport properties, namely the electrical conductivity ($\sigma$), Seebeck coefficient ($S$), and electronic thermal conductivity ($\kappa_e$), were calculated from Onsager coefficients. Given the non-cubic structure of Y$_2$Te$_3$, we report transport properties that are averaged over the three Cartesian directions.

Point defect calculations were performed using the standard supercell approach.\textsuperscript{88–90} A $2 \times 2 \times 1$ supercell of Y$_2$Te$_3$ containing 80 atoms was considered. The pylada-defects software was used to automate the point defect calculations.\textsuperscript{91} Vacancies and antisite defects in charge states ranging between $q = -3$ and $q = +3$ were considered. Additional charge states were considered where necessary e.g., $Y_{12}$ in $q = +4$. The ion positions in defect supercells were relaxed using a $4 \times 4 \times 4 \Gamma$-centered k-point mesh. The formation energy ($\Delta E_{D,q}$) of a point defect $D$ in charge state $q$ was calculated according to the equation

$$\Delta E_{D,q} = E_{D,q} - E_{\text{host}} - \sum_i n_i \mu_i + qE_F + E_{\text{corr}}$$

(3)

where $E_{D,q}$ and $E_{\text{host}}$ are the total energies of the supercell with and without the defect, respectively, and $E_F$ is the Fermi energy. $n_i$ is the number of atoms of element $i$ added ($n_i > 0$) or removed ($n_i < 0$) to create defect $D$. The elemental chemical potentials $\mu_i$ are expressed relative to the reference state chemical potentials ($\mu_i^0$) such that $\mu_i = \mu_i^0 + \Delta \mu_i$, where $\Delta \mu_i$ is the deviation from
the reference state. The reference state chemical potential $\mu_i^0$ of each element was determined by fitting to a set of experimentally-measured formation enthalpies of several compounds under standard conditions. The fitted elemental reference energies for each element considered in this study are listed in Table S1. The values of $\Delta \mu_Y$ and $\Delta \mu_{Te}$ are bounded by the condition of phase stability of $Y_2Te_3$. Mathematically, $\Delta \mu_Y$ and $\Delta \mu_{Te}$ must satisfy the equation $2\Delta \mu_Y + 3\Delta \mu_{Te} = \Delta H_{Y_2Te_3}^{0}$, where $\Delta H_{Y_2Te_3}^{0}$ is the formation enthalpy of $Y_2Te_3$. Additionally, $\Delta \mu_Y$ and $\Delta \mu_{Te}$ must also satisfy the condition that the competing phases ($YTe$, $YTe_2$, $Y_2Te_3$) are unstable.

Corrections to the defect formation energy ($E_{\text{corr}}$) arising from finite-size effects were calculated following the methodology of Lany and Zunger. Finite-size corrections are applied to address: (i) misalignment of the average electrostatic potential between supercells with and without charged defects, (ii) long-range electrostatic interactions between periodic images of point charges, and (iii) Moss-Burnstein band filling due to shallow defects.

The free carrier concentrations were calculated following the charge neutrality condition
\[
\sum_{E} \left[ q N_D e^{-\Delta E_{vbg}/k_BT} \right] + p - n = 0
\]
where $N_D$ is the site concentration, $k_B$ is the Boltzmann constant, and $T$ is the temperature. We use a typical synthesis temperature of 923 K. The hole ($p$) and electron ($n$) concentrations are calculated using the density of states $g(E)$ and the Fermi-Dirac distribution $f(E)$ as
\[
p = \int_{-\infty}^{VBM} g(E) [1 - f(E)] dE
\]
\[
n = \int_{CBM}^{0} g(E) f(E) dE
\]
The density of states was calculated using a $8 \times 8 \times 4$-k-point grid using the tetrahedron integration scheme. The free carrier concentration is the net carrier concentration i.e., $|n - p|$.

References