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High thermoelectric cooling performance of n-type Mg_3Bi_2 -based materials

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Thermoelectric materials have a large Peltier effect, making them attractive materials for solid-state cooling applications. Bi_2Te_3 -based alloys have remained as the state-of-the-art room temperature materials for many decades. However, cost partially limited wider use of thermoelectric cooling devices because of the large amounts of expensive tellurium. We report n-type Mg_3Bi_2 -based materials with a peak ZT of ~ 0.9 at 350 K, which is comparable to the commercial $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$, but much cheaper. A cooling device made of our material and p-type $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ has produced a large temperature difference of ~ 91 K at the hot-side temperature of 350 K. The n-type Mg_3Bi_2 -based materials are promising for thermoelectric cooling applications.

Thermoelectric modules can directly convert electricity into thermal energy for cooling and heating and harvest waste heat for electrical power (1, 2). The global thermoelectric module market was worth ~ 0.6 billion US dollars in 2018 and it is anticipated to reach ~ 1.7 billion US dollars by 2027 (3). Most thermoelectric modules have been used for thermal management since the market for power generation is still in its infancy. The cooling capability of a thermoelectric module largely relies on the performance of the materials used. The performance is governed by the dimensionless figure of merit $ZT = S^2 \rho^{-1} \kappa^{-1} T$, where S is the Seebeck coefficient, ρ the electrical resistivity, κ the thermal conductivity, and T the absolute temperature (4–6). Although advancements have been made on mid- and high- T materials, e.g., lead chalcogenides (7, 8), Skutterudites (9, 10), Mg_2Sn -based materials (11, 12), SnSe (13, 14), and half-Heuslers (15–17), the progress on room-temperature (RT) materials is sluggish. N-type $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ and p-type $\text{Bi}_{2-x}\text{Sb}_x\text{Te}_3$ remained as the state-of-the-art RT thermoelectric materials for the past several decades. Even though enhancements in the thermoelectric performance of nanostructured n-type $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ were reported (18, 19), it is challenging to minimize the electrical contact resistance between the contact material and $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ (20) on top of the anisotropy issue of $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ (18). Despite the progress made on materials, they have not been engineered into viable thermoelectric cooling applications yet. Additionally, the high cost of tellurium (Te) partially limits the wider applications of thermoelectric modules. Identifying new materials with high ZT , low cost, and easy to minimize the contact resistance is essential for the widespread use of thermoelectric cooling modules.

We report the n-type Mg_3Bi_2 -based materials with high ZT

around 300 K. We constructed a unicouple consisting of n-type $\text{Mg}_{3.2}\text{Bi}_{1.498}\text{Sb}_{0.5}\text{Te}_{0.002}$ and p-type $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ (Fig. 1A) and measured the cooling performance (Fig. 1B) (21). The Peltier effect (2) allows us to remove heat from the top, cold-side, copper plate and dissipates it into the bottom, hot-side, copper blocks by applying an electrical current. This results in a T difference between the hot and cold sides (Fig. 1B). This effect increased with increasing current until it eventually saturated at 91 K with the hot-side T maintained at 350 K. We found the hot-side T dependent maximum T difference (ΔT) was higher for our unicouple when compared to the commercial data (Fig. 1B, inset). Different from the nanostructured $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ that has contact issue, we found Fe and Ni were both good contact materials for $\text{Mg}_{3.2}\text{Bi}_2$ -based materials (fig. S2) and fabrication of $\text{Mg}_{3.2}\text{Bi}_{1.498}\text{Sb}_{0.5}\text{Te}_{0.002}$ leg with contact materials was easy (21). Our $\text{Mg}_{3.2}\text{Bi}_2$ -based materials should be much cheaper than $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ as they minimize the need for expensive Te. The cost of thermoelectric materials makes up nearly one third of the total cost for thermoelectric modules (22). Replacing $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ with the Mg_3Bi_2 -based materials should effectively reduce the cost of thermoelectric modules and potentially expand their usefulness for various cooling applications.

N-type Mg_3Sb_2 -based materials with promising thermoelectric performance were reported recently (23–33), mainly targeted for power generation from waste heat. Unlike the semiconducting Mg_3Sb_2 , the isostructural Mg_3Bi_2 is a semi-metal (34–36). We found stoichiometry Mg_3Bi_2 showed p-type conduction (fig. S3B), in agreement with other measurements (34, 35). We attributed the p-type conduction to the presence of a high concentration of Mg vacancies, similar to Mg_3Sb_2 (23, 29). We successfully synthesized n-type Mg_3Bi_2 samples

with excess Mg, *i.e.*, $\text{Mg}_{3+\delta}\text{Bi}_2$ ($\delta = 0.05, 0.1, \text{ and } 0.2$). The thermoelectric properties of these samples were very similar to one another (fig. S3). We focused on $\text{Mg}_{3.2}\text{Bi}_2$ and its carrier concentration (n) was $\sim 2.1 \times 10^{19} \text{ cm}^{-3}$ at 10 K (Fig. 2A, upper panel). Carrier concentration noticeably increased once T was above 150 K. Below 300 K the carrier mobility (μ) was more than $200 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and reached a high value of $\sim 4198 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at 10 K (Fig. 2A, lower panel). The high n and μ in conjunction with the low bipolar conduction T clearly indicated the semi-metallic characteristic of $\text{Mg}_{3.2}\text{Bi}_2$. Electrical resistivity of $\text{Mg}_{3.2}\text{Bi}_2$ was only $\sim 9 \mu\Omega \text{ m}$ at 300 K and $\sim 0.58 \mu\Omega \text{ m}$ at 2 K (Fig. 2B). Seebeck coefficient of $\text{Mg}_{3.2}\text{Bi}_2$ was $\sim 105 \mu\text{V K}^{-1}$ at 300 K and more than $-80 \mu\text{V K}^{-1}$ over a broad T range between 130 K and 350 K. The power factor ($S^2\rho^{-1}$) of $\text{Mg}_{3.2}\text{Bi}_2$ was $\sim 10 \mu\text{W cm}^{-1} \text{ K}^{-2}$ across a broad T range (Fig. 2D). Doping the samples with a small amount of Te effectively modulated n of $\text{Mg}_{3.2}\text{Bi}_2$ (fig. S4A), reducing ρ and slightly enhancing S (Fig. 2, B and C, respectively). This resulted in substantially higher $S^2\rho^{-1}$ on the order of $\sim 20 \mu\text{W cm}^{-1} \text{ K}^{-2}$ over a broad T range (Fig. 2D). We obtained a peak $ZT \sim 0.3$ at 350 K with $\text{Mg}_{3.2}\text{Bi}_{1.998}\text{Te}_{0.002}$ and above 0.1 down to 150 K (fig. S5B).

Semimetals usually have a low Seebeck coefficient due to cancellation between electrons and holes, but the n-type $\text{Mg}_{3.2}\text{Bi}_2$ studied here has a large S , which is essential for its high thermoelectric performance. To understand the origin of the large S , we calculated the band structure of Mg_3Bi_2 (fig. S6A). The band overlap energy we calculated between the conduction band minimum and valence band maximum was $\sim 0.4 \text{ eV}$. However, the two-band modelling estimated this at $\sim 0.1 \text{ eV}$ (fig. S7). We rigidly shifted band structure with the band overlap energy shifted to -0.1 eV (Fig. 3A). The conduction band minimum located along the L-M line with the valley degeneracy of 6 (fig. S8A) and the valence band maximum located around Γ point with the valley degeneracy of 1 (fig. S8B). Different band structures were previously reported for Mg_3Bi_2 (24, 36, 37) due to the choice of pseudo-potential and whether the spin-orbital coupling was considered (36, 37). Due to the presence of electrons and holes in a semi-metal, we expressed S as $S = (\rho_h S_e + \rho_e S_h) / (\rho_e + \rho_h)$, where S_e and S_h were partial S for electrons and holes, respectively, and ρ_e and ρ_h were partial ρ for electrons and holes, respectively. We applied a two-band model to calculate the partial S and μ for $\text{Mg}_{3.2}\text{Bi}_2$. We found the partial S for electrons was noticeably larger than that of the holes (Fig. 3B). We attributed the difference in the partial S to the disparity in density-of-states effective mass m_d^* , $\sim 0.530m_0$ (m_0 is the free electron mass) for the conduction band and $\sim 0.276m_0$ for the valence band (table S1). Density-of-states effective mass depends on the band effective mass (m^*) and the valley degeneracy (N) according to $m_d^* = N^{2/3} m^*$ (38). The different N in the conduction and

valence bands (fig. S8) accounts for the disparity in m_d^* . We also modeled the partial μ of $\text{Mg}_{3.2}\text{Bi}_2$ between 100 K and 350 K (Fig. 3C). We omitted the values under 100 K because they have relatively large uncertainties. Our modeling showed that the electrons have higher μ than that of the holes. Carrier mobility is proportional to $(m^*)^{-3/2} (m_1^*)^{-1}$ when acoustic phonon scattering is the predominant scattering process and m_1^* is the inertial effective mass (38). Based on the density functional theory results, we extracted from the model $m^* \sim 0.161m_0$ for electrons and $\sim 0.276m_0$ for holes and the $m_1^* \sim 0.133m_0$ for electrons, and $\sim 0.259m_0$ for holes (table S1). The differences in the effective masses between conduction and valence bands explained the disparity in μ between electrons and holes. We can quantify the asymmetrical transport properties between the conduction and valence bands by the electron-to-hole weighted mobility ratio $A = (N_e m_e^{*3/2} \mu_e) / (N_h m_h^{*3/2} \mu_h)$ (5, 39–41). When the transport properties were highly asymmetrical, *i.e.*, $A \gg 1$ or $A \ll 1$, a large S at 300 K can be achieved for semi-metals and semiconductors with small E_g (figs. S10 and S11). The calculated electron-to-hole mobility ratio was around 3 and A was above 8 for $\text{Mg}_{3.2}\text{Bi}_2$ (Fig. 3D). The large A contributed to the high S of n-type $\text{Mg}_{3.2}\text{Bi}_2$. Meanwhile, it partially explained why p-type Mg_3Bi_2 has a much lower S and inferior thermoelectric performance (fig. S3). The large S in n-type $\text{Mg}_{3.2}\text{Bi}_2$ is similar to that in single-crystal bismuth, which has an electron-to-hole mobility ratio of ~ 9.19 along the trigonal axis (42–44), $m_d^* \sim 0.113m_0$ for electrons, and $m_d^* \sim 0.093m_0$ for holes (44). As a result, A was as large as ~ 11 along the trigonal axis for bismuth, and thus a high S of $\sim 100 \mu\text{V K}^{-1}$ at 300 K along this direction.

The relatively high κ of $\text{Mg}_{3.2}\text{Bi}_2$ limited the thermoelectric performance (fig. S5A). Partial substitution of Bi with Sb in $\text{Mg}_{3.2}\text{Bi}_2$ should substantially reduce the lattice thermal conductivity (κ_{lat}). We prepared a range of sample with Sb, $\text{Mg}_{3.2}\text{Bi}_{1.998-x}\text{Sb}_x\text{Te}_{0.002}$ ($x = 0, 0.1, 0.3, 0.5, \text{ and } 0.7$). Increased Sb concentration increased ρ of $\text{Mg}_{3.2}\text{Bi}_{1.998-x}\text{Sb}_x\text{Te}_{0.002}$ (Fig. 4A). We measured $\rho \sim 8.1 \mu\Omega \text{ m}$ at 300 K and $\sim 2.2 \mu\Omega \text{ m}$ at 2 K for $\text{Mg}_{3.2}\text{Bi}_{1.998}\text{Te}_{0.002}$. In comparison, we measured $\rho \sim 24.4 \mu\Omega \text{ m}$ at 300 K and $\sim 9.9 \mu\Omega \text{ m}$ at 2 K for $\text{Mg}_{3.2}\text{Bi}_{1.298}\text{Sb}_{0.7}\text{Te}_{0.002}$. We attributed the increased ρ to the reduced n (fig. S13A) and μ (fig. S13B) after Sb alloying. Similarly, Sb alloying greatly enhanced S (Fig. 4B). Room-temperature S was $\sim 129 \mu\text{V K}^{-1}$ for $\text{Mg}_{3.2}\text{Bi}_{1.998}\text{Te}_{0.002}$ and $\sim 229 \mu\text{V K}^{-1}$ for $\text{Mg}_{3.2}\text{Bi}_{1.298}\text{Sb}_{0.7}\text{Te}_{0.002}$. We ascribed the enhancement of S mainly to the reduced n (fig. S13A). In addition, the modified band structure after Sb alloying partially influenced the T -dependence of S . Because Mg_3Bi_2 is a semi-metal while Mg_3Sb_2 is a semiconductor, we expected a band structure

transition from semi-metallic to semiconducting in $\text{Mg}_{3.2}\text{Bi}_{1.998-x}\text{Sb}_x\text{Te}_{0.002}$ solid solutions. To probe the variation in band structure after Sb alloying, we measured the T -dependent ρ of undoped $\text{Mg}_{3.2}\text{Bi}_{2-x}\text{Sb}_x$ ($x = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6$, and 0.7). We described this with $\rho = \rho_{300\text{K}} \exp(E_g / 2k_B T)$ (45) (Fig. 4D and fig. S15). We found a clear semi-metallic to semiconducting transition with increasing Sb concentration. We determined an $E_g \sim -0.013$ eV for $\text{Mg}_{3.2}\text{Bi}_2$ and $\text{Mg}_{3.2}\text{Bi}_{1.9}\text{Sb}_{0.1}$ showed a nearly zero E_g (~ 0.005 eV). All of the samples with Sb concentration of more than 5% ($x > 0.1$) were semiconducting and E_g increased with greater Sb concentration. The reported E_g of $\text{Mg}_{3+\delta}\text{Bi}_{0.89}\text{Sb}_{1.1}\text{Te}_{0.01}$ was ~ 0.240 eV (32) and that of $\text{Mg}_{3.2}\text{Bi}_{1.3}\text{Sb}_{0.7}$ was ~ 0.147 eV. The lower E_g is reasonable because we have a lower Sb concentration. An E_g value of -0.013 eV estimated from the temperature dependence of ρ for $\text{Mg}_{3.2}\text{Bi}_2$ is slightly smaller than the value we estimated from the two-band modelling of ~ -0.10 eV (Fig. 3A and fig. S7). This suggests the band overlap energy of Mg_3Bi_2 should be small, but require high quality single crystal measurements to completely resolve.

We can also understand the transition after Sb alloying from the variation in T -dependent n (fig. S13A). Carrier concentration of $\text{Mg}_{3.2}\text{Bi}_{1.998}\text{Te}_{0.002}$ and $\text{Mg}_{3.2}\text{Bi}_{1.898}\text{Sb}_{0.1}\text{Te}_{0.002}$ increased noticeably with T above 125 K due to the activation of electron-hole pairs from bipolar conduction. This phenomenon was greatly suppressed in $\text{Mg}_{3.2}\text{Bi}_{1.698}\text{Sb}_{0.3}\text{Te}_{0.002}$ and finally minimized in $\text{Mg}_{3.2}\text{Bi}_{1.498}\text{Sb}_{0.5}\text{Te}_{0.002}$ and $\text{Mg}_{3.2}\text{Bi}_{1.298}\text{Sb}_{0.7}\text{Te}_{0.002}$. In addition, the reduced n in $\text{Mg}_{3.2}\text{Bi}_{1.998-x}\text{Sb}_x\text{Te}_{0.002}$ with increasing Sb concentration also indicated the downward shift of the Fermi energies due to upward movement of conduction band edges that opened E_g . Despite the semi-metal to semiconductor transition after Sb alloying, the $S^2\rho^{-1}$ among $\text{Mg}_{3.2}\text{Bi}_{1.998-x}\text{Sb}_x\text{Te}_{0.002}$ samples were comparable (Fig. 4C). We observed a slight enhancement in $S^2\rho^{-1}$ in $\text{Mg}_{3.2}\text{Bi}_{1.898}\text{Sb}_{0.1}\text{Te}_{0.002}$ ($E_g \sim 0.005$ eV) and $\text{Mg}_{3.2}\text{Bi}_{1.698}\text{Sb}_{0.3}\text{Te}_{0.002}$ ($E_g \sim 0.063$ eV) compared to $\text{Mg}_{3.2}\text{Bi}_{1.998}\text{Te}_{0.002}$. Power factors at lower T were reduced due to the substantially reduced μ when the Sb concentration was above 25% ($x > 0.5$) (fig. S13B). We observed a substantial reduction in κ of $\text{Mg}_{3.2}\text{Bi}_{1.998-x}\text{Sb}_x\text{Te}_{0.002}$ with increasing Sb concentration (fig. S15). We attributed this reduction to the substantially reduced κ_{lat} due to alloying scattering (Fig. 4E). The peak κ_{lat} around 20 K was as high as $\sim 9.6 \text{ W m}^{-1} \text{ K}^{-1}$ for $\text{Mg}_{3.2}\text{Bi}_{1.998}\text{Te}_{0.002}$ and only $\sim 3.2 \text{ W m}^{-1} \text{ K}^{-1}$ for $\text{Mg}_{3.2}\text{Bi}_{1.298}\text{Sb}_{0.7}\text{Te}_{0.002}$. The reduced κ_{lat} translated into an enhanced ZT (Fig. 4F). The ZT at 350 K was ~ 0.3 for $\text{Mg}_{3.2}\text{Bi}_{1.998}\text{Te}_{0.002}$ and ~ 0.9 for $\text{Mg}_{3.2}\text{Bi}_{1.498}\text{Sb}_{0.5}\text{Te}_{0.002}$. Although the thermoelectric performance of $\text{Mg}_{3.2}\text{Bi}_{1.998-x}\text{Sb}_x\text{Te}_{0.002}$ decreased with reduced T , both $\text{Mg}_{3.2}\text{Bi}_{1.498}\text{Sb}_{0.5}\text{Te}_{0.002}$ and $\text{Mg}_{3.2}\text{Bi}_{1.298}\text{Sb}_{0.7}\text{Te}_{0.002}$ maintained a ZT above 0.3 down to 200 K. The average ZT between 200 K and 350 K was ~ 0.6 for

$\text{Mg}_{3.2}\text{Bi}_{1.298}\text{Sb}_{0.7}\text{Te}_{0.002}$, ~ 0.6 for $\text{Mg}_{3.2}\text{Bi}_{1.498}\text{Sb}_{0.5}\text{Te}_{0.002}$, and ~ 0.2 for $\text{Mg}_{3.2}\text{Bi}_{1.998}\text{Te}_{0.002}$. We measured the commercial n-type $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ ingot and it showed a ZT of ~ 0.85 at 350 K, comparable to our $\text{Mg}_{3.2}\text{Bi}_{1.998-x}\text{Sb}_x\text{Te}_{0.002}$ (fig. S17). However, the commercial $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ ingot showed a strong anisotropy in the thermoelectric properties due its highly preferred orientation. This requires the thermoelectric legs to be cut along the direction with better performance. In contrast, our $\text{Mg}_{3.2}\text{Bi}_2$ -based materials have nearly isotropic thermoelectric properties and the leg fabrication will be easier. In addition, our $\text{Mg}_{3.2}\text{Bi}_2$ -based materials are mechanically robust while the commercial $\text{Bi}_2\text{Te}_{3-x}\text{Se}_x$ ingot can easily delaminate from the cleavage plane. Further enhancements in the thermoelectric properties of Mg_3Bi_2 -based are very likely, e.g., improving μ and reducing κ_{lat} . Therefore, our n-type Mg_3Bi_2 -based materials are highly attractive for thermoelectric cooling applications.

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discussing the results and commenting on the manuscript. The project was directed and supervised by G.C. and Z.R. **Competing interests:** Z.R. and J.M. have filed a provisional patent application on the work described here. **Data and materials availability:** All data are available in the manuscript and supplementary materials.

SUPPLEMENTARY MATERIALS

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Materials and Methods

Supplementary Text

Figs. S1 to S8

Tables S1 and S2

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Fig. 1. Thermoelectric cooling measurement. (A) Experimental setup for the thermoelectric cooling measurement with a unicouple consisting of p-type $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ and n-type $\text{Mg}_{3.2}\text{Bi}_{1.498}\text{Sb}_{0.5}\text{Te}_{0.002}$. (B) Electrical current dependent T difference (ΔT) between the hot and cold sides at the hot-side T of 350 K. The inset showed the comparison of hot-side T dependent maximum ΔT between our unicouple and commercial data. The commercial data were taken from table S2.

Fig. 2. Electronic thermoelectric properties of $\text{Mg}_{3.2}\text{Bi}_{2-x}\text{Te}_x$. (A) Carrier concentration (upper panel) and mobility (lower panel) of $\text{Mg}_{3.2}\text{Bi}_2$. (B) Electrical resistivity. (C) Seebeck coefficient. (D) Power factor.

Fig. 3. Band structure and transport properties of $\text{Mg}_{3.2}\text{Bi}_2$. (A) Calculated band structure of $\text{Mg}_{3.2}\text{Bi}_2$ with the band overlap shifted to -0.1 eV. (B) Comparison of partial Seebeck coefficients between electrons and holes. (C) Comparison of mobilities between electrons and holes. (D) Electron-to-hole mobility ratio and electron-to-hole weighted mobility ratio.

Fig. 4. Thermoelectric properties of $\text{Mg}_{3.2}\text{Bi}_{1.998-x}\text{Sb}_x\text{Te}_{0.002}$. (A) Electrical resistivity. (B) Seebeck coefficient. (C) Power factor. (D) Estimated bandgap of undoped $\text{Mg}_{3.2}\text{Bi}_{2-x}\text{Sb}_x$. (E) Lattice thermal conductivity. (F) ZT . The measurement errors of $\text{Mg}_{3.2}\text{Bi}_{1.498}\text{Sb}_{0.5}\text{Te}_{0.002}$ were shown in fig. S18.