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<th>Mao, Jun et al. “Manipulation of Ionized Impurity Scattering for Achieving High Thermoelectric Performance in n-Type Mg3Sb2-Based Materials.” Proceedings of the National Academy of Sciences 114, 40 (September 2017): 10548–10553 © 2017 The Authors</th>
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<td>As Published</td>
<td><a href="http://dx.doi.org/10.1073/PNAS.1711725114">http://dx.doi.org/10.1073/PNAS.1711725114</a></td>
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<td>Publisher</td>
<td>National Academy of Sciences (U.S.)</td>
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<td>Version</td>
<td>Final published version</td>
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<td>Accessed</td>
<td>Sun Dec 30 18:39:23 EST 2018</td>
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Manipulation of ionized impurity scattering for achieving high thermoelectric performance in n-type Mg$_3$Sb$_2$-based materials

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Contributed by Ching-Wu Chu, August 24, 2017 (sent for review July 3, 2017; reviewed by Renkun Chen and Lidong Zhao)

Achieving higher carrier mobility plays a pivotal role for obtaining potentially high thermoelectric performance. In principle, the carrier mobility is governed by the band structure as well as by the carrier scattering mechanism. Here, we demonstrate that by manipulating the carrier scattering mechanism in n-type Mg$_3$Sb$_2$-based materials, a substantial improvement in carrier mobility, and hence the power factor, can be achieved. In this work, Fe, Co, Hf, and Ta are doped on the Mg site of Mg$_3$Sb$_2$, and Te$_{0.01}$ is added into the sample, where the ionized impurity scattering crosses over to mixed ionized impurity and acoustic phonon scattering. A significant improvement in Hall mobility from ∼16 to ∼81 cm$^2$/V⋅s$^{-1}$ is obtained, thus leading to a notably enhanced power factor of ∼13 μW cm$^{-1}$ K$^{-2}$ from ∼5 μW cm$^{-1}$ K$^{-2}$. A simultaneous reduction in thermal conductivity is also achieved. Collectively, a figure of merit (ZT) of ∼1.7 is obtained at 773 K in Mg$_3$Co$_{0.1}$Sb$_2$Te$_{0.01}$. The concept of manipulating the carrier scattering mechanism to improve the mobility should also be applicable to other material systems.

thermoelectric | carrier scattering mechanism | ionized impurity scattering | n-type Mg$_3$Sb$_2$ | defects

Thermoelectric devices that can directly convert heat into electricity, and vice versa, can be used in waste heat recovery and cooling applications (1–3). This solid-state conversion technology has advantages in terms of its compactness for high power density, its capability to provide cleaner energy, and its long lifetime. However, the relatively low efficiency of thermoelectric modules has limited their application to niche markets. The efficiency of thermoelectric devices is determined by the Carnot efficiency and the material’s figure of merit (ZT), which is defined as $ZT = (S^2/κT)$, where $S$ is the Seebeck coefficient, $κ$ is the electrical conductivity, $κ_T$ is the thermal conductivity ($κ = κ_{\text{ele}} + κ_{\text{lat}}$, where $κ_{\text{ele}}$ is the electronic part and $κ_{\text{lat}}$ is the lattice part), and $T$ is the absolute temperature (4–6).

The challenge of improving the ZT lies in the fact that the thermoelectric parameters $S$, $κ$, and $κ_{\text{ele}}$ are strongly interdependent (7). Therefore, two basic approaches have been used to enhance the ZT via decreasing the relatively independent lattice thermal conductivity or increasing the power factor (i.e., $S^2/κ$). Phonon scattering via defect engineering [point defects (8–11), dislocations (12–15), and grain boundaries (16, 17)] or nanostructuring (18) has led to a significant reduction in lattice thermal conductivity. On the other hand, power factors have also been enhanced via different approaches such as band engineering (19–22), inducing resonant levels (23), the carrier filtering effect (24–27), ionized impurity scattering (28), and modulation doping (29, 30).

Generally, power factors have been optimized by tuning the carrier concentration so that a compromise between the Seebeck coefficient and the electrical conductivity is reached. Strategies for further improving power factors have mainly focused on enhancing the Seebeck coefficient (e.g., resonant levels, the carrier filtering effect, ionized impurity scattering), while a few have been aimed at boosting the mobility (e.g., modulation doping). However, Seebeck coefficient enhancement is usually accompanied by a noticeable reduction in carrier mobility (23, 28), which deteriorates the electrical conductivity, and therefore results in limited power factor improvement. In fact, the importance of increasing mobility to improve the power factor should be recognized. Its importance can be understood from the fact that since the Seebeck coefficient is strongly coupled with the electrical conductivity via carrier concentration rather than mobility, the improved mobility will monotonously increase the electrical conductivity without affecting the Seebeck coefficient, thus substantially improving the power factor.

The carrier mobility, $μ$, can be expressed as follows (31):

$$μ = \frac{e\langle τ \rangle}{m^*},$$

where $e$ is the electron charge, $m^*$ is the effective mass, and $\langle τ \rangle$ is the average relaxation time. In the simplest case, the relaxation time

**Significance**

Higher carrier mobility can contribute to a larger power factor, so it is important to identify effective means for achieving higher carrier mobility. Since carrier mobility is governed by the band structure and the carrier scattering mechanism, its possible enhancement could be obtained by manipulating either or both of these. Here, we report a substantial enhancement in carrier mobility by tuning the carrier scattering mechanism in n-type Mg$_3$Sb$_2$-based materials. The ionized impurity scattering in these materials has been shifted into mixed scattering by acoustic phonons and ionized impurities. Our results clearly demonstrate that the strategy of tuning the carrier scattering mechanism is quite effective for improving the mobility and should also be applicable to other material systems.


Reviewers: R.C., University of California, San Diego; and L.Z., Beihang University.

The authors declare no conflict of interest.

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This article contains supporting information online at www.pnas.org/lookup/suppl/doi:10.1073/pnas.1711725114/-/DCSupplemental.
time is a function of carrier energy, $E$; temperature; and effective mass:

$$\tau \propto E^r T^m (m^*)^r.$$  \[2\]

Since $\tau$ varies for different scattering mechanisms, the mobility could be tuned by manipulating the carrier scattering mechanism.

Recently, a record high room temperature power factor of $\sim 106 \mu W \cdot cm^{-1} \cdot K^{-2}$ was obtained in NbFeSb-based materials by optimizing the hot-pressing temperature (32). This high power factor originates from the noticeably improved mobility, which is due to the variation in the carrier scattering mechanism. Tamaki et al. (33) reported $n$-type Mg$_2$Sb$_2$-based materials with high thermoelectric performance via introducing extra Mg and Te doping, and similar results were also reported by Zhang et al. (34). Most recently, Shuai et al. (35) reported that substantial improvements in the room temperature Hall mobility and power factor were achieved in Nb double-doped $n$-type Mg$_2$Sb$_2$-based materials. These materials showed mixed scattering due to ionized impurities and acoustic phonons, instead of being dominated by ionized impurity scattering. Therefore, these results unambiguously demonstrate that mobility can indeed be enhanced by tuning the carrier scattering mechanism.

The variation in the carrier scattering mechanism induced by Nb-doping in $n$-type Mg$_2$Sb$_2$-based materials is quite intriguing. It is natural to ask whether any other dopants have a similar effect and, more importantly, what are the underlying physics for such a phenomenon. Therefore, the motivation behind this work is to further investigate the carrier scattering mechanism in $n$-type Mg$_2$Sb$_2$-based materials. In the following discussion, it will be demonstrated that, in addition to Nb, transition-metal elements such as Fe, Co, Hf, and Ta show a similar effect in tuning the carrier scattering mechanism. In these cases, significant enhancements in the room temperature Hall mobility, $\mu_H$ (from $\sim 16 \rightarrow \sim 81 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$), and power factor (from $\sim 5$ to $\sim 13 \mu \text{W} \cdot \text{cm}^{-1} \cdot \text{K}^{-2}$) are observed. A simultaneous reduction in the thermal conductivity is also achieved, and, finally, a $ZT$ of $\sim 1.7$ is obtained in Mg$_{2.1}$Co$_{0.9}$Sb$_{1.5}$Bi$_{0.49}$Te$_{0.01}$.

**Results and Discussion**

Based upon the composition of Mg$_{3.2}$Sb$_{3.2}$Bi$_{0.49}$Te$_{0.01}$, which showed the best thermoelectric performance among the Mg$_2$Sb$_2$-based materials from the report by Tamaki et al. (33), doping on the Mg site by different elements (Hf, V, Ta, Mo, W, Fe, Co, Ni, and Zn) was investigated. Among these elements, Fe, Co, Hf, and Ta have shown an effect similar to that of Nb in tuning the carrier scattering mechanism (Fig. 1A). Detailed thermoelectric properties of Mg$_{3.2}$Co$_{0.8}$Sb$_{3.2}$Bi$_{0.49}$Te$_{0.01}$ ($T = \text{Mo, V, W, Ni, and Zn}$) are shown in SI Appendix, Fig. S1. For clarity, Mg$_{3.2}$Co$_{0.8}$Sb$_{3.2}$Bi$_{0.49}$Te$_{0.01}$ ($A = \text{Fe, Co, Hf, and Ta}$) will be referenced as double-doped specimens in the following discussion.

Although a slight difference in the magnitude of electrical conductivity is observed between Tamaki et al.’s results (33) and our data for Mg$_{3.2}$Sb$_{3.2}$Bi$_{0.49}$Te$_{0.01}$, the temperature dependences for the two specimens are quite similar. In sharp contrast, the temperature dependences at lower temperatures for double-doped specimens are noticeably different from that of Mg$_{3.2}$Sb$_{3.2}$Bi$_{0.49}$Te$_{0.01}$. Temperature-dependent Hall mobility is shown in Fig. 1B, where distinctly different temperature dependences at lower temperatures can be observed and a substantial difference in Hall mobility is noted. The room temperature Hall mobility is $\sim 16 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ for Mg$_{3.2}$Sb$_{3.2}$Bi$_{0.49}$Te$_{0.01}$, while it is more than $\sim 50 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ for the double-doped specimens. Mg$_{3.2}$Co$_{0.8}$Sb$_{3.2}$Bi$_{0.49}$Te$_{0.01}$ shows the highest mobility of $\sim 81 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$, an increase of more than 400% compared with that of Mg$_{3.2}$Sb$_{3.2}$Bi$_{0.49}$Te$_{0.01}$. It is important to note that the Hall mobilities are quite comparable at higher temperatures, which should be ascribed mainly to the similar temperature dependence (i.e., the similar carrier scattering mechanism). This clearly indicates that the carrier scattering mechanism plays a critical role in the carrier mobility.

The relationship between the temperature exponent (derived from the Hall mobility) and composition is shown in Fig. 1C. In the lower temperature range, Mg$_{3.2}$Sb$_{3.2}$Bi$_{0.49}$Te$_{0.01}$ shows ionized impurity scattering, while the double-doped specimens are dominated by mixed scattering of ionized impurities and acoustic phonons. In the higher temperature range, all of the specimens are dominated by acoustic phonon scattering. The difference between the measured temperature exponent and the theoretical value for certain carrier scattering mechanisms (1.5 for ionized impurity scattering and $-1.5$ for acoustic phonon scattering) is noted, which could be partly ascribed to the assumptions involved in deriving the carrier scattering mechanism (e.g., it is usually assumed that the band is parabolic, but it could actually be a complex band structure). Fig. 1D shows the relationship between the Hall carrier concentration, $n_{H}$, and the Hall mobility. For Mg$_{3.2}$Sb$_{3.2}$Bi$_{0.49}$Te$_{0.01}$, where the ionized impurity scattering is dominant, the Hall mobility is quite low (less than $\sim 20 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$) (35). Generally, the increased concentrations of ionized impurities and carriers will lead to enhanced ionized impurity scattering (36–38) and stronger electron-electron scattering (39–41), respectively. In other words, Hall mobility usually increases with decreasing the Hall carrier concentration. However, since the Hall carrier concentration of the double-doped specimens is similar to that of Mg$_{3.2}$Sb$_{3.2}$Bi$_{0.49}$Te$_{0.01}$ ($x < 0.01$), the noticeable enhancement in Hall mobility after doping of transition-metal elements cannot be ascribed simply to the reduced Hall carrier concentration.

Fig. 2A shows the temperature-dependent Seebeck coefficient, indicating that all of the double-doped specimens show slightly higher Seebeck coefficients than that of the Mg$_{3.2}$Sb$_{3.2}$Bi$_{0.49}$Te$_{0.01}$. The relationship between the Seebeck coefficient and the Hall carrier concentration can be understood well from the Pisarenko plot, as shown in Fig. 2B. Mg$_{3.2}$Sb$_{3.2}$Bi$_{0.49}$Te$_{0.01}$ and Mg$_{3.2}$Sb$_{3.2}$Bi$_{0.49}$Te$_{0.01}$ ($x < 0.01$) (35) show good agreement with the calculated Seebeck coefficient by considering the ionized impurity scattering. In contrast, all of the
shows the lowest thermal conductivity, which could be due to the fact that Co has the highest solubility at the Mg site among all of the dopants (SI Appendix, Figs. S2 and S3). Owing to the substantially improved power factors and reduced thermal conductivities, ZTs have been effectively improved for the double-doped specimens, where a peak ZT of ~1.7 is obtained in Mg$_{0.9}$Co$_{0.1}$Sb$_{1-x}$Te$_{0.01}$ (as shown in Fig. 4B). The engineering dimensionless ZT[$(ZT)_{eng}$] can be used to reliably and accurately predict the practical conversion efficiency (43). Therefore, the hot-side temperature ($T_H$)-dependent $(ZT)_{H}$ is calculated as shown in Fig. 4C, where a noticeable increase in $(ZT)_{H}$ is observed for the double-doped specimens. The $(ZT)_{H}$ at the cold-side temperature ($T_C$) of 323 K and $T_H$ of 773 K is ~0.67 for Mg$_{0.9}$Sb$_{1-x}$Bi$_{0.01}$Te$_{0.01}$ but ~0.97 for Mg$_{0.9}$Co$_{0.1}$Sb$_{1-x}$Bi$_{0.01}$Te$_{0.01}$, an increase of ~45%. The average ZT $(ZT)_{avg}$ is calculated by the integration method over the temperature range of 300 to 773 K. Comparison of the $(ZT)_{avg}$ is shown in Fig. 4D, where the $(ZT)_{avg}$ is ~0.87 for Mg$_{0.9}$Sb$_{1-x}$Bi$_{0.01}$Te$_{0.01}$ but more than ~1.05 for double-doped specimens. A high $(ZT)_{avg}$ of ~1.19 is obtained in Mg$_{0.9}$Co$_{0.1}$Sb$_{1-x}$Bi$_{0.01}$Te$_{0.01}$, an increase of ~37% compared with Mg$_{0.9}$Sb$_{1-x}$Bi$_{0.01}$Te$_{0.01}$. Detailed composition-dependent thermoelectric properties of Mg$_{0.9}$Co$_{0.1}$Sb$_{1-x}$Bi$_{0.01}$Te$_{0.01}$ (x = 0, x = 0.025, x = 0.05, x = 0.075, and x = 0.1) are also investigated, and an improvement in thermoelectric performance with an increased Co concentration can be observed (SI Appendix, Figs. S4 and S5).

To understand the reason for the variation in carrier scattering mechanisms, temperature-dependent Hall carrier concentrations for different specimens are compared, as shown in Fig. 5A. The Hall carrier concentrations of the double-doped specimens are either nearly temperature-independent (Fe and Co) or increase slightly with temperature (Hf and Ta). In striking contrast, Mg$_{0.9}$Sb$_{1-x}$Bi$_{0.01}$Te$_{0.01}$ shows an anomalous temperature-dependent Hall carrier concentration that decreases with temperature in the range of 300-500 K. Such unusual temperature dependence of the Hall carrier concentration has rarely been reported. To confirm the obtained results, the Hall carrier concentration was measured during both heating and cooling cycles, and similar results were observed (Fig. 5B). Repeated measurements were also conducted, in addition to the enhanced power factors in double-doped specimens, lower thermal conductivity is achieved, as shown in Fig. 4A. The reduction in thermal conductivity could be partially ascribed to the phonon scattering by point defects. Mg$_{0.9}$Co$_{0.1}$Sb$_{1-x}$Bi$_{0.01}$Te$_{0.01}$ shows the lowest thermal conductivity, which could be due to the fact that Co has the highest solubility at the Mg site among all of the dopants (SI Appendix, Figs. S2 and S3). Owing to the substantially improved power factors and reduced thermal conductivities, ZTs have been effectively improved for the double-doped specimens, where a peak ZT of ~1.7 is obtained in Mg$_{0.9}$Co$_{0.1}$Sb$_{1-x}$Te$_{0.01}$ (as shown in Fig. 4B).
The thermal equilibrium concentration of the neutral Mg vacancy is expressed as follows (46):

\[
c_{V_{Mg}}^0 = c_0 \exp \left[ -\frac{E_{V_{Mg}}}{kT} \right],
\]

where \(c_0\) is the crystal atom density and \(g_{V_{Mg}}\) is the Gibbs free energy of formation of \(V_{Mg}^0\).

Therefore, the concentration of charged Mg vacancies is strongly temperature-dependent. In fact, the charged vacancies usually tend to increase with temperature. The charged Mg vacancies will inevitably change with the measured Hall carrier concentration according to the charge neutrality condition (45):

\[
n = c_{V_{Mg}}^0 - 2c_{V_{Mg}}^{-} - 3c_{V_{Mg}}^{+} + p.
\]

Clearly, the carrier concentration depends upon the concentrations of dopant (Te) and charged defects \((V_{Mg}^{\pm}\) and \(V_{Mg}^{0}\)), as well as minority carrier (hole) concentration. To explain the temperature dependence of the Hall carrier concentration in MgSb-based materials, neutron powder diffraction was conducted for MgSb-based materials. The Rietveld refinements for the two specimens are shown in SI Appendix, Fig. S7. To achieve stable and converging refinement for the neutron powder diffraction of the samples, some assumptions were made, and the details can be found in SI Appendix. The refinement for MgSb indicates that Mg1 site, [1/3, 2/3, 0.6292(7)], is 100% occupied, while the Mg2 site, (0, 0, 0), is only 89% occupied. This implies that Mg vacancies indeed exist in MgSb and that they preferentially locate at the Mg2 site with a concentration of 11 ± 2%. Likewise, in MgSb, the Mg1 site, [1/3, 2/3, 0.6236(9)], was found to be fully occupied. Co only dopes onto the Mg2 site, and the total occupancy of this site was found to be 91 ± 2% (SI Appendix, Fig. S7 and Table S1). This implies that the Co doping reduces the concentration of Mg vacancies, which could explain why the transition-metal-doped samples do not show the anomalous temperature dependence of the Hall carrier concentration (Fig. 5A). In addition, it is worth noting that a proposed Mg interstitial site, (0, 0, 1/2), (33) did not fit well to the data, and refinement for MgSb was found to be fully occupied. Neutron powder diffraction was conducted for MgSb-based materials.

Fig. 5. Temperature-dependent Hall carrier concentrations of MgSb-based materials (A) and MgSb (B) (A = Fe, Co, Hf, and Ta) (insets) Schematic views of ionization and deionization of the Mg vacancy.
One critical question is how the unique temperature dependence of the Hall carrier concentration relates to the variation in the carrier scattering mechanism. In principle, the carrier mobility, when ionized impurity scattering is dominant, can be expressed as follows (39):

\[
\mu_1 = \frac{2^{1/2}}{\pi^{3/2}} K^2 (K^2) (m^*)^{1/2} e^2 N_i \ln(1 + b) - b/1 + b^2 \frac{1}{4},
\]

where \( K \) is the dielectric constant, \( N_i \) is the ionized impurity concentration, \( k \) is the Boltzmann constant, and \( h \) is the reduced Planck constant.

According to the Pisarenko plot (Fig. 2B), all of the specimens can be described well by considering different carrier scattering mechanisms with an identical \( m^* \), which means the \( m^* \) should remain unchanged or quite similar after doping. It was previously assumed that the improved mobility is due to an increased dielectric constant after the transition-metal doping (35). Indeed, the dielectric constant is sensitive to the trace amounts of dopants in various material systems (47–53). However, this seems not to be the case for the n-type MgSb-based materials, where the calculated dielectric constants for MgSb and MgSb\(_{1.5}\)Bi\(_0.5\) are quite comparable considering the fact that up to 25% of the Sb has been replaced by Bi (SI Appendix, Table S2).

Therefore, the variation in the Hall mobility should not come from the variation in the material’s intrinsic parameters (\( m^* \) and \( K \)). It should be noted that the ionized impurity concentration can be approximated to be the carrier concentration only when one type of dopant is present. In the case of multiple types of dopants, the ionized impurity concentration could be larger than the carrier concentration. In the n-type MgSb-based materials, the ionized impurities include both the ionized Te atoms and the charged Mg vacancies. The Rietveld refinement of neutron powder diffraction and the temperature-dependent Hall carrier concentration show that the double-doped specimens have lower concentrations of charged Mg vacancies. The noticeable difference in thermoelectric properties between the double-doped specimens and MgS\(_2\)Sb\(_{1.5}\)Bi\(_0.5\) indicates that charged Mg vacancies play a central role in the carrier scattering mechanism, and hence the thermoelectric properties of n-type MgSb-based materials.

In both NbFeSb (32) and n-type MgSb-based materials (35), the carrier scattering mechanism at a lower temperature shifted from extrinsic scattering mechanisms (i.e., grain boundary scattering, ionized impurity scattering) toward acoustic phonon scattering. Although different approaches (i.e., increasing hot-pressing temperature, doping) were used, the key idea of manipulating the carrier scattering mechanisms is identical, and relies on the control of defects (i.e., grain boundaries, Mg vacancies). Therefore, to apply this strategy to other material systems, it is first necessary to identify the defect that is responsible for the dominant carrier scattering mechanism and then to try to control it. In fact, since the dominant carrier scattering mechanism (especially in the lower temperature range) could be different for different materials, this concept should be applicable to a variety of other material systems for enhancing thermoelectric performance.

Conclusions

Ionized impurity scattering in the n-type MgSb-based materials is investigated further. Our results demonstrate that by doping transition-metal elements such as Fe, Co, Hf, and Ta at the Mg site of Mg\(_3\)Sb\(_1.5\)Bi\(_0.49\)Te\(_{0.01}\), the dominant ionized impurity scattering at a lower temperature changes to a mixed scattering of acoustic phonons and ionized impurities, thus noticeably improving the Hall mobility and power factor. A simultaneous reduction in thermal conductivity is achieved, and, finally, a ZT of ~1.7 is obtained in Mg\(_3\)Co\(_0.5\)Sb\(_1.5\)Bi\(_0.49\)Te\(_{0.01}\). Our work demonstrates that the carrier scattering mechanism could play a vital role in the thermoelectric properties of the material, and the concept of tuning the carrier scattering mechanism should be widely applicable to a variety of material systems.

Experimental Section

Synthesis. Mg turnings (99.98%; Alfa Aesar), Bi pieces (99.99%; Alfa Aesar), Sb shots (99.8%; Alfa Aesar), Te pieces (99.999%; Alfa Aesar), Hf crystals (99.9%; Altantic Metals & Alloys), V powders (99.5%; Alfa Aesar), Ta powders (99.9%; Alfa Aesar), Mo powders (99.95%; Alfa Aesar), W powders (99.9%; Alfa Aesar), Fe powders (99%; Alfa Aesar), Co powders (99.9%; Alfa Aesar), Ni powders (99%; Alfa Aesar), and Zn powders (99.9%; Alfa Aesar) were weighed according to the composition of Mg\(_3\)Sb\(_1.5\)Bi\(_0.49\)Te\(_{0.01}\) (A = Hf, Te, Co, Ni, and Zn). The elements were loaded into a stainless-steel ball-milling jar in a glove box under an argon atmosphere with an oxygen level below 0.1 ppm. The materials were ball-milled for 10 h and then loaded into a graphite die with an inner diameter of 12.7 mm. The graphite die with the ball-loaded powder was then removed from the glove box and immediately sintered by hot pressing at 923 K under a pressure of ~80 MPa for 2 min. The hot-pressed disks are about 2–3 mm thick.

Thermoelectric Property Characterizations. All of the samples were cut into pieces with dimensions of about 2 mm × 2 mm × 12 mm for simultaneous electrical resistivity and Seebeck coefficient characterizations under an He atmosphere (ZEM-3; ULVAC Riko). Thermal conductivity, \( k \), was calculated using the measured density, \( \rho \), determined by the Archimean method, thermal diffusivity, \( D \), and the thermal effusivity, \( \kappa \), by the laser flash method (LFA 457; Netzsch), and specific heat, \( c_p \) (SI Appendix, Fig. S8B) by differential scanning calorimetry (DSC 404 C; Netzsch). The Hall coefficient, \( R_H \), was measured at room temperature on a commercial system (PPMS; Quantum Design) using a four-probe configuration, with the magnetic field sweeping between +3 T and −3 T and an electrical current between 10 mA and 20 mA. The temperature-dependent Hall measurement was conducted under a reversible magnetic field of 1.5 T using the Van der Pauw technique from 300 to 773 K. The Hall carrier concentration, \( n_H \), and the carrier mobility, \( \mu \), were calculated via \( n_H = 1/(e R_H) \) and \( \mu = D/\rho \).

Thermoelectric properties show good thermal stability during the cooling and heating cycles (SI Appendix, Fig. S9).

Structure and Phase Composition. The phase composition of the samples was characterized by X-ray diffraction (PANalytical X’pert PRO diffractometer with a Cu K\(_\alpha\) radiation source).

Neutron Diffraction. Neutron powder diffraction data were taken on samples of Mg\(_3\)Sb\(_1.5\)Bi\(_0.49\)Te\(_{0.01}\) and Mg\(_3\)Co\(_0.5\)Sb\(_1.5\)Bi\(_0.49\)Te\(_{0.01}\) in an ambient environment on HB-2A at the High Flux Isotope Reactor at Oak Ridge National Laboratory, A Ge (115) monochromator (\( \lambda = 1.54 \) Å) and open 2\( \theta \) = 12’ collimation corresponding to before the monochromator, before the sample, and before the detector, respectively, were used. Pattern refinement was performed using the Rietveld method in FullProf (S4), and the details for the refinement are shown in SI Appendix, Fig. S7 and Table S1.

First Principles Density Functional Calculations. Dielectric tensors were calculated using the density functional perturbation theory implemented in the VASP code (55). We used the generalized gradient approximation of Perdew et al. (56) and standard projector-augmented wave pseudopotentials. A plane-wave cutoff of 520 eV was used for the valence wavefunctions, and the Mg 2p and Bi 5d orbitals were included as valence states. We used relaxed lattice parameters and atomic coordinates for the calculations of dielectric tensors in both MgSb\(_2\) and MgSb\(_{1.5}\)Bi\(_0.5\).

ACKNOWLEDGMENTS. The work performed at the University of Houston and the University of Missouri is supported by the Solid State Solar-Thermal Energy Conversion Center, an Energy Frontier Research Center funded by the US Department of Energy, Office of Science, Office of Basic Energy Sciences under Award DE-SC0001299, as well as by US Air Force Office of Scientific Research Grant FA9550-15-0236, the T. L. L. Temple Foundation, the John J. and Rebecca Moores Endowment, and the State of Texas through the Texas Center...