The Electronic Transport Channel Protection and Tuning in Real Space to Boost the Thermoelectric Performance of Mg$_{3+\delta}$Sb$_2$-$y$Bi$_y$ near Room Temperature

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The optimization of thermoelectric materials involves the decoupling of the transport of electrons and phonons. In this work, an increased Mg$_1$-Mg$_2$ distance, together with the carrier conduction network protection, has been shown as an effective strategy to increase the weighted mobility ($U = \mu m^{3/2}$) and hence thermoelectric power factor of Mg$_{3+\delta}$Sb$_2$-$y$Bi$_y$ family near room temperature. Mg$_{3+\delta}$Sb$_{0.5}$Bi$_{1.5}$ has a high carrier mobility of 247 cm$^2$ V$^{-1}$ s$^{-1}$ and a record power factor of 3470 $\mu$W m$^{-1}$ K$^{-2}$ at room temperature. Considering both efficiency and power density, Mg$_{3+\delta}$Sb$_{1.0}$Bi$_{1.0}$ with a high average ZT of 1.13 and an average power factor of 3184 $\mu$W m$^{-1}$ K$^{-2}$ in the temperature range of 50-250°C would be a strong candidate to replace the conventional n-type thermoelectric material Bi$_2$Te$_2.7$Se$_{0.3}$. The protection of the transport channel through Mg sublattice means alloying on Sb sublattice has little effect on electron while it significantly reduces phonon thermal conductivity, providing us an approach to decouple electron and phonon transport for better thermoelectric materials.

1. Introduction

Thermoelectric (TE) materials offer the convenience to convert the widely distributed waste heat into electric power directly, which is highly desired for the autonomous operation of the Internet of things (IoT) in recent years. The conventional room temperature (RT) thermoelectric material, Bi$_3$Te$_3$ family, dominates the market of the solid-state refrigeration [1, 2]. However, its mediocre mechanical property and the extremely low abundance of Te element limit its application [3]. The past years have witnessed great progress in developing medium-temperature thermoelectric materials, but not so much in near room temperature TE materials. So far, there is no candidate material that can compete with the Bi$_2$(Te$_{0.5}$Se$_{0.5}$)$_3$ family in terms of near room temperature TE performance. In our previous report, we have shown that the Mn-doped Mg$_{3+\delta}$Sb$_{1.5}$Bi$_{0.5}$ ((ZT)$_{\text{avg}}$ = 1.05, $K_{\text{IC}}$ = 2.2-3.0 MPa m$^{1/2}$) would be a very promising candidate for substituting the Bi$_2$Te$_{2-x}$Se$_x$ family ((ZT)$_{\text{avg}}$ = 0.9 – 1.0, $K_{\text{IC}}$ = 0.6-1.3 MPa m$^{1/2}$) in the temperature range of 50-250°C because of the comparable average ZT and much higher fracture toughness [4]. It is noted that intensive efforts have been made into searching high ZT composition in the Bi-rich Mg$_{3+\delta}$Sb$_2$-$y$Bi$_y$ with varying doping [5-7]. Imasato et al. researched Bi content-dependent thermoelectric properties and discovered that Mg$_{3+\delta}$Sb$_{0.5}$Bi$_{1.4}$ shows exceptional thermoelectric performance [8]. Ren et al. produced a thermoelectric cooling couple with Mg$_{3+\delta}$Sb$_0.5$Bi$_{1.5}$ and Bi$_0.5$Sb$_{1.5}$Te$_3$, which realized $\Delta T$ around 90 K at the hot-side $T$ of 350 K. Further improvement on the power factor is desirable for power generation applications [9]. However, the power factor of the reported
Mg vacancy and obtain stable n-type samples [19]. How-
tally, excess Mg is necessary to suppress the formation of
but not to the disordering Bi/Sb [18, 27, 28]. Experimen-
tially, we found the Bi-rich Mg3+0.5Sb0.5Bi with interstitial dopant Mn and anionic dopant Te has a recorded high carrier mobility of 247 cm² V⁻¹ s⁻¹ and a high power factor of 3470 μW m⁻¹ K⁻² at room temperature in the Mg8.5Sb0.5Bi,5 sample. The Mg3+0.5Sb0.5Bi,0 possesses a high average ZT of 1.13 and an average PF of 3184 μW m⁻¹ K⁻² in the temperature range of 50-250°C.

2. Results and Discussion

Figure 1 shows the effect of increased Mg₁-Mg₂ distance in real space on the band structure and Hall mobility. Our moti-
vation was to find a way to further tailor the charge conduc-
tive network in real space and make it more favorable for the
transport of electrons. Mg₂Sb₂ has a trigonal structure (space
group: P3m1) and a layered structure with alternate layers of
Mg and [Mg₂Sb₂] in the ab-plane [18], as shown in Figure 1(a). Recently, Sun et al. suggested that part of the conduction band minimum (CBM) originates from the covalence-like bonding state of Mg₁ 3s orbital and Mg₂ 3s orbital and there was also a small amount of antibonding-
like interaction between Mg₁ 3s and Sb 5s orbitals, where Mg₁ represents the Mg at the Sb-octahedral center (0, 0, 0) while Mg₂ is the Mg at the tetrahedral center (0.3333, 0.6667, 0.3718(4)) [29]. Figure 1(b) shows the charge density in (011) plane of the trigonal Mg₂Sb₂. Detailed analysis of the band composition near CBM shows that the states near CBM consist of Mg₁ 3s orbitals, Mg₂ 3s orbitals, and Sb 5s orbitals. The most weighted contribution to the conduction network comes from the dispersive Mg₁ 3s orbitals. Furthermore, our first-principles calculations also suggest that an increase in Mg₁-Mg₂ distance reduces the overlap of Mg₁ 3s and Mg₂ 3s orbitals that constitute the Mg₁-Mg₂ “bond.” As the distance between Mg₁ and Mg₂ increases with strain, the difference of the squared wave function, between pristine and
the one with 4% strain, shows that (i) the overlap of Mg₁ 3s and Mg₂ 3s orbitals at CBM reduces and (ii) the released charge would go to Mg₁ 3s orbitals and enhance the anti-
bonding between Mg₁ 3s orbitals that is the most pro-
nounced constituent around CBM (see Figure 1(c)). Therefore, it leads to a more dispersive band (i.e., lighter band) (see Figure 1(d)). The red line with solid circles in Figure 1(d) plots the DOS effective mass of conduction band minimum of Mg₂Sb₂ as a function of the strain along the c-axis. An almost linear decrease in the band effective mass is observed when the strain increases from 1% to 4%. When acoustic phonon scattering is considered as the dominant scattering mechanism, the maximum power fac-
tor is proportional to the ratio N_e/m* (the derivation is
given in SI A). A smaller effective mass (lighter band)
corresponds to the higher carrier mobility and the increased power factor [27, 30, 31]. Li et al. also suggested an enhanced power factor of Mg$_3$SbBi as a biaxial strain was used in their first-principles calculation [28].

Figure 2 provides more information on the relation between carrier effective mass of Mg$_3$Sb$_2$ and Mg$_{1-Mg_2}$ distance according to our first-principles calculations. Experimentally, partial substitution of Sb atoms with Bi atoms expands the crystalline lattice, as shown in Figure 2(a). The XRD patterns of Mg$_3$Sb$_{1.5}$Bi$_{0.5}$ ($y = 1.0–2.0$) powders (grinded by SPS bulks) are given in Fig. S1 (SI). All the samples show a single phase with a La$_2$O$_3$-type trigonal structure. The lattice parameters and distance of Mg$_1$-Mg$_2$ are derived from the Rietveld refinement. An almost linear expansion is observed that the lattice parameter $c$ varies from 7.296 Å to 7.416 Å (Fig. S2, SI) with increasing Bi content, indicating a complete solid solution of Mg$_3$Sb$_2$ and Mg$_3$Bi$_2$, and the $c/a$ ratio remained around 1.587, which is close to that of pure Mg$_3$Sb$_2$. As a result, the Mg$_1$-Mg$_2$ distance increases from 3.832 Å to 3.891 Å as the Bi content increases from $y = 1.0$ to $y = 2.0$. The estimated Mg$_1$-Mg$_2$ distances in Mg$_3$Sb$_2$ and Mg$_3$Sb$_{1.5}$Bi$_{0.5}$ are 3.761 Å and 3.786 Å, respectively. Figure 2(b) plots the effective mass at the conduction band edge. The inset compares the calculated charge density distribution of the two cases in the a-b cross section at the c-axis fractional coordinate $z = 0.18$, with the same setting of isosurface around 15% of the maximum values.

Figure 1: (a) Crystalline structure of Mg$_3$Sb$_2$ with Mn at the interstitial site. (b) Charge density in (011) plane. (c) The square of real-space wave function (i.e., the "charge" density) at CBM along Mg$_1$-Mg$_2$ line for Mg$_3$Sb$_2$ bulk (black solid line), under 4% strain (red solid line) along the c-axis and the difference (black dotted line) between "charge" density of Mg$_3$Sb$_2$ under 4% strain and bulk. Clear reduction of the covalence-like overlap of Mg$_1$ and Mg$_2$ 3s orbitals between Mg$_1$ and Mg$_2$ is shown with the strain and the released "charge" mostly goes to Mg$_1$. (d) Strain-dependent effective mass at conduction band edge. The inset compares the calculated charge density distribution of the two cases in the a-b cross section at the c-axis fractional coordinate $z = 0.18$, with the same setting of isosurface around 15% of the maximum values.
distance between Mg$_1$ and Mg$_2$ and weakens the covalence-like bonding between Mg$_1$ 3s and Mg$_2$ 3s orbitals. However, the slopes of the two curves, as shown in Figure 2(b), are slightly different. The change in band effective mass $m_b^*$ from Bi alloying is more complicated because (1) adding Bi into the system expands the lattice not only along the c-axis but also in the a-b plane (Fig. S2, SI) and (2) adding Bi leads to the upward shifting of valence bands and the narrowing of band gaps. The upward shifting of valence bands brings hybridization between Bi p orbitals from valence bands and Mg$_1$ 3s orbitals from conduction bands. Such hybridization makes bands more dispersive, therefore lighter effective mass. A similar tensile strain-dependent reduction of band DOS effective mass was also reported in the typical semiconductor with well-known covalent bonds, such as Ge [32] and Si [33].

A closing band gap of Mg$_3$Sb$_2-y$Bi$_y$ with increasing Bi content has been theoretically predicted by many researchers [27, 34]. Our previous experiments also proved this [4]. Zhang et al. suggested a transition from semiconductor to semimetal as the Bi content increases and goes higher than $y = 1.5$ (Mg$_{3}$Sb$_{2.5}$Bi$_{1.5}$) [34]. However, in our calculation, the band gap remains as large as 0.17 eV for the sample Mg$_{3}$Sb$_{0.5}$Bi$_{1.5}$ without spin-orbit correction. Our calculations for the Mg$_{3}$Sb$_{2-y}$Bi$_y$ ($y = 0, 0.5, 0.75, 1, 1.25, 1.5, 2.0$) family give the same trend as shown in Figures 2(c)–2(e) and Table 1. The narrowing of the band gap with increasing Bi concentration is attributed to the upward shift of valence band maximum since the valence band maximum mainly consists of Sb and Bi p orbitals, and Bi p orbitals are more dispersive and lie at higher energy levels than Sb p orbitals. The band shape at CBM does not change much within the calculated Sb/Bi ratio window, but the effective mass at CBM decreases monotonically. Furthermore, the color indicator also shows that all the Mg$_{3}$Sb$_{2-y}$Bi$_y$ family members have a similar CBM between $M^*$ and $L^*$, mainly raised from the Mg3s orbital. This suggests that the alloying disordering at the Sb site might have less impact on the transport of the electron since its transport channel in the real space is around the Mg site.

Figure 3 shows the Hall measurement of the as-fabricated Mg$_{3}$Sb$_{2-y}$Bi$_y$, together with reported theoretical
and experimental data from literature. The carrier concentrations of as-fabricated $\text{Mg}_{3}\text{Sb}_2\text{Bi}_y$ samples show a weak dependence on Bi content in the range of $y = 1.0$–1.6, with an average Hall carrier concentration of $\sim 4 \times 10^{19} \text{ cm}^{-3}$, as shown in Figure 3(a). For the composition of $\text{Mg}_{3.0}\text{Sb}_{1.5}\text{Bi}_{0.5}$ with 1% Te and 1% Mn, our measured Hall carrier concentration $(3.52 \times 10^{19} \text{ cm}^{-3})$ is slightly higher than the reported data [8, 27, 35]. The effective charge carrier per Te was estimated to be $0.30, 0.47$, and $0.56$ electron/atom as Bi content is $y = 0, 0.5$, and 1.0, respectively. Then, it reached a saturated value of about 0.55 electron/atom when Bi content gets larger than $y = 1.0$, which indicates that Te is a strong donor in $\text{Mg}_{3}\text{Sb}_2\text{Bi}_y$ that is comparable with Te in CoSb$_3$-Te$_x$ (0.4 electron/atom) [36]. Figure 3(b) shows that the Hall mobility of as-fabricated $\text{Mg}_{3.0}\text{Sb}_{2.0}\text{Bi}_1$ increases from 48.0 to 68.8, 169.8, 195.9, 201.8, 247.0, and 247.3 cm$^2$ V$^{-1}$ s$^{-1}$ as the Bi content increases from $y = 0.0, 0.5, 1.0, 1.2, 1.4$, and 1.6, respectively. Based on our measured data together with theoretical and experimental ones from literature, a weak alloying effect was found [4, 5, 7, 8, 18, 35–40], suggesting that the disordering Sb/Bi has a weak coupling effect on the charge transport channel. The Pisarenko curve was also used to analyze the alloying effect (Fig. S3, SI). The charge carrier effective masses were derived from an equivalent single band model and carrier mobility by Hall measurement. The weighted mobility increases from 85.5 to 183.7, 163.8, 169.7, 217.6, and 195.9 cm$^2$ V$^{-1}$ s$^{-1}$ as the Bi content decreases from $y = 0.5$ to $y = 1.0, 1.2, 1.4, 1.5$, and 1.6, respectively. This trend is consistent with our theoretical interpretation of the increasing $\text{Mg}_1\text{Mg}_2$ distance and decreasing DOS-m$^*$ at CBM.

Figure 4 shows the temperature-dependent electrical transport properties of as-fabricated $\text{Mg}_{3.0}\text{Sb}_{2.0}\text{Bi}_y$ $(y = 1.0–2.0)$ with 1% Te and 1% Mn. The data of our previously reported $\text{Mg}_{3.0}\text{Sb}_{1.5}\text{Bi}_{0.5}$ is also shown for comparison [4]. Firstly, a positive correlation between temperature and electrical resistivity is found in all samples without notable abnormal negative $d\rho/dT$ near room temperature. It should be resulted from suppressed formation of Mg vacancy by using excess Mg [22] and interstitial Mn [4] and less grain boundary scattering [21] due to a large grain size of 5–10 µm and high carrier concentration. The SEM images of the fracture section of as-fabricated $\text{Mg}_{3.0}\text{Sb}_2\text{Bi}_y$ samples are shown in Fig. S4, indicating a grain size of 5–10 µm. Secondly, due to the nearly unchanged carrier concentration and increasing carrier mobility with increasing Bi/Sb ratio, the room temperature electrical resistivity decreases from 8.8 to 8.2, 7.6, 6.0, 6.7, 6.2, 5.7, and 5.0 µΩ m as the content of Bi increases from $y = 1.0$ to $y = 1.2, 1.4, 1.5, 1.6, 1.7, 1.8$, and 2.0, respectively (Figure 4(a)). It is noted that the $\text{Mg}_{3.0}\text{Sb}_{2.0}\text{Bi}_{1.5}$ sample has a low electric resistivity that is only half of that of the previously reported $\text{Mg}_{3.0}\text{Sb}_{1.5}\text{Bi}_{0.5}$ because of its high carrier mobility. Furthermore, the room temperature Seebeck coefficient of $\text{Mg}_{3.0}\text{Sb}_2\text{Bi}_1$ $(y = 1.0–1.7)$ shows a weak Bi/Sb ratio dependence (staying at almost constant around 145 μV K$^{-1}$) which is consistent with the trend of carrier concentration. As Bi content increases from $y = 1.7$ to $y = 1.8$ and 2.0, the Seebeck starts to decrease from -145 μV K$^{-1}$ to -126.7 μV K$^{-1}$ and -81.4 μV K$^{-1}$, respectively, shown in Figure 4(b). Figure 4(c) plots the temperature-dependent power factor of $\text{Mg}_{3.0}\text{Sb}_2\text{Bi}_1$ $(y = 1.0–2.0)$ calculated from the measured electrical resistivity and Seebeck coefficient. All the as-fabricated $\text{Mg}_{3.0}\text{Sb}_2\text{Bi}_1$ $(y = 1.0–2.0)$ samples, except for $\text{Mg}_{3.0}\text{Bi}_{0.5}$, have a large power factor over 2500 μW m$^{-1}$ K$^{-2}$ near room temperature. The largest room temperature power factor of 3470 μW m$^{-1}$ K$^{-2}$ is obtained in $\text{Mg}_{3.0}\text{Sb}_{0.5}\text{Bi}_{0.5}$, which is 50% larger than that of our previously reported $\text{Mg}_{3.0}\text{Sb}_{1.5}\text{Bi}_{0.5}$ and also 17% larger than a recently reported.

| $y$  | Band gap at $\Gamma$-CBM (eV) | Band gap at $\Gamma$-K (eV) | Effective mass at $\Gamma$-CBM (m$^*$) | Lattice constant $a$ (Å) | Lattice constant $c$ (Å) | $\text{Mg}_1\text{Mg}_2$ distance (Å) |
|------|-----------------------------|-----------------------------|----------------------------------|-----------------------------|-----------------------------|----------------------------------|
| 0.00 | 0.50                        | 0.72                        | 0.139                            | 4.596                       | 7.276                       | 3.770                            |
| 0.50 | 0.39                        | 0.68                        | 0.123                            | 4.625                       | 7.324                       | 3.801                            |
| 0.75 | 0.33                        | 0.66                        | 0.114                            | 4.639                       | 7.344                       | 3.817                            |
| 1.00 | 0.28                        | 0.64                        | 0.107                            | 4.644                       | 7.363                       | 3.832                            |
| 1.25 | 0.22                        | 0.62                        | 0.102                            | 4.664                       | 7.387                       | 3.847                            |
| 1.50 | 0.17                        | 0.61                        | 0.097                            | 4.681                       | 7.409                       | 3.862                            |
| 2.00 | 0.14                        | 0.58                        | 0.083                            | 4.718                       | 7.453                       | 3.891                            |

*Note: The data is calculated using the effective mass at the CBM and carrier mobility by Hall measurement.
Bi-rich Mg$_{3.05}$Sb$_2$-$y$Bi$_y$ ($\sim 2750 \mu Wm^{-1}K^{-2}$) and 26% larger than Mg$_{3.05}$Sb$_2$-$y$Bi$_y$-Te$_x$ ($\sim 2750 \mu Wm^{-1}K^{-2}$) [7, 8]. More comparisons were included in Fig. S5 (SI). Figure 4(d) plots room temperature power factor as a function of reduced Fermi level under the acoustic phonon dominant scattering (calculation details are given in SI A), suggesting that the sample Mg$_{3.05}$Sb$_2$-$y$Bi$_y$ was very close to the optimized carrier concentration while Mg$_{3.05}$Sb$_2$-$y$Bi$_y$ ($y = 1.2-1.8$) would be overdoped. The optimized reduced Fermi energy ($E_F/k_BT$) is estimated to be around 0.67, equal to $E_F = 0.017$ eV at room temperature, which corresponds to a Seebeck coefficient of $-167 \mu VK^{-1}$.

Figure 4(e) compares the average power factor of Mg$_{3.05}$Sb$_2$-$y$Bi$_y$ ($y = 1.0-2.0$) in the temperature range of 50-250°C. All the samples (except $y = 2.0$) have a value over $\sim 3000 \mu Wm^{-1}K^{-2}$, which is 166% higher than Tamaki’s Mg$_{3.05}$Sb$_2$Bi$_{0.5}$ (1130 $\mu Wm^{-1}K^{-2}$) and also about 16% higher than that of previously reported Mg$_{3.05}$Sb$_2$Bi$_{y}$Te$_{0.01}$-Mn$_{0.01}$ solid solutions ($y = 0.5-2.0$).

This work

Ref.

$y = 0.5$  Mn0.1  Co0.1
$y = 1.0$  Fe0.1  Nd0.1
$y = 1.2$  Hf0.1  Bi$_{1.4}$Te$_{0.01}$
$y = 1.4$  Ta0.1
$y = 1.6$

Figure 3: (a) Hall carrier measurement of Mg$_{3.05}$Sb$_2$-$y$Bi$_y$ solid solutions ($y = 0.5, 1, 1.2, 1.4, and 1.6$). (b) Bi content-dependent Hall mobility, theoretical and experimental data from literature as references [5, 7, 8, 18, 28, 35, 39]. (c) Comparison of Hall carrier concentration and mobility in this work and reference reported Mg$_{3.05}$Sb$_2$-$y$Bi$_y$ system [8, 38-40]. (d) Weighted mobility and electron effective mass of Mg$_{3.05}$Sb$_2$-$y$Bi$_y$-Te$_{0.01}$-Mn$_{0.01}$ solid solutions ($y = 0.5-2.0$).
Figure 4: Temperature dependence of (a) electrical resistivity, (b) Seebeck coefficient, and (c) power factor of Mg$_{1-y}$Sb$_2$Bi$_y$ ($y = 1.0, 1.2, 1.4, 1.5, 1.6, 1.7, 1.8, and 2.0$), previous $y = 0.5$ as reference [4]. (d) Power factor as a function of reduced Fermi level at room temperature in condition of different weighted mobility. (e) Average power factor and (f) engineering power factor in the temperature range of 50-250°C, with Bi$_2$Te$_2$.Se$_{0.7}$ as a reference [41].
\[
\langle \text{PF}\rangle_{\text{eng}} = \left( \frac{\int_{T_1}^{T_2} S(T) dT}{\int_{T_1}^{T_2} \rho(T) dT} \right)^2,
\]

where \(\Delta T\) is the temperature difference, \(L\) is the TE-leg length, and \(S(T)\) and \(\rho(T)\) are temperature-dependent Seebeck coefficient and electrical resistivity. In the temperature range of 50-250°C, all the samples (except \(y = 2.0\)) have an engineering power factor of about 0.6 W m\(^{-1}\) K\(^{-1}\), which is 100% larger than Tamaki’s Mg\(_{3+}\delta\)Sb\(_2\)-Bi\(_y\) (0.3 W m\(^{-1}\) K\(^{-1}\)) and also 20% larger than that of previously reported Mg\(_{3+}\delta\)Sb\(_2\)-Bi\(_y\) and Bi\(_2\) (Te, Se)\(_3\) as reference.

This work

Other MgSbBi system

\[\bullet y = 1\]
\[\bullet y = 1.5\]
\[\bullet y = 1.6\]
\[\bullet y = 1.7\]
\[\bullet y = 2.0\]

BiTeSe system

\[\bullet y = 1\]
\[\bullet y = 1.2\]
\[\bullet y = 1.4\]
\[\bullet y = 1.5\]
\[\bullet y = 1.6\]
\[\bullet y = 1.7\]
\[\bullet y = 2.0\]

Mg\(_{3+}\delta\)Sb\(_2\)-Bi\(_y\) - 0.01Te0.01:Mn0.01 solid solutions in the temperature range of 50-250°C, compared with literature reported Mg\(_{3+}\delta\)Sb\(_2\)-Bi\(_y\) and Bi\(_2\) (Te, Se)\(_3\) as reference.

Figures 5(a) and 5(b) show the temperature-dependent thermal properties of Mg\(_{3+}\delta\)Sb\(_2\)-Bi\(_y\) (\(y = 1.0\)-2.0). At room temperature, the thermal conductivity increases from 1.31 to 1.34, 1.47, 1.64, 1.41, 1.90, 2.13, and 2.18 W m\(^{-1}\) K\(^{-2}\), as the Bi content increases from \(y = 1.0\) to 1.2, 1.4, 1.5, 1.6,
1.5, 1.6, 1.7, 1.8, and 2.0, respectively. A notable bipolar effect is observed in all the samples which are characterized by an increasing thermal conductivity with temperature at the high temperature end. Furthermore, the samples with more Bi (i.e., larger y value in the formula of Mg$_{3+x}$Sb$_2$-$y$Bi$_y$) have a lower starting temperature, which is consistent with narrowing band gap predicted by our theoretical calculations. The lattice thermal conductivity is estimated by subtracting the contribution of electronic part ($\kappa_{ele}$) and bipolar part ($\kappa_{bip}$) from the total thermal conductivity ($\kappa_{tot}$), i.e., $\kappa_{lat} = \kappa_{tot} - \kappa_{ele} - \kappa_{bip}$ (Figure 5(b)). The details of the calculation relative to the electronic thermal conductivity ($\kappa_{ele}$) and bipolar thermal conductivity ($\kappa_{bip}$) are given in SI B. At room temperature, $\kappa_{lat}$ changes from 0.75 to 0.69, 0.77, 0.76, 0.61, 1.00, 1.12, and 0.82 W m$^{-1}$K$^{-1}$ as the Bi content increases from y = 1.0 to 1.2, 1.4, 1.5, 1.6, 1.7, 1.8, and 2.0, respectively. For comparison, $\kappa_{lat}$ of Mg$_3$Sb$_2$ and Mg$_3$Sb$_1$Bi$_0.5$ from our previous work are estimated to be 1.46 W m$^{-1}$K$^{-2}$ and 0.73 W m$^{-1}$K$^{-2}$ [4]. $\kappa_{lat}$ of Mg$_3.2$Bi$_1.998$-Sb$_0$Te$_0.002$ for its high average ZT of 1.13 and higher than Mg$_3$Bi$_2$. Moreover, in the temperature range of 50-250 °C, which gives an efficiency of 8.5% under ideal adiabatic condition. Furthermore, the electronic transport channel protection and tuning in real space could be a new electronic engineering strategy to increase the carrier mobility.

4. Experimental Procedures

4.1. Sample Synthesis. The samples with nominal compositions of Mg$_{3+y}$Sb$_2$-$y$Bi$_y$Te$_0.5$:$\delta$Mn$_{0.01}$ were synthesized by mechanical alloying and spark plasma sintering (SPS). High-purity magnesium turnings (Mg, 99.99%; Acros Organics), antimony shots (Sb, 99.999%; 5N Plus), bismuth shots (Bi, 99.999%; 5N Plus), tellurium shots (Te, 99.999%; 5N Plus), and manganese powders (Mn, 99.95%; Alfa Aesar) were weighed according to the composition of Mg$_{3+y}$Sb$_2$-$y$Bi$_y$Te$_0.5$:$\delta$Mn$_{0.01}$ (\(\delta = 0.2, y = 1.0, 1.2, 1.4, 1.5, 1.6, 1.7, 1.8, 2.0\)) simplified as Mg$_3$Sb$_2$-$y$Bi$_y$ in the text, and were then loaded into a stainless steel ball milling jar together with stainless steel balls in a glove box in an argon atmosphere with the oxygen level < 1 ppm. After ball milling for 8 hours in SPEX 8000D, or 8000 M, the ball-milled powders were loaded into a graphite die with an inner diameter of 15 mm in a glove box. Graphite die with loading powder was immediately sintered at 675 °C under a pressure of 50 MPa for 5 min in SPS division (SPS-211Lx, Fuji Electronic Industrial Co. LTD). The SPS bulks are ~15 mm in diameter and ~8 mm in thickness. The Seebeck coefficient, electrical resistivity, and thermal diffusivity were measured in the directions perpendicular to pressure.

4.2. Thermoelectric Characterization. Electrical properties, including Seebeck coefficient, electrical resistivity, and power factor, were measured by ZEM-3, ULVAC Riko, under a 0.01 MPa pressure helium atmosphere from RT to 400°C. Measured samples were cut into about 2.5 mm × 3 mm × 13 mm pieces. Thermal conductivity was calculated by equation $\kappa = \frac{DC}{\rho}$, where D is thermal diffusivity measured by laser flash method (LFA 467; Netzsch) using about 6 mm × 6 mm × 1 mm pieces, $C$ is density measured by the Archimedeans method, and specific heat ($C_p$) is tested by differential scanning calorimetry (Discovery, DSC, Waters LLC), shown in Fig. S9 (SI).

4.2.1. Hall Effect Measurement. Hall coefficient was measured by Physical Property Measurement System (PPMS-14L, Quantum Design) with four-point method in magnetic field from -5 T to 5 T. Tested samples were cut into about

3. Conclusion

We have successfully enhanced the room temperature thermoelectric performance of Mg$_{3+y}$Sb$_2$-$y$Bi$_y$ by the strategy of electronic transport channel protection and tuning in real space. It was found that the increased carrier mobility was closely related to the weakening covalence-like bonding between Mg$_3$Sb and Mg$_3$Sb orbi...
6 mm × 6 mm × 1 mm pieces and then soldered to Φ0.1 mm enamelled wire with In as the solder. Hall carrier concentration was calculated by \( n_H = 1/|S_H|e \), and Hall mobility was calculated by \( \mu_H = |R_H|/\rho \), where \( e \) is elementary charge and \( \rho \) is measured electrical resistivity.

4.3. X-Ray Diffraction. SPS bulks were grinded into powder in a glove box, and then, the phase composition was characterized by X-ray diffraction (Rigaku SmartLab) with Cu Kα radiation (\( \lambda = 1.54 \) Å, operating at 40 kV/15 mA with Kα, foil filter). XRD patterns were further refined by the Rietveld method to calculate lattice parameter and Mg\(_{1}\)-Mg\(_{2}\) distance.

4.4. Calculation Methods. The first-principles calculations are based on density functional theory (DFT) [48, 49] and the screened hybrid functional HSE06 [50, 51] as implemented in the Vienna Ab Initio Simulation Package (VASP) code [52]. Projected augmented wave (PAW) potentials [53] with plane-wave basis set and an energy cutoff of 550 eV are used. The valence electronic configurations for Mg, Sb, and Bi are 3s\(^2\), 5s\(^2\)5p\(^3\), and 6s\(^2\)6p\(^3\) in the pseudopotentials, respectively. For integrations over the Brillouin zone, we use 5 × 5 × 3 Monkhorst-Pack k-point mesh [54] for 40-atom cells (2 × 2 × 2). The atomic positions are fully relaxed until the forces on each atom are less than 0.005 eV/Å and total energy differences between two consecutive steps are less than 10\(^{-6}\) eV. The lowest-energy structural configurations for alloy systems are constructed by Supercell program [55] and direct energy comparison.

Conflicts of Interest

There are no conflicts to declare.

Authors’ Contributions

W.S. Liu and Z.J. Han designed the experiment; Z.J. Han conducted the synthesis and TE transport property measurement; Z.G. Gui contributed to the first-principles calculation; P. Qin and Y.B. Zhu conducted the Hall measurement; Z.J. Han and Z.G. Gui complete the writing of the manuscript; B.P. Zhang, W.Q. Zhang, L. Huang, and W.S. Liu were responsible for the interpretation of the results and revision of the manuscript. All authors discussed the results and gave comments regarding the manuscript. Z.J. Han and Z.G. Gui have equivalent contribution.

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Supplementary Materials

Fig. S1: XRD patterns of the Mg\(_{3+}\)Sb\(_{2}\)Bi\(_{y}\) (\( y = 1.0, 1.2, 1.4, 1.5, 1.6, 1.7, 1.8, 2.0 \)) solid solution powder. Fig. S2: lattice parameter and \( c \) of Mg\(_{3+}\)Sb\(_{2}\)Bi\(_{y}\) as function of Bi content, and dash lines show Vegard’s law between MgSb\(_{2}\) and MgBi\(_{2}\). Fig. S3: Pisarenko’s plot for Mg\(_{3+}\)Sb\(_{2}\)Bi\(_{y}\). It shows a decrease effective mass with higher Bi content. Fig. S4: SEM images of the fractured surface of Mg\(_{3+}\)Sb\(_{2}\)Bi\(_{y}\): (a) \( y = 1.0 \), (b) \( y = 1.2 \), (c) \( y = 1.4 \), (d) \( y = 1.5 \), and (e) \( y = 1.6 \). Fig. S5: comparison of power factor of the Mg\(_{3+}\) (Sb, Bi) system [1–18]. Fig. S6: reproducibility and cycling test of as-fabricated Mg\(_{3+}\)Sb\(_{2}\)Bi\(_{y}\) and Bi\(_{y}\)(Te,Se)\(_{3}\) from references [8, 9, 12, 15, 17–23]. Fig. S7: temperature dependence of (a) power factor and (b) ZT of as-fabricated Mg\(_{3+}\)Sb\(_{2}\)Bi\(_{y}\) and Bi\(_{y}\)(Te,Se)\(_{3}\) in the temperature range of 50–250°C. Fig. S9: specific heat of the Mg\(_{3+}\)Sb\(_{2}\)Bi\(_{y}\)\(_{0.01}\)Te\(_{0.01}\)Mn\(_{0.01}\) solid solution powder. (Supplementary Materials)

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