### Exceptional Thermoelectric Performance in Mg₃Sb₀.₃Bi₁.₄ for low-grade waste heat recovery

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Exceptional Thermoelectric Performance in Mg$_3$Sb$_{0.6}$Bi$_{1.4}$ for low-grade waste heat recovery

Kazuki Imasato$^1$, Stephen Dongmin Kang$^{1,2}$ and G. Jeffrey Snyder$^1$

$^1$Northwestern University, Evanston, IL 60208, USA, $^2$California Institute of Technology, Pasadena, CA 91125, USA

Bi$_2$Te$_3$ alloys have been the most widely used n-type material for low temperature thermoelectric power generation for over 50 years, thanks to the highest efficiency in the 300 – 500 K temperature range relevant for low-grade waste-heat recovery. Here we show that n-type Mg$_3$Sb$_{0.6}$Bi$_{1.4}$, with a thermoelectric figure-of-merit $zT$ of 1.0–1.2 at 400–500 K, finally surpasses n-type Bi$_2$Te$_3$. This exceptional performance is achieved by tuning the alloy composition of Mg$_3$(Sb$_{1-x}$Bi$_x$)$_2$. The two primary mechanisms of the improvement are the band effective-mass reduction and grain size enhancement as the Mg$_3$Bi$_2$ content increases. The benefit of the effective-mass reduction is only effective up to the optimum composition Mg$_3$Sb$_{0.6}$Bi$_{1.4}$, after which a different band dominates charge transport. The larger grains are important for minimizing grain-boundary electrical resistance. Considering the limited choice for low temperature n-type thermoelectric materials, the development of Mg$_3$Sb$_{0.6}$Bi$_{1.4}$ is a significant advancement towards sustainable heat recovery technology.

Broader Context

One of the bottlenecks for low-grade waste-heat recovery using thermoelectrics is the lack of a good n-type material that performs well around 400–500 K. For more than 50 years, n-type Bi$_2$Te$_3$ has been the standard material for this application, and the field has not seen any superior alternatives. Having only one material option can also greatly limit the device design space that one could utilize. When designing thermoelectric devices, many more properties other than just the maximum performance can be restricting factors: cost and availability of the material; chemical stability when interfaced with other materials; mechanical reliability; thermal shock resistance; thermoelectric compatibility for segmenting. With the demonstration of n-type Mg$_3$Sb$_{0.6}$Bi$_{1.4}$ with properties offering higher energy conversion efficiency than Bi$_2$Te$_3$ for low-grade waste-heat recovery, the material could become a next-generation material for low temperature thermoelectrics.

Globally, more than half of the energy in fuels is lost as waste heat to the environment. Strategies for converting this wasted energy into a useful form like electricity depends on the temperature of the waste heat. In particular, low-grade waste heat (temperatures lower than 250°C) offers a great opportunity because of its huge portion amounting to 300 TBTu/yr of work potential$^1$. Thermoelectric generation is one of the most promising technologies for recovering this low-grade waste heat and solving today’s energy challenges$^{2,3}$.

The maximum energy conversion efficiency of a thermoelectric material is assessed by using the dimensionless figure-of-merit $zT$, defined as $zT = S^2\sigma T/\kappa$ where $S$ is the Seebeck coefficient, $\sigma$ is the electrical conductivity, $\kappa$ is the thermal conductivity, and $T$ is the temperature. An average $zT$ value near unity in the temperature range of use is typically needed to make thermoelectric conversion a useful process.
In the temperature range for low-grade waste heat recovery (below 250°C), there are few high performance thermoelectric materials, especially on the n-type side. Currently, Bi₂Te₃ and its related compounds are the only practical n-type materials in this temperature range (typically exhibiting $zT \approx 1$ at 400 K), a material that dates back to 1954⁴,⁵. The situation is in contrast to p-type materials where Bi₂Te₃ has higher $zT$ values (when nano-engineered⁶,⁷) and also other potentially good materials exist⁸.

The Mg₃Sb₂-Mg₃Bi₂ alloy is one of the few high performance n-type materials, recently discovered⁸,⁹ and originally optimized for its mid-temperature (above 500 K) application with the specific composition Mg₃₋ₓSb₁ₓBi₀.₅Te₀.₀₁ ($zT \approx 1.5$ at 700 K)¹⁰. Alloying with Mg₃Bi₂ reduces the thermal conductivity⁸,¹¹, but also significantly changes the electrical band structure¹². The alloying effect on bands implies that one should be able to tune this material for low temperatures by employing band engineering strategies.

**Figure 1: Conduction band optimization in the solid solution of Mg₃Sb₂-Mg₃Bi₂ for low-temperature thermoelectrics.** a Schematic of how the relative energy of bands change with alloying. The effective mass of all bands reduces with increasing Mg₃Bi₂ content in the solid solution. The single-valley $\Gamma$ band (blue) crosses over the six-fold valley conduction band CB₁ (red), eventually circumventing the multi-valley benefit of CB₁. The optimum band structure is obtained near the conduction band crossing, when the effective mass is minimized while maintaining valley degeneracy. b Weighted mobility of the conduction band at 450 K shows a maximum peak around 70% alloying (Mg₃Sb₀.₆Bi₁.₄). c The Seebeck effective mass of the conduction band decreases with Mg₃Bi₂ alloying because of the increased curvature of the bands. Since a lighter band mass is favorable for mobility, the optimum thermoelectric composition is where the six-fold CB₁ band is lighter but still the lowest conduction band. The lack of a noticeable peak in $m^*_S$ at 70% indicates that the convergence effect is minimal. The lines in b and c are guides to the eyes.

**Band Engineering Strategy**

The goal of band engineering in thermoelectrics is to increase the weighted mobility $\mu_w$, which is the electronic part of the material quality factor¹³,¹⁴ $B$:

$$B \propto \frac{\mu_w}{\kappa_L} \propto \frac{N_V}{m^*_I \kappa_L}.$$  

(1)
Here, $\kappa_L$ is lattice thermal conductivity, $N_V$ is valley degeneracy, and $m^*_1$ is inertial effective mass of the charge carriers. Since a higher maximum $zT$ is obtainable with higher $B$, maximizing $\mu_w$ is desired, which can be achieved through either increasing $N_V$ or reducing $m^*_1$. The typical band engineering strategy is to converge multiple bands to have the same band edge\textsuperscript {15–17}, which effectively increases $N_V$. A different strategy often overlooked is to reduce $m^*_1$. The conduction bands of Mg$_{70}$Sb$_{30}$ can be made lighter by alloying with Mg$_{53}$Bi$_{27}$, which has the same band structure but with bands that have more curvature and therefore have lighter charge carriers (smaller $m^*_1$) \textsuperscript {12}.

Decreasing the conduction band mass by increasing the Mg$_{53}$Bi$_{27}$ content of Mg$_{53}$Sb$_{27}$-Mg$_{53}$Bi$_{27}$ alloys should increase $\mu_w$ and therefore $zT$. Increasing the Mg$_{53}$Bi$_{27}$ content also shrinks the band gap (Fig.1a) and brings the peak in $zT$ with respect to $T$ to a lower temperature\textsuperscript {12}. Although a narrow gap is not usually desired as the thermally excited bipolar conduction (by holes and electrons) effectively limits the maximum operation temperature, the benefit of the reduced band mass for use at lower temperature can outweigh the disadvantage of a more limited operation temperature.

The benefit of increasing the Mg$_{53}$Bi$_{27}$ content should only be effective up to an optimum composition due to the band crossing of the conduction bands. According to band structure calculations\textsuperscript {18,19}, the lowest conduction band in Mg$_{53}$Bi$_{27}$ is the single-valley $\Gamma$ band rather than the six-valley MLA$\Gamma$ band (CB1). Thus, one can expect a band crossing to occur in Mg$_{53}$Sb$_{27}$-Mg$_{53}$Bi$_{27}$ alloys when the Mg$_{53}$Bi$_{27}$ content is high, at about 70 % of Mg$_{53}$Bi$_{27}$ (see Fig.1a). Once the $\Gamma$ band becomes the lowest and dominant conduction band, the effective valley degeneracy is reduced and the band gap rapidly decreases, which will lead to detrimental bipolar conduction. Therefore, the optimum composition is expected to be around 70 % of Mg$_{53}$Bi$_{27}$, or Mg$_{53}$Sb$_{0.6}$Bi$_{1.4}$, which is the composition with maximum Mg$_{53}$Bi$_{27}$ content before the band crossing. Regardless of whether the $\Gamma$ band makes a meaningful contribution at the band crossing composition, highest thermoelectric performance is expected at this alloy composition due to the decreased band mass of CB1. The n-type Goldsmid-Sharp band gap (the effective band gap for transport) at the band crossing composition Mg$_{53}$Sb$_{0.6}$Bi$_{1.4}$ is 0.2 eV, which is still suitable for applications below 500 K (the true gap is smaller\textsuperscript {12}; see ESI).

**Results**

**Optimum Composition from Weighted Mobility**

To experimentally identify the composition at which the electronic transport properties are optimal, the weighted mobilities, $\mu_w$, are determined from the measured electrical conductivity and Seebeck coefficient values (see Methods). Weighted mobility is a Fermi-level independent quantity that is most directly relevant in determining the conductivity one can get from a given Seebeck coefficient\textsuperscript {13,14}. It is the most useful form for this analysis because, in principle, it does not change strongly with doping concentration like Seebeck or conductivity does. Fig.1b shows the weighted mobilities of the n-type charge carriers in Mg$_{53}$(Sb$_{0.2}$Bi$_{0.8}$)$_2$.

A maximum in the $\mu_w$ ($T = 450$ K) is found at a composition of 70 % Mg$_{53}$Bi$_{27}$ (Fig.1b), consistent with the expected band engineering strategy. The increase in $\mu_w$ (red line) with Mg$_{53}$Bi$_{27}$ content up to the maximum at 70 % Mg$_{53}$Bi$_{27}$ is attributed primarily to the reduction in $m^*_1$ (Eq.1). The abrupt change to a decreasing trend (blue line) is attributed to the band crossover, which reduces the effective $N_V$ as the singly degenerate conduction band at $\Gamma$ becomes increasingly more dominant. Therefore, the optimum electronic structure found by transport measurements coincides with the composition Mg$_{53}$Sb$_{0.6}$Bi$_{1.4}$.

Furthermore, the change in the Seebeck effective mass\textsuperscript {12,13} ($m^*_S$, which is a density-of-states mass that depends on both $N_V$ and band curvature) also supports the understanding of band structure optimization. The decrease in $m^*_S$ with alloying (Fig.1c, red line) is due to the curvature increase of the CB1 bands. One can also notice that the kink in the $m^*_S$ trend at the band crossover is not as pronounced because of the strong remaining influence of CB1. This subtlety indicates that the band convergence effect is minimal as expected from the small valley degeneracy of the $\Gamma$ band. Even after the crossing, the CB1 bands still contribute to the Seebeck coefficient because of the much higher valley degeneracy ($\times 6$) and small energy offset from the $\Gamma$ band.
Figure 2: Thermoelectric performance in n-type Mg$_3$Sb$_{0.6}$Bi$_{1.4}$ for low-grade waste-heat recovery exceeding that of standard n-type materials. a The material figure-of-merit with various n-type doping levels, compared with the current commercial material n-type Bi$_2$Te$_3$. Nominal compositions are indicated in the legend. The error bar represents an estimated standard deviation including variations in Seebeck, resistance, and thickness measurements. b The maximum conversion efficiency obtainable with a 500 K hot-side leg-temperature and room temperature cold-side leg-temperature. An efficiency of > 8 % is possible with the best composition. The efficiencies were calculated from individual transport properties and by considering self-compatibility$^{20}$ (see SI). c Electrical conductivity, d Seebeck coefficient, e Hall carrier concentration (inverse of the Hall coefficient), and f Thermal conductivity of Mg$_3$Sb$_{0.6}$Bi$_{1.4}$ doped with various amounts of Te on the anion site. Reference data from: [21] (Bi$_2$Te$_3$); [22] (CoSb$_3$); [23, 24] (PbTe); [10] (Mg$_3$Sb$_{1.5}$Bi$_{0.5}$).
Mitigation of Grain Boundary Resistance

A critical prerequisite for fully taking advantage of the benefits from band engineering in this material is the minimization of grain boundary resistance. It has been shown in recent studies that the grain boundary resistance is the reason for low and thermally activated conduction below 500 K (rather than ionized impurity scattering). This grain boundary resistance leads to poor thermoelectric performance at low-grade waste-heat temperatures, which is one reason why the material was not seriously considered for low temperatures in previous investigations. An effective solution for such a material is to maximize the grain size and thereby minimize the grain boundary density.

Increasing the \( \text{Mg}_3\text{Bi}_2 \) content greatly enhances the grain growth kinetics, allowing the samples to have larger grains and minimal grain boundary resistance. Electron microscopy of the 75 and 25 % \( \text{Mg}_3\text{Bi}_2 \) samples shows a 5-10 times grain size difference (Fig.3a-b) when prepared under identical conditions (consolidated at 800°C for 20 min to limit Mg loss\(^{25,28}\)). The thermally-activated behavior in the low temperature electrical conductivity (Fig.3c) is substantially removed with larger grains. This microstructure enables the material to take full advantage of the band structure optimized for low temperature. Enhanced grain growth kinetics can be expected from the decreasing melting temperature as the \( \text{Mg}_3\text{Bi}_2 \) content increases (\( \text{Mg}_3\text{Bi}_2 \) melts at 820°C while \( \text{Mg}_3\text{Sb} \) melts at 1120°C). We note that, the increase in grain size does not compromise the low thermal conductivity in this material due to the inherently short mean free paths of phonons\(^{10,29,30} \), unlike other materials such as \( \text{Bi}_2\text{Te}_3 \) where grain size reduction is a useful strategy\(^7 \).

Thermoelectric performance at the optimal composition \( \text{Mg}_3\text{Sb}_{0.6}\text{Bi}_{1.4} \)

The optimal composition \( \text{Mg}_3\text{Sb}_{0.6}\text{Bi}_{1.4} \) indeed shows excellent low-temperature thermoelectric performance, much better than standard n-type materials (Fig.2). By varying the doping concentration of \( \text{Mg}_3\text{Sb}_{0.6}\text{Bi}_{1.4} \) where best \( \mu_\text{w} \) was found, we find \( zT \) values higher than unity in the range of 350-600 K, a significant improvement compared with the commercial n-type \( \text{Bi}_2\text{Te}_3 \) material (Fig.2a). The maximum obtainable energy conversion efficiency exceeds 8 % for a thermoelectric leg at 300 and 500 K at each side, corresponding to a device figure-of-merit\(^{20} \) \( ZT > 1 \) (Fig.1b), also higher than both the commercial n-type \( \text{Bi}_2\text{Te}_3 \) and the \( \text{Mg}_3\text{Sb}_{0.5}\text{Bi}_{0.5} \) composition previously optimized for mid-temperature. The detailed nominal composition of the sample with highest conversion efficiency was \( \text{Mg}_5\text{Sb}_{0.3}\text{Bi}_{0.7} \) (red circles in Fig.1). Here, excess Mg (3 + \( \delta \) in the formula) is required to ensure the stable acquirement of n-type properties\(^{25} \), but is minimized to not increase thermal conductivity\(^{26} \). Te is the n-type dopant that provides the optimum carrier concentration. The individual transport properties are shown in Fig.2c-f.
Thermal conductivity

Alloying has a beneficial effect also for reducing thermal conductivity (Fig.4) because the Sb-Bi disorder helps to scatter phonons; however, near the electronic optimal composition (70 % Mg$_3$Bi$_2$), the lattice thermal conductivity is not very sensitive to the composition (consistent with the alloy scattering model). Therefore, in terms of finding the optimum composition, the electronic consideration on $\mu_w$ is much more important than controlling the thermal conductivity. The quality factor evaluation is discussed in the ESI.

Conclusions

To summarize, the band structure of Mg$_3$(Sb$_{1-x}$Bi$_x$)$_2$ can be tuned such that the thermoelectric performance is optimized for low-grade waste-heat temperatures. The primary benefit comes from the decrease in the band mass of the six-valley conduction band as the Mg$_3$Bi$_2$ content is increased. This benefit is maximum at the band crossing point, beyond which the single-valley $\Gamma$ band becomes the lowest conduction band. Bipolar conduction at the band-crossing composition is not as severe as what the true band gap might suggest, thanks to the large contrast between n-type and p-type weighted mobilities that gives a larger effective gap for n-type Mg$_3$(Sb$_{1-x}$Bi$_x$)$_2$.

Methods

Weighted Mobility Analysis

To determine the weighted mobilities from the measured electrical conductivity and Seebeck coefficient data, it is important to obtain values representing the intrinsic properties of the majority carriers. From the raw measurement data, we identify temperature regions that are not affected by bipolar conduction (which would reduce the extracted $\mu_w$ to below the intrinsic value). Furthermore, we also exclude regions where grain boundary resistance is significant. Use of the remaining regions ensures the values obtained are closest to the intrinsic $\mu_w$ values (See ESI for details of the analysis procedure and also the raw data). It should be noted that an energy dependency of $E^{-1/2}$ for scattering time, rather than $E^{3/2}$, should be used for the analysis. It has been shown$^{27}$ through the log $|S| - \log \sigma$ analysis$^{31,32}$ that such energy dependency is indeed the case at and above room temperature, as opposed to some earlier suggestions about ionized impurity scattering$^{33}$.
Sample Synthesis

Samples with nominal compositions of \( \text{Mg}_{3.05}(\text{Sb}_{1-x}\text{Bi}_x)_{1.99}\text{Te}_{0.01} \) (\( x = 0 \) to \( 1.0 \)) and \( \text{Mg}_{3.05}(\text{Sb}_{0.3}\text{Bi}_{0.7})_{2-y}\text{Te}_y \) (\( y = 0.0025 \) to \( 0.01 \)) were synthesized. Weighed magnesium turnings (99.98%, metals basis, Alfa Aesar), antimony shots (99.999%, metals basis, Alfa Aesar), bismuth granules (99.997%, metals basis, Alfa Aesar), and tellurium lumps (99.999%, metals basis, Alfa Aesar) were loaded into stainless steel vials together with stainless steel balls. All weighing and loading were done inside an argon-filled glove box. Elements were reacted by mechanical alloying with a shaker (SPEX 8000D) for two hours. The product powder was extracted from the vial and loaded into a carbon die, in which the powder was consolidated into pellets by rapid hot pressing with 45 MPa at 1073 K for 20 min, under dynamic argon atmosphere.

Property Characterization

The Seebeck coefficients were measured under high vacuum by a two-probe configuration with Chromel/Nb thermocouples embedded in heater blocks to prevent cold finger effects. The Hall coefficients and electrical conductivities were measured under high vacuum by using the four-probe van der Pauw method with Mo probes and a 2 T electromagnet. Thermal diffusivities were measured by using the laser flash method (Netzsch LFA 457) under dynamic argon atmosphere. Pellet densities were measured with the geometric method. Heat capacity values based on experimental measurements (see SI or Ref.[36]) were used to calculate thermal conductivities from diffusivity measurements. Electron backscattering diffraction maps were obtained using a scanning electron microscope (Quanta 650 FEG) equipped with a detector (Oxford Instruments Nordlys).

Author Contributions

KI synthesized and measured the samples. KI and SDK analyzed the data. SDK and KI wrote the manuscript. SDK supervised the project with the advice from GJS. All authors reviewed or edited the manuscript.

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Competing interests

The authors declare no competing interests.

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