Electronic Supplementary Information
for
"Exceptional Thermoelectric Performance in $Mg_3Sb_{0.6}Bi_{1.4}$ 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*

1 Transport property characterization

1.1 Varied Mg_3Bi_2 content: $Mg_{3.05}(Sb_{1-x}Bi_x)_{1.99}Te_{0.01}$

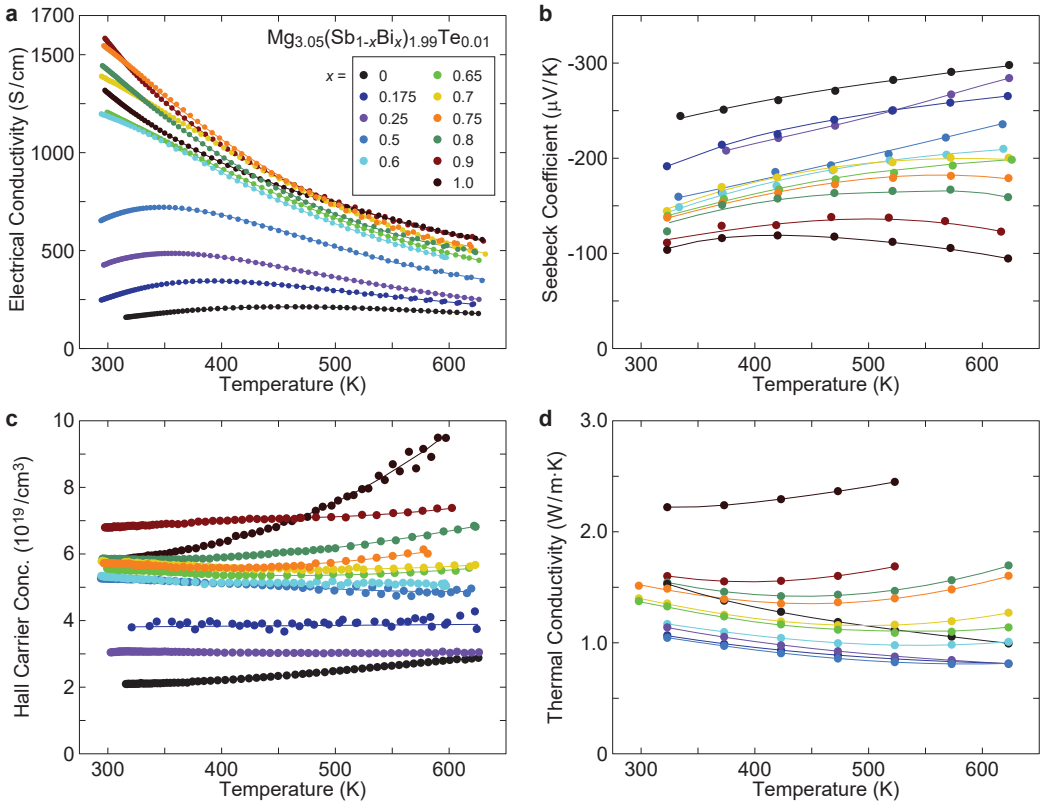

Figure S1: Transport properties of $Mg_{3.05}(Sb_{1-x}Bi_x)_{1.99}Te_{0.01}$. **a** Electrical conductivity. **b** Seebeck coefficient. **c** Hall carrier concentration. **d** Thermal conductivity. Solid lines are guides to the eyes.

1.2 Band gap estimation from transport analysis

The change in the band gap with respect to alloy composition can be estimated from the temperature dependent Seebeck coefficient (for finding Goldsmid-Sharp gaps[1]) and the weighted mobilities (for finding the true gap). The results are shown in Fig.S2. Note that the effective band gap for n-type is higher than the true gap.

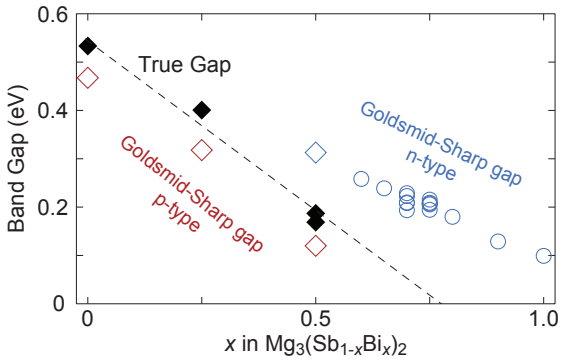

Figure S2: Band gaps estimated as a function of alloy compositions. The Goldsmid-Sharp gaps are estimated from the peak in the magnitude of Seebeck coefficient (thermopower) with respect to temperature. These Goldsmid-Sharp gaps represent effective gaps for transport, which are larger than the true gap when the majority carriers have higher weighted mobility than the minority carriers. The true gap can be estimated (black solid points) if the weighted mobility ratio is known[1]. Diamonds indicate data from Ref.[2]. Circles indicate data from the current study.

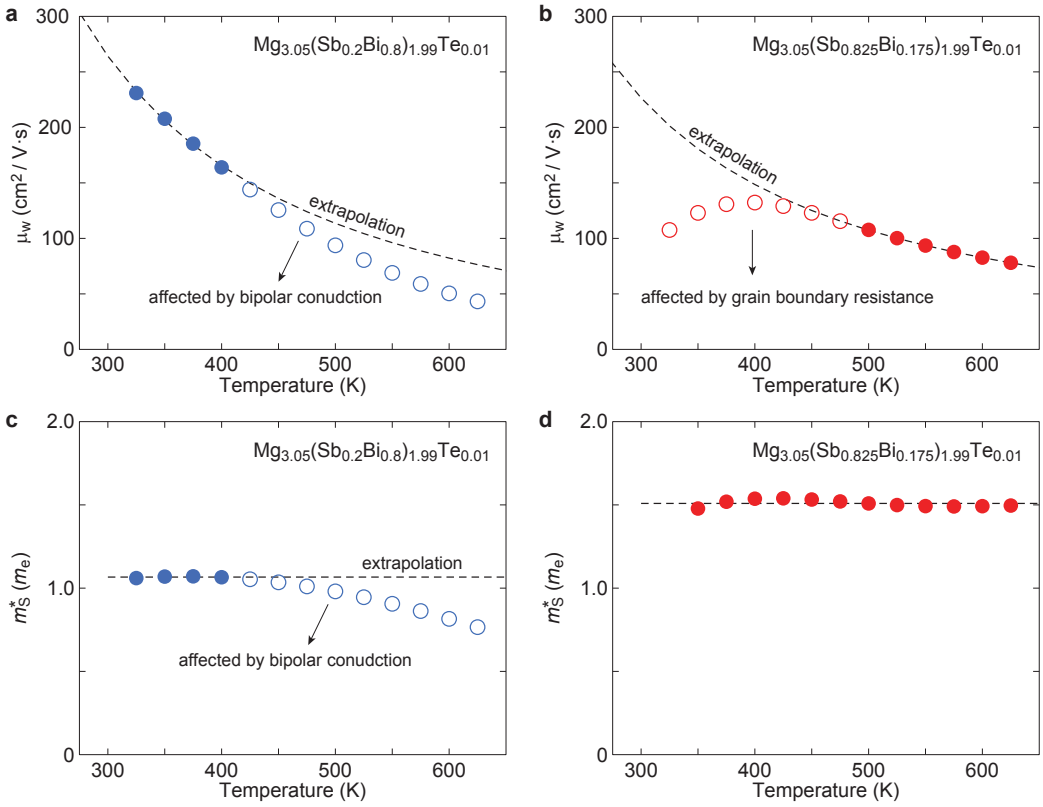

Figure S3: Extrapolation scheme for extracting μ_w and m_S^* values. Extrapolation examples of weighted mobilities (**a** and **b**) and Seebeck effective masses (**c** and **d**). Note that Hall measurements tend to be unaffected by grain boundary resistance, similar to Seebeck coefficient measurements.

1.3 Obtaining μ_w and m_S^*

Weighted mobilities and the Seebeck effective mass can be obtained by combining the measured Seebeck coefficients with electrical conductivity and Hall carrier concentrations, respectively. The method and equations are described in Ref.[2]. To work around the influence from bipolar conduction and grain boundary resistance, values from the unaffected temperatures were extrapolated as shown in Fig.S3. Bipolar conduction is significant only at high temperature with higher Mg_3Bi_2 content (Fig.S3a,c); grain boundary resistance is dominant mostly at low

temperature and at Mg_3Sb_2-rich compositions (Fig.S3b,d).

Table S1: Heat capacity for $Mg_3(Sb_{1-x}Bi_x)_2$.

Temperature (K)	Heat Capacity (J/mol·K)
298	123.6
323	124.8
373	126.9
423	128.6
473	130.0
523	131.2
573	132.4
623	133.4

1.4 Note on heat capacity

For converting thermal diffusivity measurements to thermal conductivity, we use heat capacity values from a thermodynamic model curve that fits experimental measurements. Above room temperature, the Mg_3Sb_2-Mg_3Bi_2 composition has minimal effect on the molar heat capacity values. Details of this study can be found in Ref.[3]. Here we tabulate values (Table S1) in the temperature range of interest for the current study.

2 Thermoelectric conversion efficiency

The maximum obtainable energy conversion efficiency of a thermoelectric leg can be calculated by considering thermoelectric compatibility[4,5]. By treating the material to be a series of segments each at different temperatures, the temperature dependent transport properties are taken into account. Conversion efficiency calculated in such a way can be significantly different than the naive approach of using constant property models or just averaging zT over a temperautre range. With the precise maximum conversion efficiency, one can also exactly define a device figure-of-merit ZT (as opposed to the material figure-of-merit zT). The conversion efficiencies and device figure-of-merit ZT shown in Fig.2 were calculated using this method, which is described in detail in Ref.[5].

3 Alloy scattering in $Mg_3(Sb_{1-x}Bi_x)_2$

We model the point defect scattering effect due to Sb/Bi disorder by using the relation between the alloy thermal conductivity $\kappa_{\mathrm{L,alloy}}$ and non-alloyed thermal conductivity $\kappa_{\mathrm{L,pure}}$ as proposed by Callaway[6] and Klemens[7]:

$$\frac{\kappa_{\mathrm{L,alloy}}}{\kappa_{\mathrm{L,pure}}} = \frac{\arctan(u)}{u}, \tag{S1}$$

$$u^2 = \frac{\pi\theta_{\mathrm{D}}\Omega}{2\hbar v^2}\kappa_{\mathrm{L,pure}}\Gamma. \tag{S2}$$

Here, θ_{D} is the Debye temperature, Ω is the atomic volume, and v is the average speed of sound. Γ is a scattering parameter which we assume to be dominated by the mass difference contribution:

$$\Gamma \approx \Gamma_{\mathrm{M}} = \frac{\sum_{i=1}^{n} c_i \left(\frac{\overline{M_i}}{\hat{M}_i}\right)^2 f_i^{\mathrm{Sb}} f_i^{\mathrm{Bi}} \left(\frac{M_i^{\mathrm{Sb}} - M_i^{\mathrm{Bi}}}{\overline{M_i}}\right)^2}{\sum_{i=1}^{n} c_i}. \tag{S3}$$

Here i is the index of sublattice sites, M_i^k is the mass on site i due to atom k, f_k^k is the fractional occupation of site i due to atom k, $\overline{M_i} = \sum_k f_i^k M_i^k$, and $\hat{M}_i = \frac{\sum_{i=1}^{n} c_i \overline{M_i}}{\sum_{i=1}^{n} c_i}$. We use $\theta_{\mathrm{D}} = 230$ K and $v = 2260$ m/s. The best fit was found for the data points on the Mg_3Sb_2 side where bipolar thermal conduction is not pronounced.

4 Material quality factor analysis

The material quality factor[8,9] for thermoelectrics is devised to provide a doping-independent metric that determines the maximum zT obtainable from the majority carriers of a material, assuming that the material can be optimally doped. The dimensionless material quality factor is defined as:

$$B = \left(\frac{k_B}{e}\right)^2 \frac{e(2m_e k_B)^{3/2} T^{5/2}}{3\pi^2 \hbar^3} \frac{\mu_w}{\kappa_L}. \tag{S4}$$

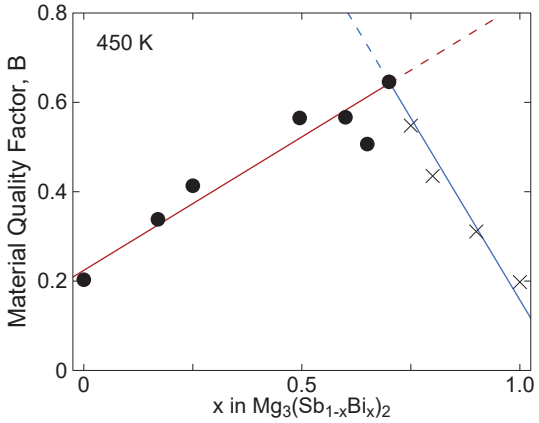

Figure S4: Material quality factors at 450 **K, representing the property of the majority carriers.** Cross-markers (×) are calculated using κ_L from the alloy scattering model values in Fig.4. The actual maximum zT obtainable is lower than that simply extracted from B due to bipolar conduction, especially at the high Mg_3Bi_2 content side.

References

1. Gibbs, Z. M., Kim, H.-S., Wang, H. & Snyder, G. J. Band gap estimation from temperature dependent Seebeck measurement-Deviations from the $2e|S|_{max}T_{max}$ relation. *Applied Physics Letters* **106,** 022112 (2015).
2. Imasato, K., Kang, S. D., Ohno, S. & Snyder, G. J. Band engineering in Mg_3Sb_2 by alloying with Mg_3Bi_2 for enhanced thermoelectric performance. *Materials Horizons* **5,** 59–64 (2018).
3. Agne, M. T. *et al.* Heat capacity of Mg_3Sb_2, Mg_3Bi_2, and their alloys at high temperature. *Materials Today Physics* **6,** 83–88 (2018).
4. Snyder, G. J. & Ursell, T. S. Thermoelectric Efficiency and Compatibility. *Physical Review Letters* **91** (2003).
5. Snyder, G. J. & Snyder, A. H. Figure of merit ZT of a thermoelectric device defined from materials properties. *Energy & Environmental Science* **10,** 2280–2283 (2017).
6. Callaway, J. & von Baeyer, H. C. Effect of Point Imperfections on Lattice Thermal Conductivity. *Physical Review* **120,** 1149–1154 (1960).
7. Klemens, P. G. Thermal Resistance due to Point Defects at High Temperatures. *Physical Review* **119,** 507–509 (1960).
8. Kang, S. D. & Snyder, G. J. Transport property analysis method for thermoelectric materials: material quality factor and the effective mass model. *arXiv:1710.06896 [cond-mat.mtrl-sci].*
9. Kang, S. D. *VI. Application to Thermoelectrics: Material Quality Factor* in *Charge Transport Analysis Using the Seebeck Coefficient-Conductivity Relation* 90–104 (California Institue of Technology, 2018).