Supporting Information

The *p*-type $Mg_2Si_{0.4}Sn_{0.6}$ thermoelectric materials synthesized by the flux method using Li_2CO_3 as doping agent

Peng Gao, Joshua D. Davis, Viktor V. Poltavets and Timothy P. Hogan[c]*

The calculation of the Lorenz number

The Lorenz number L is determined as (Ref 3, 4, 9, 20 and 21 in the manuscript)

$$L = \left(\frac{k_B}{q}\right)^2 \left\{ \frac{\left(\lambda + \frac{7}{2}\right) F_{\lambda + \frac{5}{2}}(\eta)}{\left(\lambda + \frac{7}{2}\right) F_{\lambda + \frac{1}{2}}(\eta)} - \delta^2 \right\}$$

$$\delta = \frac{\left(\lambda + \frac{5}{2}\right) F_{\lambda + \frac{3}{2}}(\eta)}{\left(\lambda + \frac{3}{2}\right) F_{\lambda + \frac{1}{2}}(\eta)}$$

where the scattering mechanism is taken as λ = -1/2 for phonon scattering dominated transport as discussed in the manuscript.

The Boltzmann constant is denoted by k_B and q is the charge per electron or hole. The Fermi-Dirac integral is calculated numerically as a function of η and stored in data files.

$$F_r(\eta) = \int_0^\infty x^r \frac{1}{1 + e^{x - \eta}} dx$$

In a single parabolic band conduction model, the Seebeck coefficients could be calculated as

$$S = \frac{k_B}{q} \left[\frac{\left(\lambda + \frac{5}{2}\right) F_{\lambda + \frac{3}{2}}(\eta)}{\left(\lambda + \frac{3}{2}\right) F_{\lambda + \frac{1}{2}}(\eta)} - \eta \right]$$

Knowing the experimental values of S, the value of η could be solved by looking up the Fermi-Dirac integral data files. Once η is solved, the Lorenz number and the electronic thermal conductivity (Fig. 4 in the manuscript) could be calculated by Equation 3 in the manuscript.

The calculation of the thermal conductivity for the MgO-$Mg_2Si_{0.4}Sn_{0.6}$ two-phase system

As summarized by Hashin and Shtrikman, for an N-phase composite with component volume fraction v_i and conductivities k_i, the effective conductivity k* of the composite should falls into the region defined by a lower and upper bound.[1,2]

$$k_L \leq k^* \leq k_U$$

where

$$k_L = k_m + A_m/(1 - \alpha_m A_m)$$

$$k_U = k_n + A_n/(1 - \alpha_n A_n)$$

$$A_s = f(x) = \sum_{j=1}^{N} v_j\left[(k_j - k_s)^{-1} + \alpha_s\right]^{-1} \qquad s = m,n$$

$$\alpha_S = (3k_s)^{-1}$$

and k_m and k_n denote the minimum and the maximum of the phase conductivities, respectively.

The parameters used for our calculation are listed in the following tables, where the density data are used to convert the XRD-RIR calculated weight percentage to volume percentage.

Temperature / K	k_m ($Mg_2Si_{0.4}Sn_{0.6}$) / $W{\cdot}m^{-1}{\cdot}K^{-1}$	k_n $(MgO)^3$ / $W{\cdot}m^{-1}{\cdot}K^{-1}$	ρ($Mg_2Si_{0.4}Sn_{0.6}$) / $g{\cdot}cm^{-3}$	ρ(MgO) / $g{\cdot}cm^{-3}$
375	1.2615	28.4	3	3.58

Supporting figures

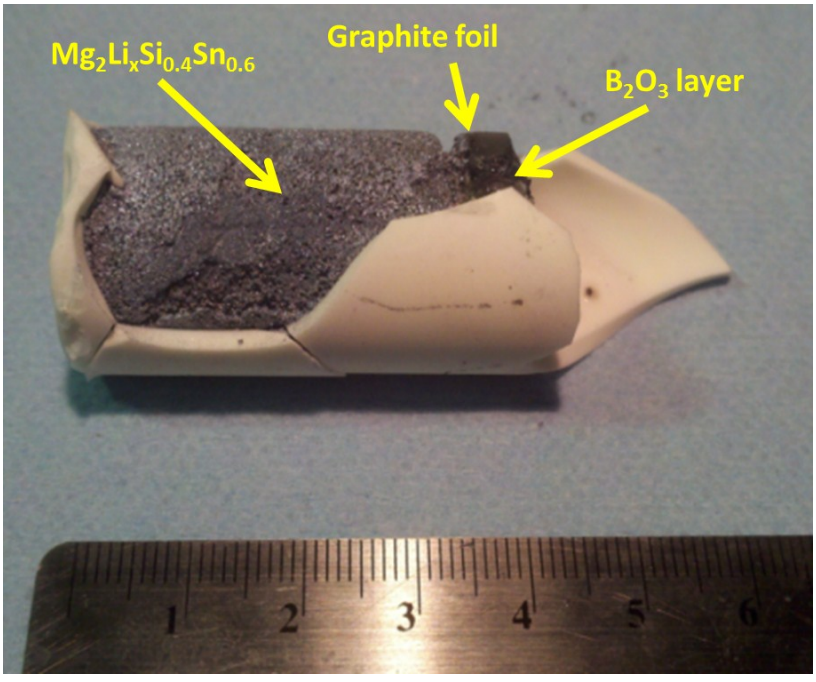

Fig. S1 Photo of the sample ingot

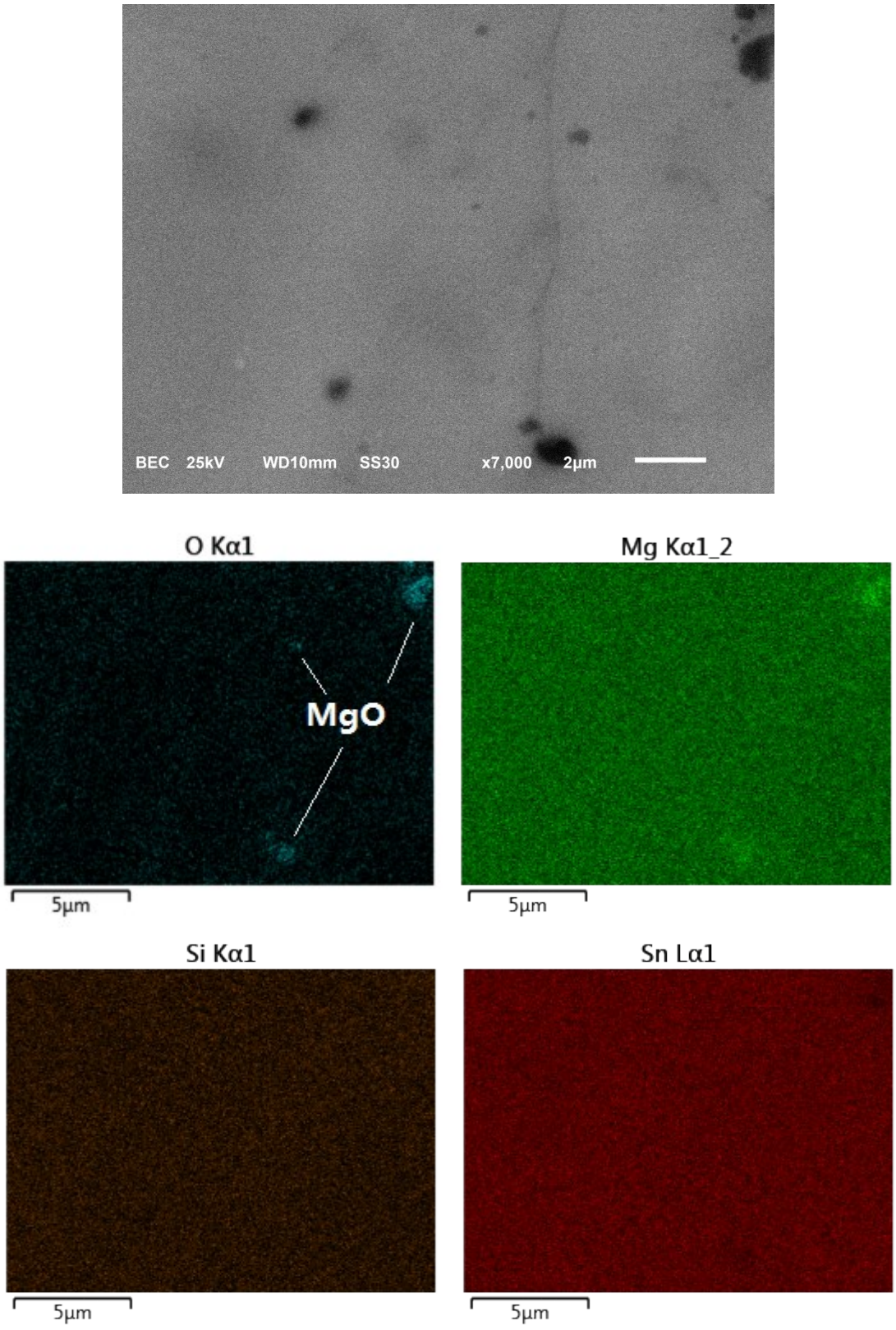

Fig. S2 The SEM images of the doped sample and the EDS mapping results

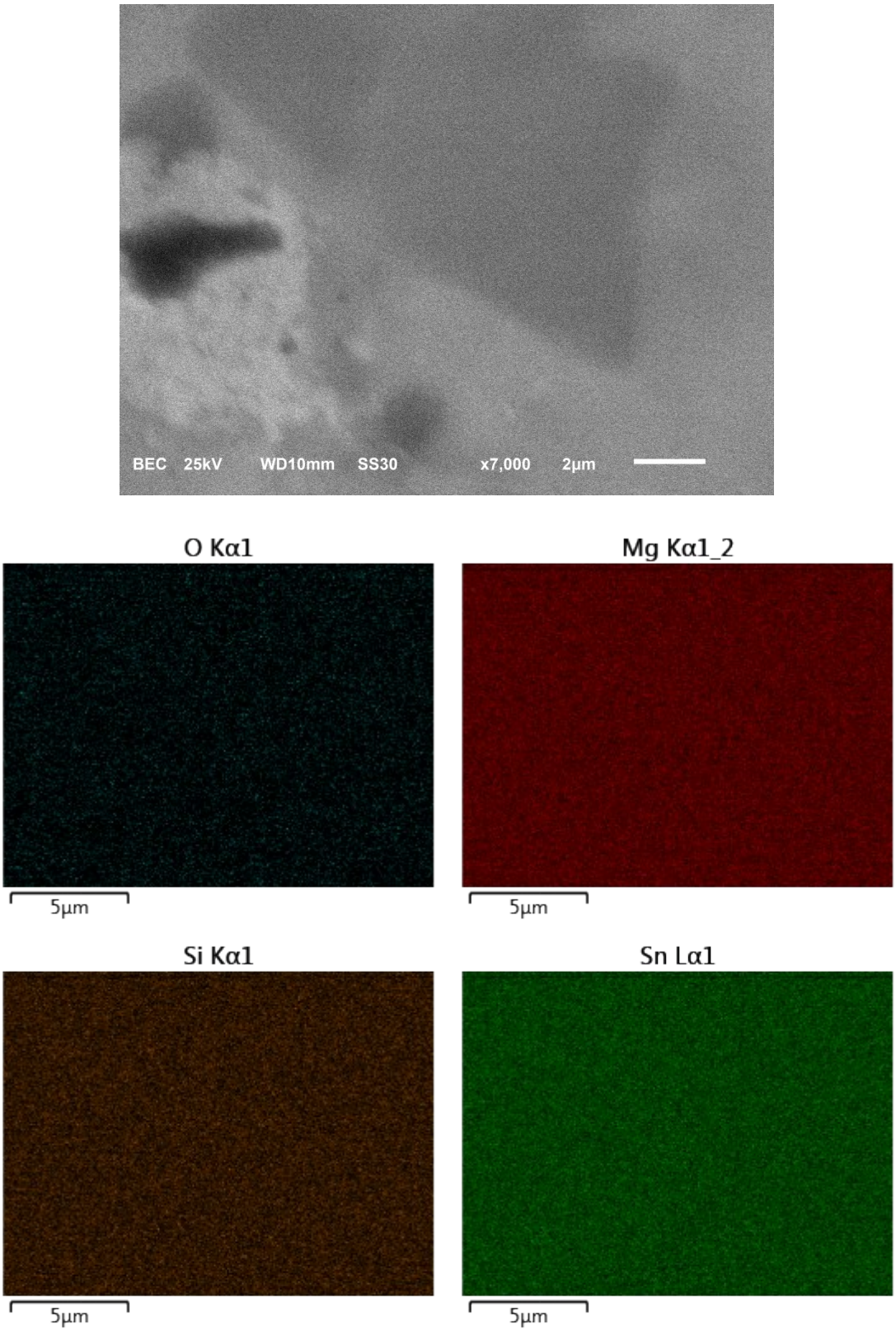

Fig. S3 The SEM images of the undoped sample and the EDS mapping results

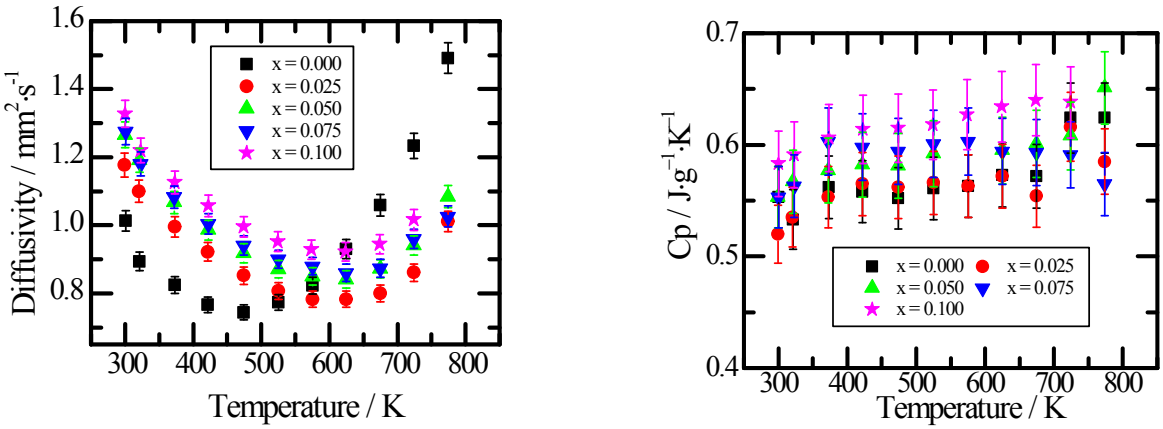

Fig. S4 The raw data of thermal diffusivity and specific heat for $Mg_2Li_xSi_{0.4}Sn_{0.6}$ samples

Fig. S5 Photo of two pieces of sample from the same pellet (the one the left is the one that has not been tested and the one on the right is the one that has been measured to 775K.)

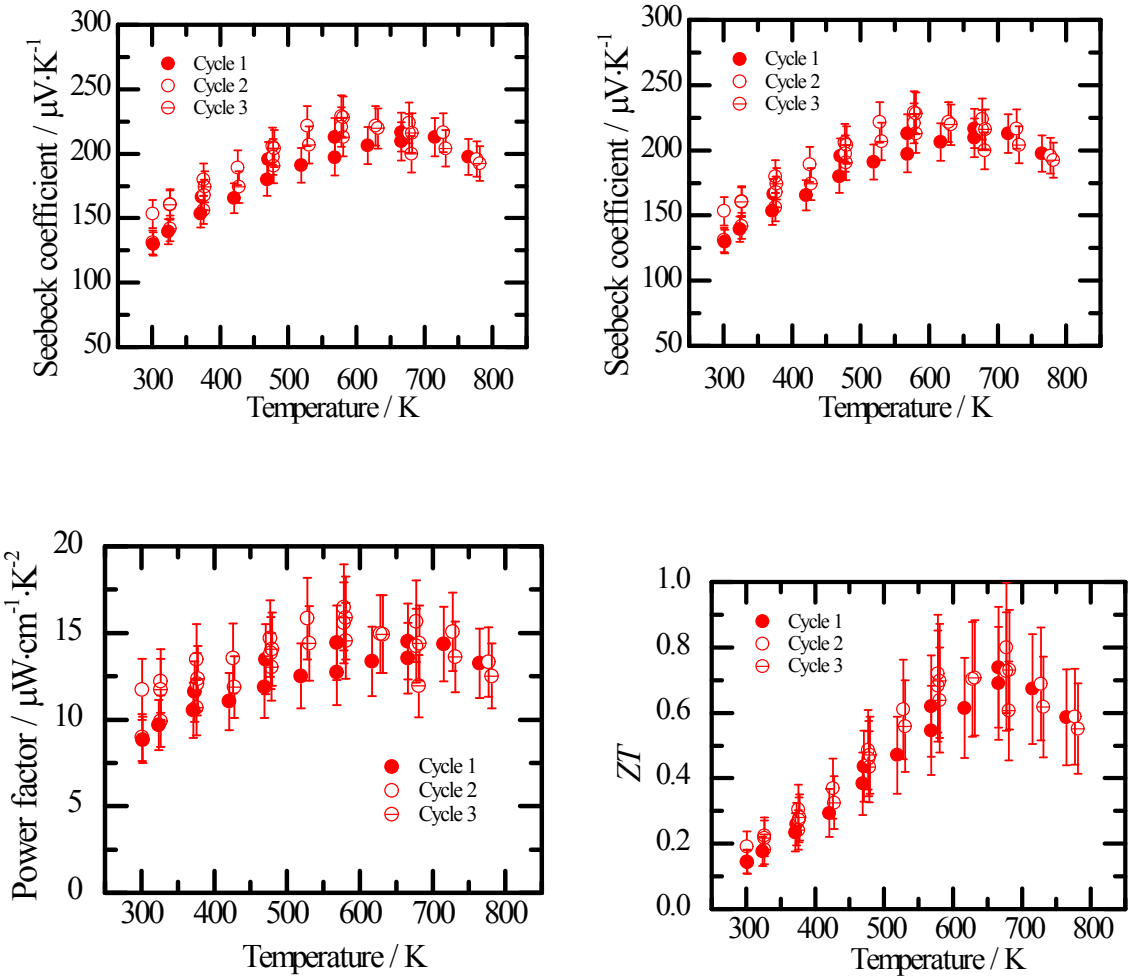

Fig. S6 Cycling measurement of (S and σ) on $Mg_2Li_{0.025}Si_{0.4}Sn_{0.6}$ (ZT is calculated using S and σ from each cycle and κ from Fig. 3e)

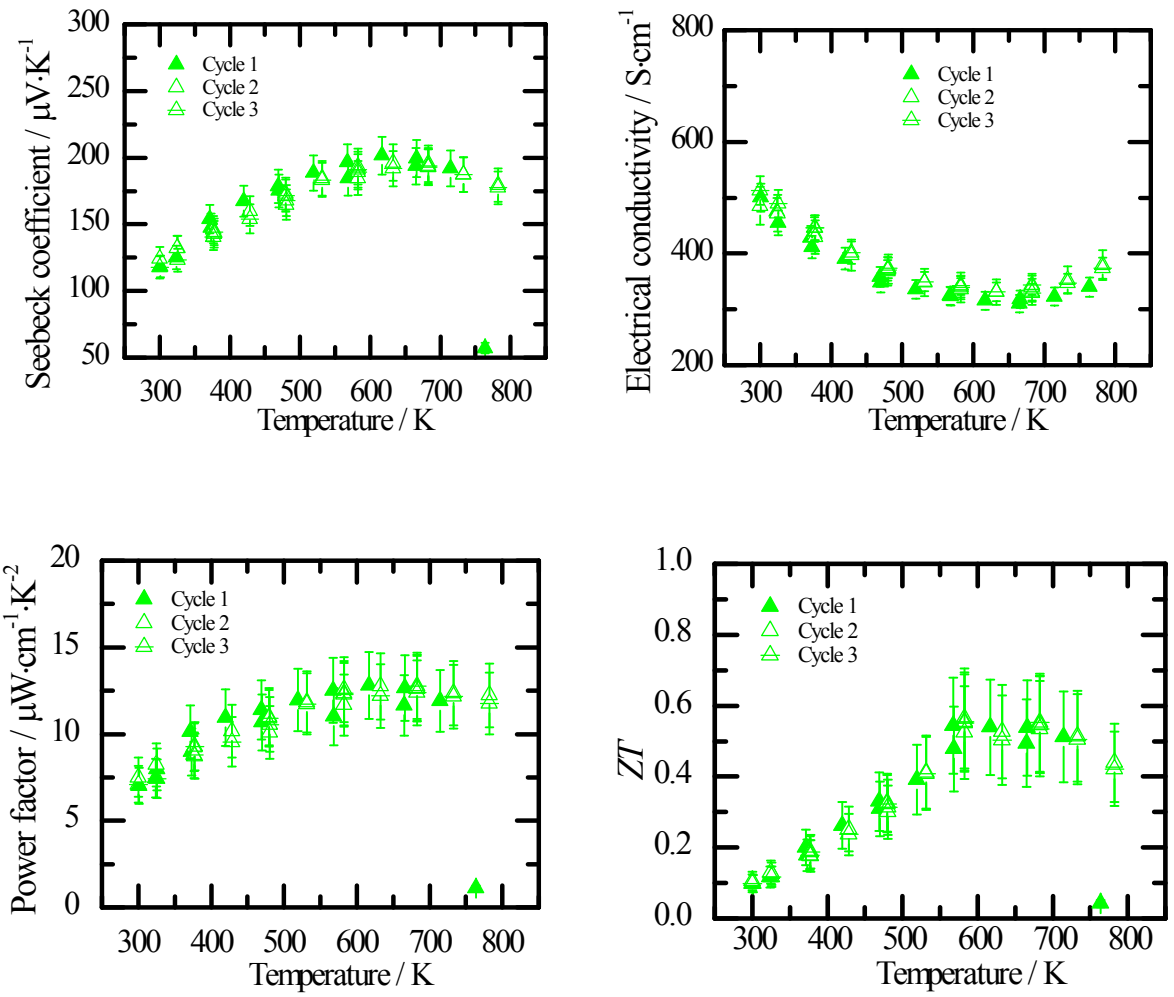

Fig. S7 Cycling measurement of (S and σ) on $Mg_2Li_{0.050}Si_{0.4}Sn_{0.6}$ (ZT is calculated using S and σ from each cycle and κ from Fig. 3e)

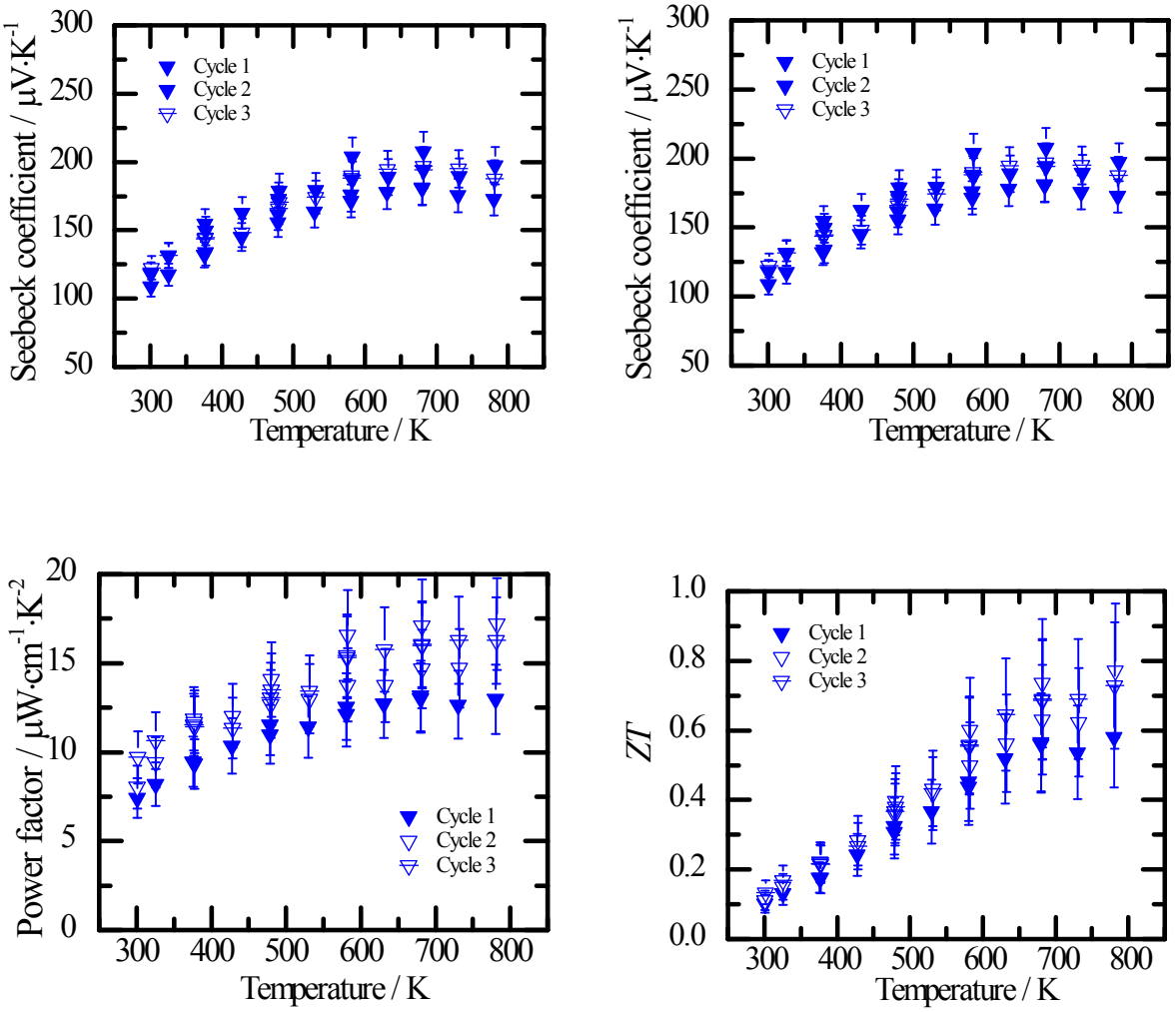

Fig. S8 Cycling measurement of (S and σ) on $Mg_2Li_{0.075}Si_{0.4}Sn_{0.6}$ (ZT is calculated using S and σ from each cycle and κ from Fig. 3e)

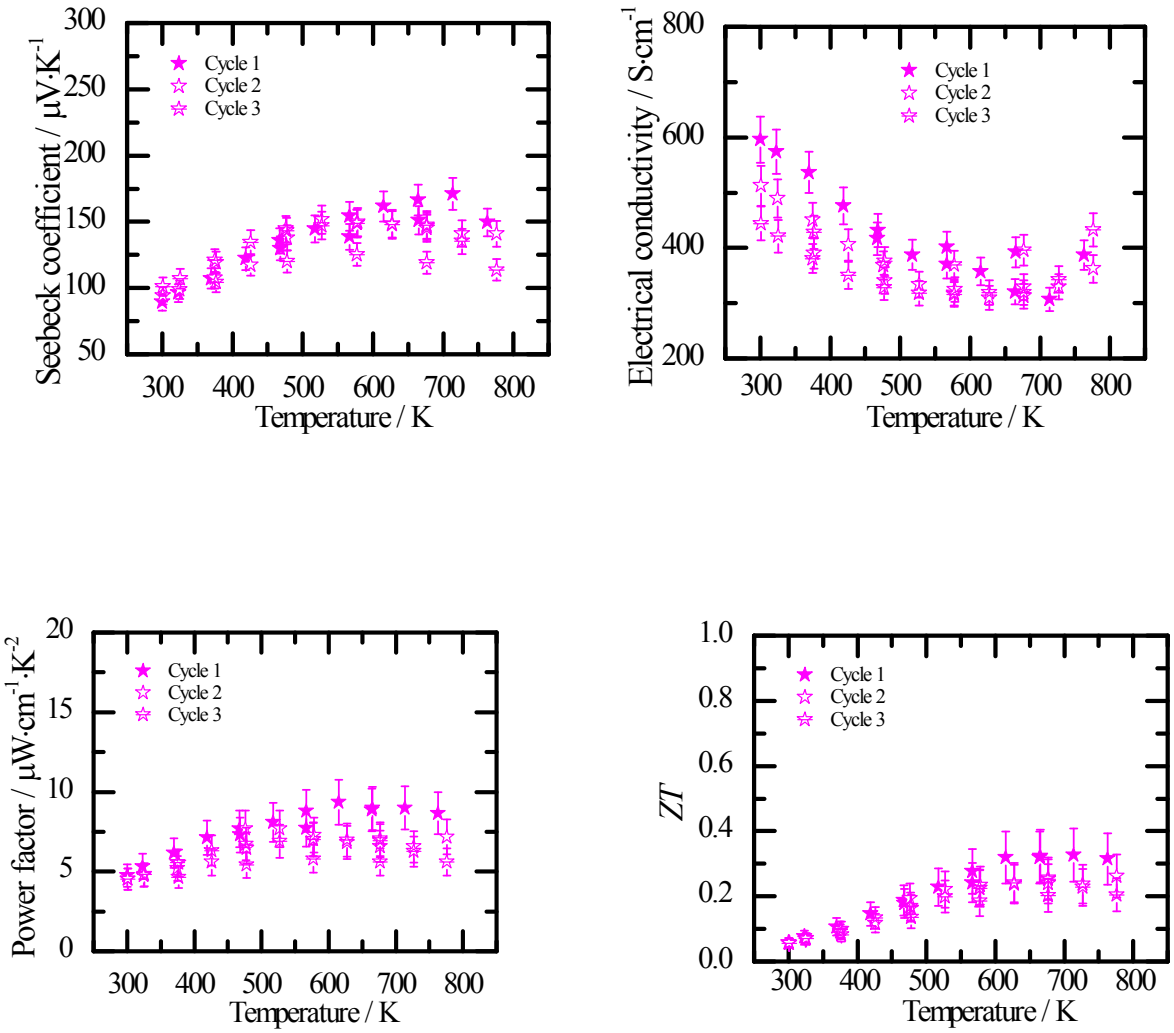

Fig. S9 Cycling measurement of (S and σ) on $Mg_2Li_{0.100}Si_{0.4}Sn_{0.6}$ (ZT is calculated using S and σ from each cycle and κ from Fig. 3e)

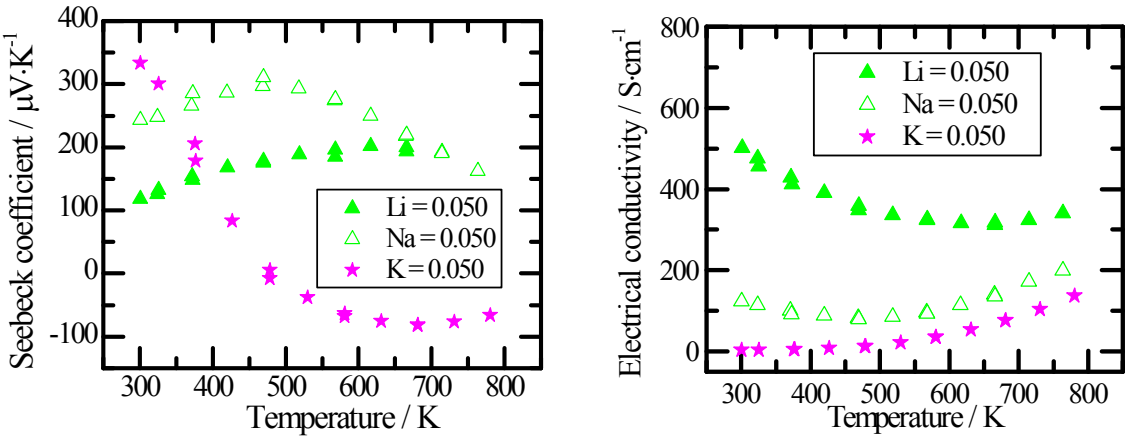

Fig. S10 Transport property of Na_2CO_3, K_2CO_3 and Li_2CO_3 doped sample

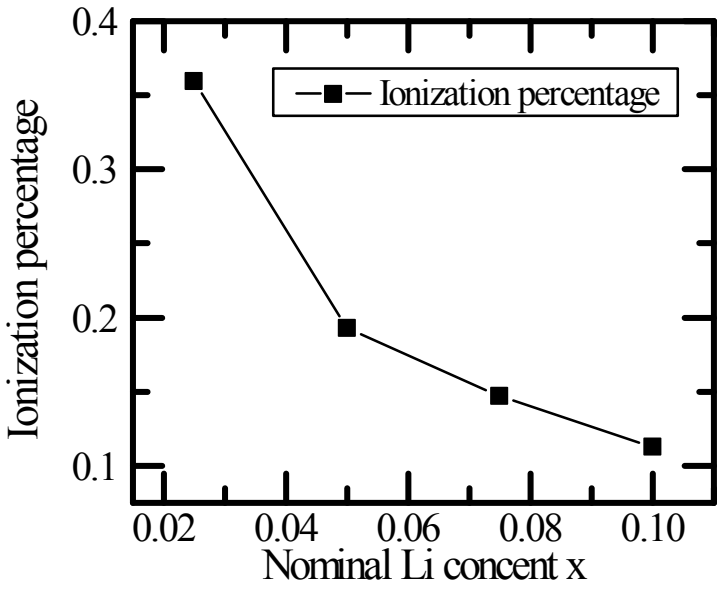

Fig. S11 "Ionization" percentage

Reference

1. Y. Benveniste, *J. Appl. Math. Phys.*, 1986, 37, 696.

2. Z. Hashin and S. Shtrikman, *J. Appl. Phys.*, 1962, 33, 3125.

3. A. J. Slifka, B. J. Filla, and J. M. Phelps, *J. Res. Natl. Inst. Stand. Technol.*, 1998, **103**, 357.