Supporting Information

Synergistic Modulation on the Thermoelectric Performance of Melt-spun p-Type Mg_2Sn via Na_2S and Si Alloying

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Calculation of density of state effective mass by single parabolic band model [1]

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

$$n_H = \frac{1}{eR_H} = \frac{\left(2m^* k_B T\right)^{3/2}(r+3/2)^2 F_{(r+1/2)}(\eta)}{3\pi^2\hbar^3 \quad (2r+3/2)F_{(2r+1/2)}(\eta)}$$

where η, k_B, e, r, R_H, m^*, T and $\hbar$ are reduced Fermi level, the Boltzmann constant, the electronic charge, carrier scattering parameter, the Hole coefficient, effective mass, absolute temperature and the reduced Pulank constant, respectively.

$$F_j(\eta) = \int_0^\infty \frac{\xi^j d\xi}{1 + e^{(\xi - \eta)}}$$

where $F_j(\eta)$is the Fermi integral.

Calculation of thermal conductivity by Debye-Callaway model

In order to understand the impacts of different phonon scattering process and lattice thermal conductivity, Debye-Callaway model and the relaxation time are carried out here to calculate the contribution of different scattering effects[2,3]. Within the Debye-Callaway model, the lattice thermal conductivity can be expressed via the following equation:

$$\kappa_L = \frac{k_B}{2\pi^2 v}\left(\frac{k_B}{\hbar}\right)^3 T^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{\tau_c^{-1}\left(e^x - 1\right)^2} dx$$

where k_B is the Boltzmann constant, v is the the average sound velocity, $\hbar$ is the reduced Plank constant, T is the absolute temperature, θ_D is the Debye temperature, τ_c is the phonon relaxation time, and x is defined as $x = \hbar\omega/k_B T$, where ω is the phonon frequency.

In this work, we took Umklapp scattering (τ_U), grain boundary scattering (τ_B), and point defect scattering (τ_{PD}) into consideration. The phonon relaxation time can be given by:

$$\tau_U^{-1} = \frac{h\gamma^2\omega^2 T}{Mv^2\theta_D} exp\left(-\frac{\theta_D}{3T}\right)$$

$$\tau_B^{-1} = \frac{v}{L}$$

$$\tau_{PD}^{-1} = \frac{V\omega^4}{4\pi v^2}\Gamma$$

$$\tau_c^{-1} = \tau_U^{-1} + \tau_B^{-1} + \tau_{PD}^{-1} = B\omega^2 T e^{-\theta_D/3T} + \frac{v}{L} + A\omega^4$$

where M is average atomic mass, γ is the Gruneisen parameter, θ_D is the Debye temperature, L is grain size, V is average atomic volume, and Γ is point defect scattering parameter of $(Mg_2Sn_{0.9}Si_{0.1})_{0.93}(Na_2S)_{0.07}$[4].

The mass-fluctuation phonon-scattering parameter can be given by:

$$\Gamma = \sum_i f_i \left(1 - \frac{M_i}{M}\right)^2$$

where M is the mass of a unit cell, f_i is the fraction of unit cells with mass M_i, and M is the average mass of all cells.

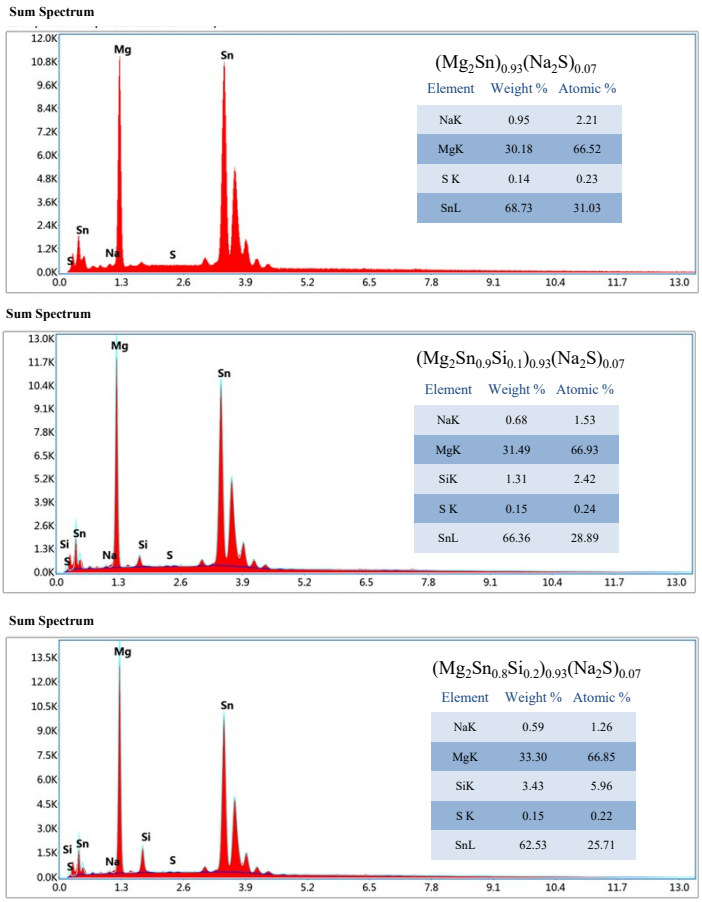

Figure S1 EDS spectra and chemical compositions of $(Mg_2Sn_{1-y}Si_y)_{0.93}(Na_2S)_{0.07}$ (y = 0, 0.1, 0.2).

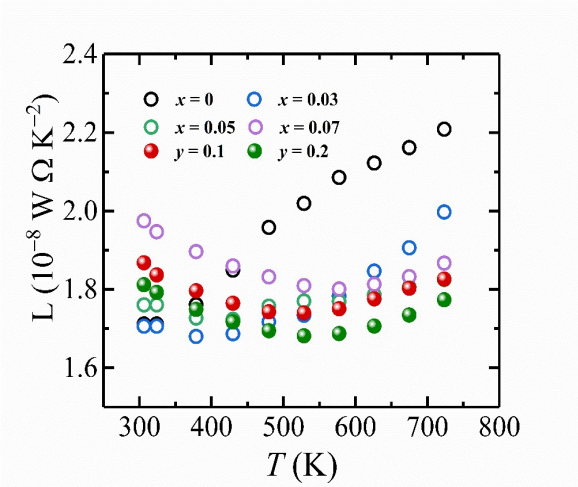

Figure S2 Temperature dependence of calculated Lorentz constant for $(Mg_2Sn)_{1-x}(Na_2S)_x$ (x = 0, 0.03, 0.05, 0.07), and $(Mg_2Sn_{1-y}Si_y)_{0.93}(Na_2S)_{0.07}$ (y = 0.1, 0.2) compounds.

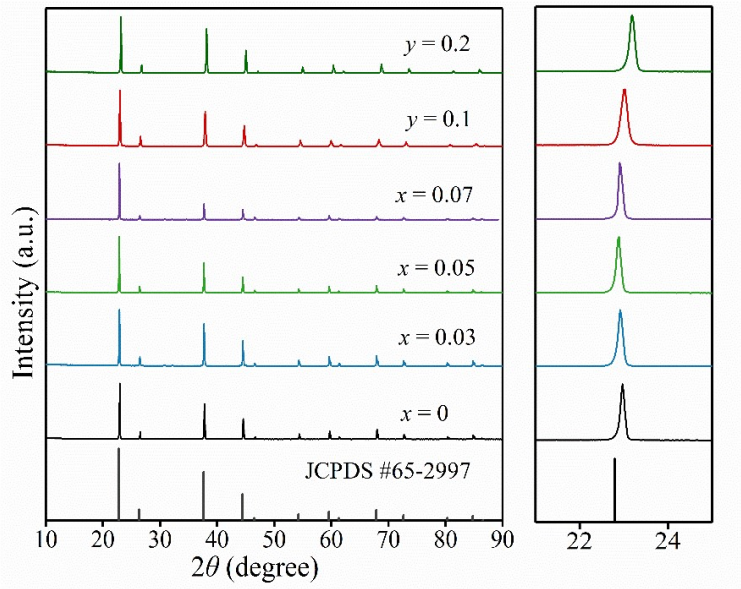

Figure S3 XRD patterns for the $(Mg_2Sn)_{1-x}(Na_2S)_x$ (x = 0, 0.03, 0.05, 0.07) sample, and $(Mg_2Sn_{1-y}Si_y)_{0.93}(Na_2S)_{0.07}$ (y = 0.1, 0.2) samples. All the diffraction peaks can be indexed to Mg_2Sn phase with an anti-fluorite structure.

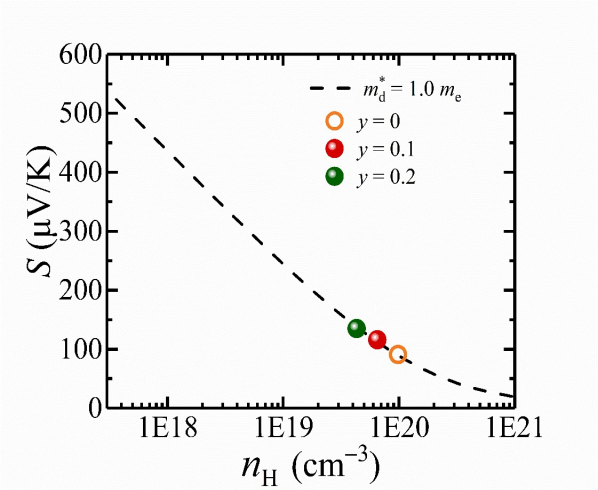

Figure S4 The relationship between Seebeck coefficient and carrier concentration of $(Mg_2Sn_{1-y}Si_y)_{0.93}(Na_2S)_{0.07}$ (y = 0, 0.1, 0.2) compounds. The dashed line is the Pisarenko curve calculated by the SPB model (m^* = 1.0 m_e).

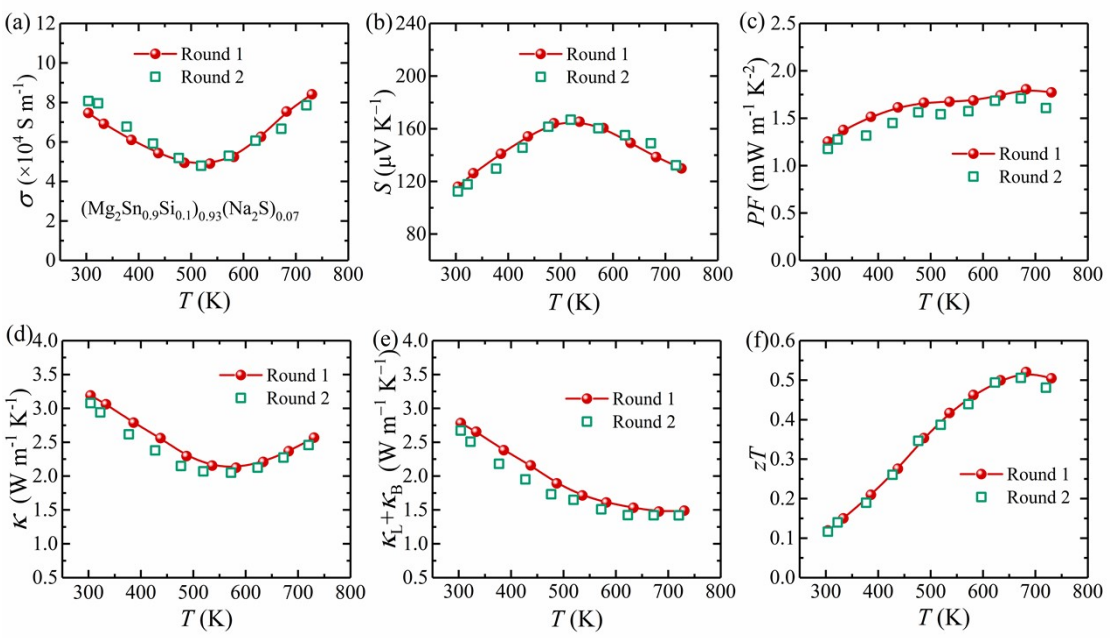

Figure S5 The temperature-dependent (a) electrical conductivity, (b) Seebeck coefficient, (c) power factor, (d) total thermal conductivity, (e) lattice and bipolar thermal conductivity, and (f) zT values of $(Mg_2Sn_{0.9}Si_{0.1})_{0.93}(Na_2S)_{0.07}$ measured during two consecutive cycles during heating up to 723 K.

Table S1 Room temperature properties of the $(Mg_2Sn)_{1-x}(Na_2S)_x$ (x = 0, 0.03, 0.05, 0.07), and $(Mg_2Sn_{1-y}Si_y)_{0.93}(Na_2S)_{0.07}$ (y = 0.1, 0.2) compounds.

Composition	**carrier concentration (cm^{-3})**	**Hall mobility ($cm^2\ V^{-1}\ s^{-1}$)**	**Effective mass ($cm^2\ V^{-1}\ s^{-1}$)**
x = 0	-5.3×10^{18}	153	1.0
x = 0.03	2.8×10^{19}	82	1.0
x = 0.05	3.1×10^{19}	93	1.1
x = 0.07	9.8×10^{19}	69	1.1
y = 0.1	6.5×10^{19}	77	1.1
y = 0.2	4.3×10^{19}	75	1.2

Table S2 Room temperature physical parameters of $(Mg_2Sn_{0.9}Si_{0.1})_{0.93}(Na_2S)_{0.07}$ used to calculate κ_L based on different scattering process mentioned above.

Parameter	Values
Longitudinal sound velocity v_l (m s^{-1})	4324
Transverse sound velocity v_t (m s^{-1})	3601
Average sound velocity v (m s^{-1})	3787
Gruneisen parameter γ	1.41
Debye temperature θ_D (K)	270
Average atomic volume V (m^3)	7.5×10^{-29}
Grain size L (μm)	1

References

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2. J. Callaway, and H. C. von Baeyer, *Phys. Rev.*, 1960, **120**, 1149–1154.
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4. D. T. Morelli, J. P. Heremans, and G. A. Slack, *Phys. Rev. B*, 2002, **66**, 195304.