Thermoelectric properties of materials in Mg₂Sn-Mg₂Ge-Mg₂Si system

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Abstract

Thermoelectric properties of $\text{Mg}_2(\text{Sn}_{0.765}\text{Ge}_{0.22}\text{Sb}_{0.015})_{1-x}(\text{Sn}_{0.685}\text{Si}_{0.3}\text{Sb}_{0.015})_x$ materials with compositions on and near the line connecting $\text{Mg}_2\text{Sn}_{0.765}\text{Ge}_{0.22}\text{Sb}_{0.015}$ and $\text{Mg}_2\text{Sn}_{0.685}\text{Si}_{0.3}\text{Sb}_{0.015}$ in the Mg₂Sn-Mg₂Ge-Mg₂Si system are investigated. Although ZT s are very similar, power factors are different. On the line, the power factor decreases from $\text{Mg}_2\text{Sn}_{0.765}\text{Ge}_{0.22}\text{Sb}_{0.015}$ to $\text{Mg}_2\text{Sn}_{0.685}\text{Si}_{0.3}\text{Sb}_{0.015}$, and off the line, the power factor also decreases. The output power and energy conversion efficiency are calculated using engineering power factor $(PF)_{\text{eng}}$ and figure of merit $(ZT)_{\text{eng}}$. It is shown that although similar energy conversion efficiency of ~11% could be achieved for all compositions studied, the output power are different, increasing from ~9.1 W cm⁻² for $\text{Mg}_2\text{Sn}_{0.685}\text{Si}_{0.3}\text{Sb}_{0.015}$ to ~10.3 W cm⁻² for $\text{Mg}_2\text{Sn}_{0.765}\text{Ge}_{0.22}\text{Sb}_{0.015}$, due to the different power factors.

Keywords: Mg₂Sn-Mg₂Ge-Mg₂Si; Thermoelectric; Output power; Efficiency

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1. Introduction

Thermoelectric materials, converting heat energy into electricity, have received extensive attentions due to their potential roles in increasing energy conversion efficiency in vehicles, boilers, solar generators, etc. [1-5]. Thermoelectric performance of power generation devices requires not only high conversion efficiency but also large output power [6, 7]. On the basis of constant property model, the maximum energy conversion efficiency (η_{max}) and output power (ω_{max}) are related to material parameters figure of merit (ZT) and power factor (PF), respectively, as following [7].

$$\eta_{max} = \frac{T_H - T_C}{T_H} \left(\frac{\sqrt{1 + Z\bar{T}} - 1}{\sqrt{1 + Z\bar{T}} + T_C / T_H} \right) \quad (1)$$

$$\omega_{max} = \frac{1}{4} \frac{(T_H - T_C)^2}{L_{leg}} PF \quad (2)$$

where $Z\bar{T} = S^2\bar{T}/\rho\kappa$, $PF = S^2/\rho$, and $\bar{T} = (T_H + T_C)/2$, S is Seebeck coefficient, ρ is electrical resistivity, κ is thermal conductivity, L_{leg} is leg length, T_H is hot side temperature, and T_C is cold side temperature.

For the Mg_2Sn - Mg_2Ge - Mg_2Si system, most of the research has focused on Mg_2Sn - Mg_2Si [8-23], with limited reports on Mg_2Sn - Mg_2Ge [7, 24] and Mg_2Ge - Mg_2Si [25-29]. Improved ZT from Si alloying effects were early demonstrated in Mg_2Sn - Mg_2Si system, and the best property was achieved in $Mg_2Sn_{0.6}Si_{0.4}$ [9]. Recently, there are increasing interests in reinvestigating the Mg_2Sn - Mg_2Si system around the composition of $Mg_2Sn_{0.6}Si_{0.4}$ [10, 11, 16, 19, 22, 23]. One of the investigations found that $Mg_2Sn_{0.7}Si_{0.3}$ has higher power factor ($\sim 47 \mu W cm^{-1} K^{-2}$ at 523 K) and hence higher ZT (~ 1.3 at 700 K) than $Mg_2Sn_{0.6}Si_{0.4}$ due to the composition caused band crossing (or band convergence) [16]. Recently, Liu *et al.* reported $Mg_2Sn_{0.75}Ge_{0.25}$ is even better than $Mg_2Sn_{0.7}Si_{0.3}$ with higher PF ($\sim 55 \mu W cm^{-1} K^{-2}$ at 623 K) and higher ZT (~ 1.4 at 723 K) with a similar band crossing in Mg_2Sn - Mg_2Ge system happened near the composition of $Mg_2Sn_{0.75}Ge_{0.25}$ [7]. According to our recent understanding [30], in the Sn-poor region (purple in Fig. 1a), it would have a

light band (C_L -band) at the bottom which is mainly from the hybridized 3p orbital of Mg with the s-orbital and d- e_g orbital of IV elements (*i.e.*, Sn, Ge, Si) as shown in Fig. 1b. In contrast, in the Sn-rich region (blue in Fig. 1a), it has a heavy band (C_H -band) at the bottom which is the hybridization between 3s-orbital of Mg with the d- t_{2g} orbital of IV elements, shown in Fig. 1d. Thus, at certain composition, the C_L -band and C_H -band would converge, shown in Fig. 1c.

For $Mg_2Sn_{0.7}Si_{0.3}$ and $Mg_2Sn_{0.75}Ge_{0.25}$, their high thermoelectric performance are mainly attributed to the band crossing. It is expected that the band crossing would also occur in compositions on and near the line connecting $Mg_2Sn_{0.7}Si_{0.3}$ and $Mg_2Sn_{0.75}Ge_{0.25}$ in the Mg_2Sn - Mg_2Ge - Mg_2Si system with a possibility of even higher thermoelectric performance. It is noted that there are several reports on thermoelectric properties of Mg_2Sn - Mg_2Ge - Mg_2Si system [23, 24, 31-33], as shown in Fig. 1a. Most of them are about partial substitution of Sn by Ge in $Mg_2Sn_{0.6}Si_{0.4}$, such as $Mg_2Sn_{0.55}Ge_{0.05}Si_{0.4}$ and $Mg_2Sn_{0.5}Ge_{0.10}Si_{0.4}$ [6]. However, from the band crossing map (Fig. 1b, c, d), substitution of Ge for Sn in $Mg_2Sn_{0.6-y}Ge_ySi_{0.4}$ brings the material away from the line connecting $Mg_2Sn_{0.75}Ge_{0.25}$ and $Mg_2Sn_{0.7}Si_{0.3}$, which lose the benefits of the unique band structure. Tada *et al.* [24] has conducted an investigation on $Mg_2Sn_xGe_{0.1}Si_{0.9-x}$ ($x = 0.6, 0.65, 0.75, 0.9$), near the line. However, they only did the composition $Mg_2Sn_{0.6}Ge_{0.1}Si_{0.3}$, showing an n-type behavior and also poor electrical conductivity. To our best knowledge, there is still lack of investigation about the compositions on and near the line connecting $Mg_2Sn_{0.75}Ge_{0.25}$ and $Mg_2Sn_{0.7}Si_{0.3}$ in the Mg_2Sn - Mg_2Ge - Mg_2Si system.

Therefore, the motivation of this work is to investigate the thermoelectric properties of $Mg_2(Sn_{0.765}Ge_{0.22}Sb_{0.015})_{1-x}(Sn_{0.685}Si_{0.3}Sb_{0.015})_x$ in the Mg_2Sn - Mg_2Ge - Mg_2Si system on and near the line connecting $Mg_2Sn_{0.765}Ge_{0.22}Sb_{0.015}$ and $Mg_2Sn_{0.685}Si_{0.3}Sb_{0.015}$. It is noted that $Mg_2Sn_{0.75}Ge_{0.25}$ is slightly deviate from the theoretically predicted band crossing point of $Mg_2Sn_{0.78}Ge_{0.22}$ [10]. In our previous work, $Mg_2Sn_{0.75}Ge_{0.25}$ was investigated, while $Mg_2Sn_{0.78}Ge_{0.22}$ has not yet been studied. In this work, we have studied compositions on and near the line connecting $Mg_2Sn_{0.765}Ge_{0.22}Sb_{0.015}$ and $Mg_2Sn_{0.685}Si_{0.3}Sb_{0.015}$. The thermoelectric performances were further evaluated by using engineering

power factor $(PF)_{eng}$ and figure of merit $(ZT)_{eng}$ [34], which consider the temperature dependence of thermoelectric properties over the whole temperature range of the hot and cold sides.

2. Experimental Section

2.1 Synthesis

High purity magnesium turnings (Mg, 99.98%; Alfa Aesar), tin powder (Sn, 99.8%; Alfa Aesar), germanium powder (Ge, 99.9999%; Alfa Aesar), silicon shots (Si, 99.9999%; Alfa Aesar) were weighed according to the composition of $Mg_2(Sn_{0.765}Ge_{0.22}Sb_{0.015})_{1-x}(Sn_{0.685}Si_{0.3}Sb_{0.015})_x$ ($x = 0, 0.2, 0.4, 0.6, 0.8, 1$). Moreover, samples near the line connecting $Mg_2Sn_{0.765}Ge_{0.22}Sb_{0.015}$ and $Mg_2Sn_{0.685}Si_{0.3}Sb_{0.015}$ were also prepared, *i.e.*, $Mg_2Sn_{0.685}Ge_{0.25}Si_{0.05}Sb_{0.015}$, $Mg_2Sn_{0.685}Ge_{0.15}Si_{0.15}Sb_{0.015}$, $Mg_2Sn_{0.735}Ge_{0.15}Si_{0.1}Sb_{0.015}$, $Mg_2Sn_{0.735}Ge_{0.05}Si_{0.2}Sb_{0.015}$. For all the samples, 3 at% extra Mg were added in order to compensate the loss of Mg during the preparation. The elements were loaded into stainless steel ball milling jar in glove box under argon atmosphere with oxygen level below 3.5 ppm. The materials were ball milled for 20 hours at 1200 rpm. The ball-milled powders were then loaded into a graphite die with an inner diameter of 12.7 mm in glove box. Then, the graphite die with loaded powder was removed from glove box and immediately sintered by direct current-induced hot pressing at 1023 K for 2 min. The hot pressed disks are about 2-3 mm thick.

2.2 Thermoelectric property characterizations

All the samples were cut into about 2 mm × 2 mm × 12 mm for simultaneous electrical resistivity and Seebeck coefficient characterizations under Helium atmosphere (ZEM-3; ULVAC Riko). Thermal conductivity $\kappa = dDC_p$ was calculated using the measured density (d) by Archimedeian method, specific heat (C_p) by differential scanning calorimetry (DSC 404C; Netzsch) and thermal diffusivity (D) by laser flash method (LAF457; Netzsch). It should be pointed out that

$\text{Mg}_2(\text{Sn}_{0.765}\text{Ge}_{0.22}\text{Sb}_{0.015})_{1-x}(\text{Sn}_{0.685}\text{Si}_{0.3}\text{Sb}_{0.015})_x$ materials become unstable when the temperature is above 723 K. (*i.e.*, the measured thermoelectric properties during the cooling process are totally different from the measured values during the heating process). Therefore, all the thermoelectric parameters were measured from room temperature to 723 K only. The errors of measurement for electrical resistivity, Seebeck coefficient, and thermal conductivity are $\pm 5\%$, $\pm 5\%$, and $\pm 7\%$, respectively. Hall coefficient R_H was measured at room temperature on a commercial system (PPMS; Quantum Design) using a four-probe configuration, with the magnetic field sweeping between ± 3 T and an electrical current between 10 and 20 mA. The Hall carrier concentration n_H and Hall carrier mobility μ_H were calculated via the relations $n_H = 1/(e R_H)$ and $\mu_H = R_H/\rho$.

2.3 Microstructure and phase composition

The phase composition of the samples was characterized by X-ray diffraction (PANalytical X'pert PRO diffractometer with a Cu K α radiation source). The lattice constants of $\text{Mg}_2(\text{Sn}_{0.765}\text{Ge}_{0.22}\text{Sb}_{0.015})_{1-x}(\text{Sn}_{0.685}\text{Si}_{0.3}\text{Sb}_{0.015})_x$ were calculated by Rietveld refinement using the Fullprof software. The crystal structure of Mg_2Sn (#642850, ICSD database) was chosen as the starting structure. The microstructures of the samples were studied by a JEOL 6340F scanning electron microscope (SEM). The elemental mapping was conducted by energy-dispersive X-ray spectroscopy (EDS) inside the SEM. The actual compositions were determined by the electron probe micro analyzer (EPMA, JEOL JXA 8600).

3. Results and Discussion

3.1 On the line connecting $\text{Mg}_2\text{Sn}_{0.765}\text{Ge}_{0.22}\text{Sb}_{0.015}$ and $\text{Mg}_2\text{Sn}_{0.685}\text{Si}_{0.3}\text{Sb}_{0.015}$

Fig. 2 shows the XRD patterns of $\text{Mg}_2(\text{Sn}_{0.765}\text{Ge}_{0.22}\text{Sb}_{0.015})_{1-x}(\text{Sn}_{0.685}\text{Si}_{0.3}\text{Sb}_{0.015})_x$ which can be indexed to the CaF_2 crystal structure (PDF-#07-0274, Fig. 2a). No impurity phases such as Mg or MgO are observed within the detection limit of the XRD machine. As shown in Fig. 2b, the

diffraction peak shifts to higher angle with increase of x . By Rietveld refinement the lattice parameters of each sample are calculated (Fig. 3). The lattice parameters of $\text{Mg}_2\text{Sn}_{0.765}\text{Ge}_{0.22}\text{Sb}_{0.015}$ and $\text{Mg}_2\text{Sn}_{0.685}\text{Si}_{0.3}\text{Sb}_{0.015}$ are ~ 6.685 Å and ~ 6.643 Å, respectively. It decreases linearly with the increase of x , which obeys the Vegard's law (inset of Fig. 3). The decrease of lattice constants should be mainly due to the smaller atomic radius of Si atom (1.11 Å) than that of Ge atom (1.22 Å) and Sn atom (1.40 Å). The linear dependence of lattice constants on the composition indicates the formation of solid solution in the whole range of x . In order to investigate the microstructure of $\text{Mg}_2(\text{Sn}_{0.765}\text{Ge}_{0.22}\text{Sb}_{0.015})_{1-x}(\text{Sn}_{0.685}\text{Si}_{0.3}\text{Sb}_{0.015})_x$, the SEM and EDS characterization are also taken. As shown in Fig. 4a, there are no pores in our hot pressed sample which indicates its high relative density. Fig. 4b-4f show the uniformly distribution of each elements. It is noted that within the detection limit of the SEM machine, no impurity phases are observed which showed a good agreement with the XRD results. Moreover, the actual compositions measured by EPMA also show a reasonable agreement with the nominal compositions (Table 1).

Fig. 5 shows the thermoelectric properties as a function of temperature for $\text{Mg}_2(\text{Sn}_{0.765}\text{Ge}_{0.22}\text{Sb}_{0.015})_{1-x}(\text{Sn}_{0.685}\text{Si}_{0.3}\text{Sb}_{0.015})_x$. The electrical resistivity of $\text{Mg}_2(\text{Sn}_{0.765}\text{Ge}_{0.22}\text{Sb}_{0.015})_{1-x}(\text{Sn}_{0.685}\text{Si}_{0.3}\text{Sb}_{0.015})_x$ increases with temperature which indicates the characteristics of degenerate semiconductors (Fig. 5a). For $\text{Mg}_2\text{Sn}_{0.765}\text{Ge}_{0.22}\text{Sb}_{0.015}$, the room temperature electrical resistivity is ~ 4.7 $\mu\Omega$ m and it reaches ~ 10.2 $\mu\Omega$ m at 723 K. As shown in Fig. 5b, all the samples showed negative Seebeck coefficient indicating n-type conduction. The Seebeck coefficient of $\text{Mg}_2\text{Sn}_{0.765}\text{Ge}_{0.22}\text{Sb}_{0.015}$ is ~ -148 $\mu\text{V K}^{-1}$ at room temperature and ~ -227 $\mu\text{V K}^{-1}$ at 723 K. However, the Seebeck coefficient decreases gradually with x , which is clearly shown in the inset of Fig. 5b. It is noted that although identical amount of Sb is added, the Hall carrier concentration increases with x , which could partly explain the decrease of Seebeck coefficient (Fig. 9a). The power factor is ~ 46 $\mu\text{W cm}^{-1} \text{K}^{-2}$ at room temperature and ~ 55 $\mu\text{W cm}^{-1} \text{K}^{-2}$ at 523 K for $\text{Mg}_2\text{Sn}_{0.765}\text{Ge}_{0.22}\text{Sb}_{0.015}$ (Fig. 5c). The power factor decreases with the increase of x , as shown in the inset of Fig. 5c. For $\text{Mg}_2\text{Sn}_{0.685}\text{Si}_{0.3}\text{Sb}_{0.015}$, the room temperature PF is ~ 36 $\mu\text{W cm}^{-1} \text{K}^{-2}$ and peak PF is ~ 49 $\mu\text{W cm}^{-1} \text{K}^{-2}$, lower than those of $\text{Mg}_2\text{Sn}_{0.765}\text{Ge}_{0.22}\text{Sb}_{0.015}$. Liu *et al.* [16] reported that

Mg₂Sn_{0.7}Si_{0.3} can achieve a room temperature PF of $\sim 43 \mu\text{W cm}^{-1} \text{K}^{-2}$ and a peak PF of $\sim 47 \mu\text{W cm}^{-1} \text{K}^{-2}$. It is noted that their sample was prepared by a two-step solid-state reaction method followed by spark plasma sintering. Besides, the Hall carrier concentration is $\sim 2.2 \times 10^{20} \text{ cm}^{-3}$ for our sample (Table 1) and it is $\sim 1.7 \times 10^{20} \text{ cm}^{-3}$ for the sample prepared by Liu *et al.* Therefore, the difference in the thermoelectric properties can be ascribed to the different preparation methods and variation in carrier concentration. Moreover, comparing to Mg₂Sn_{0.765}Ge_{0.22}Sb_{0.015}, Mg₂Sn_{0.685}Si_{0.3}Sb_{0.015} showed $\sim 19.5\%$ and $\sim 10.9\%$ reduction in room temperature PF and peak PF , respectively. For Mg₂Sn_{0.735}Ge_{0.25}Sb_{0.015}, its power factor at room temperature is $\sim 45 \mu\text{W cm}^{-1} \text{K}^{-2}$ and it increases to $\sim 55 \mu\text{W cm}^{-1} \text{K}^{-2}$ at 523 K [7]. The comparable thermoelectric properties of Mg₂Sn_{0.765}Ge_{0.22}Sb_{0.015} and Mg₂Sn_{0.735}Ge_{0.25}Sb_{0.015} suggests their band structures are similar.

The total thermal conductivity of Mg₂(Sn_{0.765}Ge_{0.22}Sb_{0.015})_{1-x}(Sn_{0.685}Si_{0.3}Sb_{0.015})_x decreases with increase of x (Fig. 5d). The total thermal conductivity (κ_{tot}) is the sum of electronic thermal conductivity (κ_{ele}), lattice thermal conductivity (κ_{lat}), and bipolar thermal conductivity (κ_{bip}). According to the Wiedemann–Franz relation, the electronic thermal conductivity is $\kappa_{ele} = LT/\rho$, where L is the Lorenz number which can be estimated using single parabolic band model with measured Seebeck coefficient:

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

$$F_i(\eta_F) = \int_0^\infty \frac{x^i dx}{1 + \exp(x - \eta_F)} \quad (4)$$

$$\eta_F = E_F / k_B T \quad (5)$$

$$L = \left(\frac{k_B}{e} \right)^2 \left\{ \frac{(r+7/2)F_{r+5/2}(\eta_F)}{(r+3/2)F_{r+1/2}(\eta_F)} - \left[\frac{(r+5/2)F_{r+3/2}(\eta_F)}{(r+3/2)F_{r+1/2}(\eta_F)} \right]^2 \right\} \quad (6)$$

where k_B is the Boltzmann constant, e is the electron charge, η_F is the reduced Fermi energy, r is the scattering factor, considering acoustic phonon scattering its value can be chosen as $-1/2$, $F_i(\eta_F)$ is the

Fermi-Dirac integral.

The calculated Lorenz numbers, all about 1.7, are shown in Tab. 1. $\kappa_{lat} + \kappa_{bip}$ can be calculated by reduction of κ_{ele} from κ_{tot} . As shown in Fig. 5e, $\kappa_{lat} + \kappa_{bip}$ decreases significantly with increase of x . For $\text{Mg}_2\text{Sn}_{0.765}\text{Ge}_{0.22}\text{Sb}_{0.015}$, its value is $\sim 2.5 \text{ W m}^{-1} \text{ K}^{-1}$ at room temperature, while it is only $\sim 2.0 \text{ W m}^{-1} \text{ K}^{-1}$ for $\text{Mg}_2(\text{Sn}_{0.765}\text{Ge}_{0.22}\text{Sb}_{0.015})_{0.4}(\text{Sn}_{0.685}\text{Si}_{0.3}\text{Sb}_{0.015})_{0.6}$ at the same temperature, a $\sim 20\%$ reduction. It means that the lattice thermal conductivity of $\text{Mg}_2\text{Sn}_{0.765}\text{Ge}_{0.22}\text{Sb}_{0.015}$ can be significantly reduced by the formation of pseudo ternary solid solution. The dependence of thermal conductivity on composition will be quantitatively discussed later. Fig. 5f shows the temperature dependence of ZT for $\text{Mg}_2(\text{Sn}_{0.765}\text{Ge}_{0.22}\text{Sb}_{0.015})_{1-x}(\text{Sn}_{0.685}\text{Si}_{0.3}\text{Sb}_{0.015})_x$. Since the decrease of PF is compensated by the reduction of thermal conductivity, all the samples showed similar ZT s in the whole temperature range with the room temperature ZT of ~ 0.4 and peak ZT of ~ 1.3 (at 723 K). Moreover, it is worth pointing out that all the samples showed repeatable properties upon thermal cycling, which indicates good thermal stability.

3.2 Near the line

In addition to the compositions on the line connecting $\text{Mg}_2\text{Sn}_{0.765}\text{Ge}_{0.22}\text{Sb}_{0.015}$ and $\text{Mg}_2\text{Sn}_{0.685}\text{Si}_{0.3}\text{Sb}_{0.015}$, samples with compositions near the line are also studied. Thermoelectric properties of these samples are shown in Fig. 6. Comparing to $\text{Mg}_2\text{Sn}_{0.5}\text{Ge}_{0.1}\text{Si}_{0.4}$ [23] and $\text{Mg}_2\text{Sn}_{0.4}\text{Ge}_{0.05}\text{Si}_{0.55}$ [32] that are far away from the line, samples near the line showed significantly higher PF and ZT in the whole temperature range. It indicates that the ratio of Sn/Ge/Si plays a decisive role for the thermoelectric performance of materials in the Mg_2Sn - Mg_2Ge - Mg_2Si system. This is similar to the ratio of Sn/Si and Sn/Ge which determines the thermoelectric performance of materials in Mg_2Sn - Mg_2Si and Mg_2Sn - Mg_2Ge systems, respectively. Therefore, it suggests that better thermoelectric properties of samples near the line should be mainly due to the unique band structure (band convergence of light and heavy conduction bands). Furthermore, when comparing $\text{Mg}_2\text{Sn}_{0.685}\text{Ge}_{0.25}\text{Si}_{0.05}\text{Sb}_{0.015}$ with $\text{Mg}_2\text{Sn}_{0.685}\text{Ge}_{0.15}\text{Si}_{0.15}\text{Sb}_{0.015}$, $\text{Mg}_2\text{Sn}_{0.735}\text{Ge}_{0.15}\text{Si}_{0.1}\text{Sb}_{0.015}$ with

$\text{Mg}_2\text{Sn}_{0.735}\text{Ge}_{0.05}\text{Si}_{0.2}\text{Sb}_{0.015}$, it shows that for the same Sn content Ge rich samples showed indeed higher PF than that of Si rich samples. For power generation, higher power factor is desired, which is very important to produce larger output power at a given ZT . Therefore, in the Mg_2Sn - Mg_2Ge - Mg_2Si system with suitable Sn content, Ge rich compositions possess better thermoelectric performance than that of Si rich compositions.

3.3 Evaluation of thermoelectric performance by $(ZT)_{eng}$ and $(PF)_{eng}$

The conventional ZT and PF have been used for more than half a century to guide the research of thermoelectric materials. Recently, Kim *et al.* showed that the conventional ZT often lead to large errors in calculation of output power and leg efficiency using the conventional output power and energy conversion efficiency formulas [34, 35]. Therefore, they introduced new formulas to accurately calculate the maximum output power and maximum energy conversion efficiency by defining a new engineering power factor $(PF)_{eng}$ and figure of merit $(ZT)_{eng}$ and taking into account of temperature dependent individual thermoelectric properties and the Thomson effect (supporting information).

Fundamentally, $(ZT)_{eng}$ and $(PF)_{eng}$ are global indexes while conventional ZT and PF are local indexes for thermoelectric performance [35]. In section 3.1 and 3.2, we have shown the local thermoelectric performance of materials in the Mg_2Sn - Mg_2Ge - Mg_2Si system. Here, we discuss their global thermoelectric performance. The boundary conditions are $T_C = 323$ K, $L_{leg} = 2$ mm, T_H is from 323 to 723 K. The engineering $(PF)_{eng}$ and $(ZT)_{eng}$ as a function of T_H are shown in Fig. 7a and Fig. 7b. Both $(PF)_{eng}$ and $(ZT)_{eng}$ increase linearly with T_H . For $(PF)_{eng}$, it decreases with the increase of x (inset of Fig. 7a). At $T_H = 723$ K, $(PF)_{eng}$ is ~ 2.1 W m⁻¹ K⁻¹ for $\text{Mg}_2\text{Sn}_{0.765}\text{Ge}_{0.22}\text{Sb}_{0.015}$ and ~ 1.8 W m⁻¹ K⁻¹ for $\text{Mg}_2\text{Sn}_{0.685}\text{Si}_{0.3}\text{Sb}_{0.015}$. For $(ZT)_{eng}$, all the samples showed similar values. By using $(PF)_{eng}$ and $(ZT)_{eng}$, the output power and energy conversion efficiency can be calculated and are shown in Fig. 7c and Fig. 7d, respectively. Clearly, the output power decreases with x which is shown in the inset of Fig. 7c. The output power is ~ 9.1 W cm⁻² for $\text{Mg}_2\text{Sn}_{0.685}\text{Si}_{0.3}\text{Sb}_{0.015}$ and ~ 10.3 W cm⁻² for

$\text{Mg}_2\text{Sn}_{0.765}\text{Ge}_{0.22}\text{Sb}_{0.015}$, an enhancement of ~13% due to a higher power factor, a clear demonstration that higher output power can be achieved from higher power factor when the ZT s are similar. Moreover, as shown in Fig. 7d, all the samples showed similar energy conversion efficiency due to similar $(ZT)_{eng}$. It clearly shows that ideal thermoelectric materials should have both high $(PF)_{eng}$ and $(ZT)_{eng}$ in order to ensure higher efficiency and larger output power.

In order to further illustrate the effect of composition on the thermoelectric performance of Mg_2Sn - Mg_2Ge - Mg_2Si , the contour of $(PF)_{eng}$ is presented in Fig. 8. It is shown that on the line connecting $\text{Mg}_2\text{Sn}_{0.765}\text{Ge}_{0.22}\text{Sb}_{0.015}$ and $\text{Mg}_2\text{Sn}_{0.685}\text{Si}_{0.3}\text{Sb}_{0.015}$, the $(PF)_{eng}$ decreases from $\text{Mg}_2\text{Sn}_{0.765}\text{Ge}_{0.22}\text{Sb}_{0.015}$ to $\text{Mg}_2\text{Sn}_{0.685}\text{Si}_{0.3}\text{Sb}_{0.015}$. The $(PF)_{eng}$ also decreases for compositions which are away from the line. It is noted that due to the limited samples we have prepared and characterized, it is impossible to draw quantitatively conclusions. But it clearly shows that Ge rich compositions outperform their Si rich counterparts.

3.4 Hall carrier concentration and mobility

In order to analyze the dependence of electrical properties on composition, room temperature Hall measurement is carried out. All samples showed negative Hall coefficient R_H (Tab. 1), which is consistent with the measurement of Seebeck coefficient. As shown in Fig. 9a, the Hall carrier concentration increases gradually from $\sim 1.8 \times 10^{20} \text{ cm}^{-3}$ for $\text{Mg}_2\text{Sn}_{0.765}\text{Ge}_{0.22}\text{Sb}_{0.015}$ to $\sim 2.2 \times 10^{20} \text{ cm}^{-3}$ for $\text{Mg}_2\text{Sn}_{0.685}\text{Si}_{0.3}\text{Sb}_{0.015}$. It could be explained by the slight variation of Sb content in the actual composition determined from EPMA (Table 1). The relationship between Seebeck coefficient and Hall carrier concentration can be understood by the well-established Pisarenko plot that can be calculated by using the equations (3) and (7) [36, 37].

$$m_d^* = \frac{h^2}{2k_B T} \left(\frac{n_H r_H}{4\pi F_{1/2}(\eta_F)} \right)^{2/3} \quad (7)$$

$$r_H = \frac{3}{2} F_{1/2}(\eta_F) \frac{(1/2 + 2\lambda) F_{2\lambda-1/2}(\eta_F)}{(1+\lambda)^2 F_{\lambda}^2(\eta_F)} \quad (8)$$

where m_d^* is the density of state (DOS) effective mass, r_H is the Hall factor, and λ is related to scattering parameter r , such that $\lambda = r + 1/2$ [38].

As shown in Fig. 9b, the dash lines are the theoretical Pisarenko line corresponding to a single parabolic band model with the assumption of acoustic phonon scattering. All the samples showed good agreement with the Pisarenko line of $m_d^*/m_0 = 2.8$, where m_0 is free electron mass. The DOS effective mass m_d^* can be expressed as $N_v^{2/3} m_b$, where N_v and m_b are the number of degenerate carrier pockets and the average band mass, respectively [39, 40]. Generally, high DOS effective mass will lead to higher Seebeck coefficient at similar carrier concentration, which can be understood from the Pisarenko line [37]. However, as pointed out by Pei *et al.* [41-43] that simply increase the m_b (band flattening) will enhance Seebeck coefficient at the cost of significant reduction of Hall carrier mobility thus decrease the power factor. For $\text{Mg}_2\text{Sn}_{0.765}\text{Ge}_{0.22}\text{Sb}_{0.015}$ and $\text{Mg}_2\text{Sn}_{0.685}\text{Si}_{0.3}\text{Sb}_{0.015}$, the convergence of the light and heavy conduction bands could be considered as an equivalent effect to increase N_v rather than m_b [7, 16]. Thus, the m_d^* increases effectively without significant influence on the Hall carrier mobility leading to excellent power factor. More importantly, since all the samples achieve similar high m_d^* , it indicates that they have similar band structures. This means that the unique band structure is maintained for compositions on the line connecting $\text{Mg}_2\text{Sn}_{0.765}\text{Ge}_{0.22}\text{Sb}_{0.015}$ and $\text{Mg}_2\text{Sn}_{0.685}\text{Si}_{0.3}\text{Sb}_{0.015}$, which leads to similar high thermoelectric performance.

While the Hall carrier concentration of $\text{Mg}_2(\text{Sn}_{0.765}\text{Ge}_{0.22}\text{Sb}_{0.015})_{1-x}(\text{Sn}_{0.685}\text{Si}_{0.3}\text{Sb}_{0.015})_x$ increases with x , Hall carrier mobility decreases with x (Fig. 10). The Hall carrier mobility of $\text{Mg}_2\text{Sn}_{0.765}\text{Ge}_{0.22}\text{Sb}_{0.015}$ is $\sim 72.6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $\sim 59.4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for $\text{Mg}_2\text{Sn}_{0.685}\text{Si}_{0.3}\text{Sb}_{0.015}$, a reduction of $\sim 18\%$. In order to understand the dependence of mobility on composition, the electron scattering mechanisms are investigated. Here, the acoustic phonon scattering and alloy scattering are considered [44].

The mobility for acoustic phonon scattering μ_{ph} can be expressed as:

$$\mu_{ph} = \frac{\sqrt{2}\pi e\hbar^4}{3(k_B T)^{3/2}} \frac{v_L^2 \rho}{\Xi^2(m_b)^{5/2}} \frac{F_0(\eta)}{F_{1/2}(\eta)} \quad (9)$$

v_L is the longitudinal sound wave, ρ is the density, Ξ is the deformation potential due to the phonon wave.

When the carriers are scattered by alloy disorder, the mobility μ_{al} can be expressed as:

$$\mu_{al} = \frac{16e\hbar^4}{9\sqrt{2}\pi x(1-x)(k_B T)^{1/2}} \frac{N_0}{\psi^2(m_b)^{5/2}} \frac{F_0(\eta)}{F_{1/2}(\eta)} \quad (10)$$

N_0 is the number of atoms per unit volume, x is the fractional concentration of the solid solution, ψ is the potential energy fluctuation caused by atomic level disorder in solid solution.

When the effect of both the acoustic phonon scattering and alloy disorder scattering is considered, mobility can be expressed using the Matthiessen's rule [45]:

$$\frac{1}{\mu} = \frac{1}{\mu_{ph}} + \frac{1}{\mu_{al}} \quad (11)$$

It is clearly shown that if only consider the acoustic phonon scattering, the calculated μ_{ph} is too much higher than the measured μ (Fig. 10). So the acoustic phonon scattering is not the only mechanism for the scattering of carriers. When alloy scattering is also considered, the measured μ falls right on the calculated curve by $\mu_{ph} + \mu_{al}$ by equation (20). μ_{al} was calculated with the fitted ψ value. All the ψ is between 0.2 and 0.7 eV. **Mg₂Sn_{0.685}Si_{0.3}Sb_{0.015}** has largest ψ of 0.7 eV among all the samples. This means that alloy scattering in **Mg₂Sn_{0.685}Si_{0.3}Sb_{0.015}** is more significant and it explains the decrease of Hall carrier mobility with the increase of x . The reason for the increase of ψ can be understood from the larger difference of atomic radius between Si and Sn than Ge and Sn, which causes more severe distortion of crystal structure and disturbs the periodic potential thus leading to enhanced carrier scattering.

3.5 Weighted carrier mobility

The high power factor of $\text{Mg}_2(\text{Sn}_{0.765}\text{Ge}_{0.22}\text{Sb}_{0.015})_{1-x}(\text{Sn}_{0.685}\text{Si}_{0.3}\text{Sb}_{0.015})_x$ materials leads to high thermoelectric performance. The origin of the high power factor is discussed here. According to the previous theoretical research [36, 46-48], the weighted carrier mobility U (defined as $\mu(m_d^*/m_0)^{3/2}$) can be a good indicator for the thermoelectric performance of materials.

As shown in Fig. 11a, the weighted carrier mobility U decreases with increase of x . Considering the DOS effective mass are similar for all samples, the reduced U is mainly due to the decreased carrier mobility. $\text{Mg}_2\text{Sn}_{0.765}\text{Ge}_{0.22}\text{Sb}_{0.015}$ has a higher weighted carrier mobility of $\sim 352 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ than $\sim 273 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for $\text{Mg}_2\text{Sn}_{0.685}\text{Si}_{0.3}\text{Sb}_{0.015}$. The relationship between the weighted carrier mobility U and $(PF)_{\text{eng}}$ (at $T_H = 723 \text{ K}$) is shown in Fig. 11b. The $(PF)_{\text{eng}}$ increases monotonically with the weighted carrier mobility U . It clearly shows that higher U would leads to higher power factor that explains the reason why $\text{Mg}_2\text{Sn}_{0.765}\text{Ge}_{0.22}\text{Sb}_{0.015}$ has higher power factor than $\text{Mg}_2\text{Sn}_{0.685}\text{Si}_{0.3}\text{Sb}_{0.015}$.

3.6 Lattice thermal conductivity

The lower power factor of $\text{Mg}_2\text{Sn}_{0.685}\text{Si}_{0.3}\text{Sb}_{0.015}$ is compensated by its lower lattice thermal conductivity, yielding similar ZT s for all samples. In order to understand the effect of composition on the lattice thermal conductivity of $\text{Mg}_2(\text{Sn}_{0.765}\text{Ge}_{0.22}\text{Sb}_{0.015})_{1-x}(\text{Sn}_{0.685}\text{Si}_{0.3}\text{Sb}_{0.015})_x$, detailed phonon scattering mechanisms are considered for the room temperature lattice thermal conductivity. Generally, the dominant phonon scattering mechanisms contains the point defect scattering, phonon-phonon scattering (Normal process and Umklapp process) and boundary scattering [49]. Due to the identical preparation method for all samples, the grain size should be similar thus the boundary scattering should be similar in all cases and is not considered. Since we only discuss the room temperature lattice thermal conductivity, the Umklapp scattering is also ignored since it only becomes dominant in high temperatures, therefore only the alloying scattering is considered. The

$\text{Mg}_2(\text{Sn}_{0.765}\text{Ge}_{0.22}\text{Sb}_{0.015})_{1-x}(\text{Sn}_{0.685}\text{Si}_{0.3}\text{Sb}_{0.015})_x$ system belongs to solid solution according to the above description, thus it is understandable that alloy scattering plays a decisive role in the lattice thermal conductivity. The relation between $\kappa_{L, \text{pure}}$ and $\kappa_{L, \text{alloy}}$ is proposed by Callaway [49] and Klemens [50], according to their model the effects of alloying scattering on the lattice thermal conductivity are calculated (supporting information).

The room temperature κ_{lat} is calculated and the comparison between the calculated and measured data is shown in Fig. S1 (supporting information). Although there are differences between the calculated and measured lattice thermal conductivity, their dependence on the composition shows good agreement with the calculated results, *i.e.*, lattice thermal conductivity decrease with increase of x . According to the results of Zaitsev *et al.*, this could be explained by larger mass difference and strain field between Sn and Si than Sn and Ge [10]. Therefore, replacing Ge with Si enhances the alloy scattering and leading to the reduction of lattice thermal conductivity.

4. Conclusion

In summary, samples on and near the line connecting $\text{Mg}_2\text{Sn}_{0.765}\text{Ge}_{0.22}\text{Sb}_{0.015}$ and $\text{Mg}_2\text{Sn}_{0.685}\text{Si}_{0.3}\text{Sb}_{0.015}$ are synthesized and characterized. On the line, power factor decreases from $\text{Mg}_2\text{Sn}_{0.765}\text{Ge}_{0.22}\text{Sb}_{0.015}$ to $\text{Mg}_2\text{Sn}_{0.685}\text{Si}_{0.3}\text{Sb}_{0.015}$. Off the line, the power factor decreases from the line to the region which away from it. We also calculated the energy conversion efficiency and output power using the newly developed energy conversion efficiency and output power formulas based on the newly defined engineering figure of merit $(ZT)_{\text{eng}}$ and power factor $(PF)_{\text{eng}}$, respectively. The results showed that efficiency is similar for all samples due to their similar $(ZT)_{\text{eng}}$, but the output power differs to some extent due to the difference in $(PF)_{\text{eng}}$. The output power for $\text{Mg}_2\text{Sn}_{0.685}\text{Si}_{0.3}\text{Sb}_{0.015}$ is $\sim 9.1 \text{ W cm}^{-2}$ and $\sim 10.3 \text{ W cm}^{-2}$ for $\text{Mg}_2\text{Sn}_{0.765}\text{Ge}_{0.22}\text{Sb}_{0.015}$, an enhancement of $\sim 13\%$.

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References

- [1] U. Birkholz, E. GroB, U. Strohrer, K. Voss, D. Gruden, W. Wurster, Conversion of waste exhaust heat in automobiles using FeSi_2 thermoelements, Proc. 7th Int. Conf. on Thermoelectrics Energy Convers., Arlington, USA, (1988) 124-128.
- [2] F.J. DiSalvo, Thermoelectric cooling and power generation, Science 285 (1999) 703-706.
- [3] L.E. Bell, Cooling, heating, generating power, and recovering waste heat with thermoelectric systems, Science 321 (2008) 1457-1461.
- [4] G.J. Snyder, E.S. Toberer, Complex thermoelectric materials, Nature Mater. 7 (2008) 105-114.
- [5] D. Kraemer, B. Poudel, H.P. Feng, J.C. Caylor, B. Yu, X. Yan, Y. Ma, X.W. Wang, D.Z. Wang, A. Muto, K. McEnaney, M. Chiesa, Z.F. Ren, G. Chen, High performance flat panel solar thermoelectric generators with high thermal concentration, Nature Mater. 10 (2011) 532-538.
- [6] W.S. Liu, Q. Jie, H.S. Kim, Z.F. Ren, Current progress and future challenges in thermoelectric power generation: From materials to devices, Acta Mater. 87 (2015) 357-376.
- [7] W.S. Liu, H.S. Kim, S. Chen, Q. Jie, B. Lv, M.L. Yao, Z.S. Ren, C.P. Opeil, S. Wilson, C.W. Chu, Z.F. Ren, N-type thermoelectric material $\text{Mg}_2\text{Sn}_{0.75}\text{Ge}_{0.25}$ for high power generation, Proc. Natl. Acad. Sci. U.S.A. 112 (2015) 3269-3274.
- [8] M.I. Fedorov, V.K. Zaitsev, G.N. Isachenko, I.S. Eremin, E.A. Gurieva, A.T. Burkov, P.P. Konstantinov, A.A. Shabaldin, Kinetic properties of p-type $\text{Mg}_2\text{Ge}_{0.4}\text{Sn}_{0.6}$ solid solutions, Proc. 24th Int. Conf. on Thermoelectrics, Clemson, USA, (2005) 134-137.
- [9] V.K. Zaitsev, M.I. Fedorov, E.A. Gurieva, I.S. Eremin, P.P. Konstantinov, A.Y. Samunin, M.V. Vedernikov, Highly effective $\text{Mg}_2\text{Si}_{1-x}\text{Sn}_x$ thermoelectrics, Phys. Rev. B 74 (2006) 045207.
- [10] V.K. Zaitsev, M.I. Fedorov, I.S. Eremin, E.A. Gurieva, Thermoelectrics on the base of solid solutions of $\text{Mg}_2\text{B}^{\text{IV}}$ compounds ($\text{B}^{\text{IV}} = \text{Si, Ge, Sn}$), in Thermoelectrics handbook: macro to nano, D. M. Rowe (Ed.), CRC/Taylor & Francis, Boca Raton, USA, 2006, Ch. 29.
- [11] Q. Zhang, J. He, T.J. Zhu, S.N. Zhang, X.B. Zhao, T.M. Tritt, High figures of merit and natural nanostructures in $\text{Mg}_2\text{Si}_{0.4}\text{Sn}_{0.6}$ based thermoelectric materials, Appl. Phys. Lett. 93 (2008) 102109.
- [12] M.I. Fedorov, V.K. Zaitsev, I.S. Eremin, E.A. Gurieva, A.T. Burkov, P.P. Konstantinov, M.V. Vedernikov, A.Y. Samunin, G.N. Isachenko, A.A. Shabaldin, Transport properties of $\text{Mg}_2\text{X}_{0.4}\text{Sn}_{0.6}$ solid solutions ($\text{X} = \text{Si, Ge}$) with p-type conductivity, Phys. Solid State 48 (2006) 1486-1490.
- [13] J.I. Tani, H. Kido, Thermoelectric properties of Al doped $\text{Mg}_2\text{Si}_{1-x}\text{Sn}_x$, J. Alloys Compd. 466 (2008) 335-340.

-
- [14] H.L. Gao, T.J. Zhu, X.X. Liu, L.X. Chen, X.B. Zhao, Flux synthesis and thermoelectric properties of eco-friendly Sb doped $\text{Mg}_2\text{Si}_{0.5}\text{Sn}_{0.5}$ solid solutions for energy harvesting, *J. Mater. Chem.* 21 (2011) 5933-5937.
 - [15] W. Liu, X.F. Tang, H. Li, J. Sharp, X.Y. Zhou, C. Uher, Optimized thermoelectric properties of Sb doped $\text{Mg}_{2(1+z)}\text{Si}_{0.5-y}\text{Sn}_{0.5}\text{Sb}_y$ through adjustment of the Mg content, *Chem. Mater.* 23 (2011) 5256-5263.
 - [16] W. Liu, X.J. Tan, K. Yin, H. Liu, X.F. Tang, J. Shi, Q.J. Zhang, C. Uher, Convergence of conduction bands as a means of enhancing thermoelectric performance of n-type $\text{Mg}_2\text{Si}_{1-x}\text{Sn}_x$ solid solutions, *Phys. Rev. Lett.* 108 (2012) 166601.
 - [17] Z.L. Du, T.J. Zhu, Y. Chen, J. He, H.L. Gao, G.Y. Jiang, T.M. Tritt, X.B. Zhao, Roles of interstitial Mg in improving thermoelectric properties of Sb doped $\text{Mg}_2\text{Si}_{0.4}\text{Sn}_{0.6}$ solid solutions, *J. Mater. Chem.* 22 (2012) 6838-6844.
 - [18] W. Liu, Q. Zhang, K. Yin, H. Chi, X.Y. Zhou, X.F. Tang, C. Uher, High figure of merit and thermoelectric properties of Bi doped $\text{Mg}_2\text{Si}_{0.4}\text{Sn}_{0.6}$ solid solutions *J. Solid State Chem.* 203 (2013) 333-339.
 - [19] G.Y. Jiang, J. He, T.J. Zhu, C.G. Fu, X.H. Liu, L.P. Hu, X.B. Zhao, High performance $\text{Mg}_2(\text{Si},\text{Sn})$ solid solutions: a point defect chemistry approach to enhancing thermoelectric properties, *Adv. Funct. Mater.* 24 (2014) 3776-3781.
 - [20] H.L. Gao, T.J. Zhu, X.B. Zhao, Y. Deng, Synergetic effect of Zn substitution on the electron and phonon transport in $\text{Mg}_2\text{Si}_{0.5}\text{Sn}_{0.5}$ based thermoelectric materials, *Dalton Trans.* 43 (2014) 14072-14078.
 - [21] W. Liu, H. Chi, H. Sun, Q. Zhang, K. Yin, X.F. Tang, Q.J. Zhang, C. Uher, Advanced thermoelectrics governed by a single parabolic band: $\text{Mg}_2\text{Si}_{0.3}\text{Sn}_{0.7}$, a canonical example, *Phys. Chem. Chem. Phys.* 16 (2014) 6893-6897.
 - [22] Q. Zhang, Y. Zheng, X.L. Su, K. Yin, X.F. Tang, C. Uher, Enhanced power factor of $\text{Mg}_2\text{Si}_{0.3}\text{Sn}_{0.7}$ synthesized by a non-equilibrium rapid solidification method, *Scripta Mater.* 96 (2015) 1-4.
 - [23] L.B. Zhang, P.H. Xiao, L. Shi, G. Henkelman, J.B. Goodenough, J.S. Zhou, Suppressing the bipolar contribution to the thermoelectric properties of $\text{Mg}_2\text{Si}_{0.4}\text{Sn}_{0.6}$ by Ge substitution, *J. Appl. Phys.* 117 (2015) 155103.
 - [24] S. Tada, Y. Isoda, H. Udon, H. Fujiu, S. Kumagai, Y. Shinohara, Preparation and thermoelectric properties of $\text{Mg}_2\text{Si}_{0.9-x}\text{Sn}_x\text{Ge}_{0.1}$, *Phys. Status Solidi C* 10 (2013) 1704-1707.
 - [25] R.J. LaBotz, D.R. Mason, D.F.O. Kane, The thermoelectric properties of mixed crystals of $\text{Mg}_2\text{Ge}_x\text{Si}_{1-x}$, *J. Electrochem. Soc.* 110 (1963) 127-134.
 - [26] Y. Noda, H. Kon, Y. Furukawa, N. Otsuka, I.A. Nishida, K. Masumoto, Temperature

-
- dependence of thermoelectric properties of $\text{Mg}_2\text{Si}_{0.6}\text{Ge}_{0.4}$, *Mater. Trans.* 33 (1992) 851-855.
- [27] Y. Noda, H. Kon, Y. Furukawa, I.A. Nishida, K. Masumoto, Preparation and thermoelectric properties of $\text{Mg}_2\text{Si}_{1-x}\text{Ge}_x$ ($x = 0.0-0.4$) solid solution semiconductors, *Mater. Trans.* 33 (1992) 845-850.
 - [28] T. Aizawa, R.B. Song, A. Yamamoto, Solid-state synthesis of thermoelectric materials in Mg-Si-Ge system, *Mater. Trans.* 46 (2005) 1490-1496.
 - [29] H.I. Mouko, C. Mercier, J. Tobola, G. Pont, H. Scherrer, Thermoelectric properties and electronic structure of p-type Mg_2Si and $\text{Mg}_2\text{Si}_{0.6}\text{Ge}_{0.4}$ compounds doped with Ga, *J. Alloys Compd.* 509 (2011) 6503-6508.
 - [30] W.S. Liu, J.W. Zhou, H.S. Kim, Q. Jie, Y. Li, J.M. Bao, G. Chen, Z.F. Ren, New insight of the material parameter B that enhanced the thermoelectric performance of $\text{Mg}_2\text{Sn}_{0.75}\text{Ge}_{0.25}$, *Energy Environ. Sci.* Submitted.
 - [31] A.U. Khan, N. Vlachos, T. Kyratsi, High thermoelectric figure of merit of $\text{Mg}_2\text{Si}_{0.55}\text{Sn}_{0.4}\text{Ge}_{0.05}$ materials doped with Bi and Sb, *Scripta Mater.* 69 (2013) 606-609.
 - [32] A.U. Khan, N.V. Vlachos, E. Hatzikraniotis, G.S. Polymeris, C.B. Lioutas, E.C. Stefanaki, K.M. Paraskevopoulos, I. Giapintzakis, T. Kyratsi, Thermoelectric properties of highly efficient Bi doped $\text{Mg}_2\text{Si}_{1-x-y}\text{Sn}_x\text{Ge}_y$ materials, *Acta Mater.* 77 (2014) 43-53.
 - [33] G.S. Polymeris, N. Vlachos, A.U. Khan, E. Hatzikraniotis, C.B. Lioutas, A. Delimitis, E. Pavlidou, K.M. Paraskevopoulos, T. Kyratsi, Nanostructure and doping stimulated phase separation in high *ZT* $\text{Mg}_2\text{Si}_{0.55}\text{Sn}_{0.4}\text{Ge}_{0.05}$ compounds, *Acta Mater.* 83 (2015) 285-293.
 - [34] H.S. Kim, W.S. Liu, G. Chen, C.W. Chu, Z.F. Ren, Relationship between thermoelectric figure of merit and energy conversion efficiency, *Proc. Natl. Acad. Sci. U.S.A.* 112 (2015) 8205-8210.
 - [35] W.S. Liu, H.S. Kim, Q. Jie, Z.F. Ren, Importance of high power factor in thermoelectric materials for power generation application: A perspective, *Scripta Mater.* 111 (2015) 3-9.
 - [36] A.F. Ioffe, *Semiconductor thermoelements and thermoelectric cooling*, Infosearch, London 1957.
 - [37] J.P. Heremans, V. Jovovic, E.S. Toberer, A. Saramat, K. Kurosaki, A. Charoenphakdee, S. Yamanaka, G.J. Snyder, Enhancement of thermoelectric efficiency in PbTe by distortion of the electronic density of states, *Science* 321 (2008) 554-557.
 - [38] A.F. May, E.S. Toberer, A. Saramat, G.J. Snyder, Characterization and analysis of thermoelectric transport in n-type $\text{Ba}_8\text{Ga}_{16-x}\text{Ge}_{30+x}$, *Phys. Rev. B* 80 (2009) 125205.
 - [39] H.J. Goldsmid, *Introduction to Thermoelectricity*, Springer, New York, 2009.
 - [40] Y.Z. Pei, X.Y. Shi, A. LaLonde, H. Wang, L.D. Chen, G.J. Snyder, Convergence of electronic bands for high performance bulk thermoelectrics, *Nature* 473 (2011) 66-69.

-
- [41] Y.Z. Pei, A. LaLonde, S. Iwanaga, G.J. Snyder, High thermoelectric figure of merit in heavy hole dominated PbTe, *Energy Environ. Sci.* 4 (2011) 2085-2089.
- [42] Y.Z. Pei, H. Wang, Z.M. Gibbs, A. LaLonde, G.J. Snyder, Thermopower enhancement in $\text{Pb}_{1-x}\text{Mn}_x\text{Te}$ alloys and its effect on thermoelectric efficiency, *NPG Asia Mater.* 4 (2012) e28.
- [43] Y.Z. Pei, H. Wang, G.J. Snyder, Band engineering of thermoelectric materials, *Adv. Mater.* 24 (2012) 6125-6135.
- [44] X.H. Liu, T.J. Zhu, H. Wang, L.P. Hu, H.H. Xie, G.Y. Jiang, G.J. Snyder, X.B. Zhao, Low electron scattering potentials in high performance $\text{Mg}_2\text{Si}_{0.45}\text{Sn}_{0.55}$ based thermoelectric solid solutions with band convergence, *Adv. Energy Mater.* 3 (2013) 1238-1244.
- [45] A. Matthiessen, C. Vogt, On the influence of temperature on the electric conducting-power of alloys, *Phil. Trans. R. Soc. London* 154 (1864) 167-200.
- [46] H.J. Goldsmid. *Electronic refrigeration*, Pion Limited, London, 1986.
- [47] G.D. Mahan, Figure of merit for thermoelectrics, *J. Appl. Phys.* 65 (1989) 1578-1583.
- [48] G.A. Slack, New materials and performance limits for thermoelectric cooling, in: *Handbook of thermoelectrics*, D.M. Rowe (Ed.), CRC Press, Boca Raton, 1995, ch. 34.
- [49] J. Callaway, H.C. von Baeyer, Effect of point imperfections on lattice thermal conductivity, *Phys. Rev.* 120 (1960) 11499.
- [50] P. Klemens, Thermal resistance due to point defects at high temperatures, *Phys. Rev.* 119 (1960) 507-509.

Figures

Figure 1. (a) Research on the thermoelectric properties of materials in the Mg₂Sn-Mg₂Ge-Mg₂Si system, (b), (c) and (d) effects of alloy composition on band convergence of Mg₂Sn-Mg₂Ge-Mg₂Si.

Figure 2. (a) XRD patterns of $\text{Mg}_2(\text{Sn}_{0.765}\text{Ge}_{0.22}\text{Sb}_{0.015})_{1-x}(\text{Sn}_{0.685}\text{Si}_{0.3}\text{Sb}_{0.015})_x$, (b) enlarged view of (220) peak from (a).

Figure 3. Rietveld refinement of $\text{Mg}_2(\text{Sn}_{0.765}\text{Ge}_{0.22}\text{Sb}_{0.015})_{1-x}(\text{Sn}_{0.685}\text{Si}_{0.3}\text{Sb}_{0.015})_x$, inset shows the dependence of lattice constant on composition.

Figure 4. (a) SEM result of $\text{Mg}_2(\text{Sn}_{0.765}\text{Ge}_{0.22}\text{Sb}_{0.015})_{0.6}(\text{Sn}_{0.685}\text{Si}_{0.3}\text{Sb}_{0.015})_{0.4}$, (b)-(f) EDS results of elements mapping.

Figure 5. Temperature and composition dependent thermoelectric properties of $\text{Mg}_2(\text{Sn}_{0.765}\text{Ge}_{0.22}\text{Sb}_{0.015})_{1-x}(\text{Sn}_{0.685}\text{Si}_{0.3}\text{Sb}_{0.015})_x$. (a) Electrical resistivity ρ , (b) Seebeck coefficient S , the inset shows the Seebeck coefficient vs. composition at room temperature, (c) power factor PF , the inset shows the PF vs. composition at room temperature, (d) total thermal conductivity κ_{tot} , (e) lattice and bipolar thermal conductivity $\kappa_{\text{lat}} + \kappa_{\text{bip}}$, (f) figure of merit ZT .

Figure 6. Temperature dependent thermoelectric properties of compositions in the $\text{Mg}_2\text{Sn}-\text{Mg}_2\text{Ge}-\text{Mg}_2\text{Si}$ system near the line connecting $\text{Mg}_2\text{Sn}_{0.765}\text{Ge}_{0.22}\text{Sb}_{0.015}$ and $\text{Mg}_2\text{Sn}_{0.685}\text{Si}_{0.3}\text{Sb}_{0.015}$. (a) Electrical resistivity ρ , (b) Seebeck coefficient S , (c) power factor PF , (d) total thermal conductivity κ_{tot} , (e) lattice and bipolar thermal conductivity $\kappa_{\text{lat}} + \kappa_{\text{bip}}$, (f) figure of merit ZT .

Figure 7. (a) Dependence of $(PF)_{eng}$ on hot side temperature T_H , the inset shows the $(PF)_{eng}$ vs. composition at $T_H = 723$ K, (b) dependence of $(ZT)_{eng}$ on hot side temperature T_H , the inset shows the $(ZT)_{eng}$ vs. composition at $T_H = 723$ K, (c) dependence of output power on hot side temperature T_H , the inset shows the output power vs. composition at $T_H = 723$ K, (d) dependence of efficiency on hot side temperature T_H , the inset shows the efficiency vs. composition at $T_H = 723$ K.

Figure 8. Contour of $(PF)_{eng}$ of materials in the Mg_2Sn - Mg_2Ge - Mg_2Si system.

Figure 9. (a) Dependence of Hall carrier concentration on composition, (b) dependence of Seebeck coefficient on Hall carrier concentration.

Figure 10. Dependence of carrier mobility on composition.

Figure 11. (a) Dependence of weighted carrier mobility U on the composition, (b) dependence of $(PF)_{eng}$ (at $T_H = 723$ K) on the weighted carrier mobility U .

Table

Table 1. Physical parameters of $\text{Mg}_2(\text{Sn}_{0.765}\text{Ge}_{0.22}\text{Sb}_{0.015})_{1-x}(\text{Sn}_{0.685}\text{Si}_{0.3}\text{Sb}_{0.015})_x$ materials: Hall carrier concentration n_H (10^{20} cm^{-3}), Hall carrier mobility μ_H ($\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), Hall factor r_H (dimensionless), density of state effective mass m_d^* (m_0), reduced Fermi energy $\eta_F = E_F/k_B T$ (dimensionless), Lorenz number L ($10^{-8} \text{ V}^2 \text{ K}^{-2}$), Seebeck coefficient S ($\mu\text{V K}^{-1}$), electrical resistivity ($\mu\Omega \text{ m}$).

Composition	Nominal composition	Measured composition	n_H	μ_H	r_H	m_d^*	η_F	L	S	ρ
$x = 0$	$\text{Mg}_{2.06}\text{Sn}_{0.765}\text{Ge}_{0.22}\text{Sb}_{0.015}$	$\text{Mg}_{2.01}\text{Sn}_{0.759}\text{Ge}_{0.219}\text{Sb}_{0.015}$	1.81	72.62	1.10	2.86	1.06	1.73	-148	4.74
$x = 0.2$	$\text{Mg}_{2.06}\text{Sn}_{0.752}\text{Si}_{0.06}\text{Ge}_{0.173}\text{Sb}_{0.015}$	$\text{Mg}_{2.02}\text{Sn}_{0.757}\text{Si}_{0.054}\text{Ge}_{0.173}\text{Sb}_{0.016}$	1.94	68.24	1.10	2.91	1.13	1.74	-145	4.71
$x = 0.4$	$\text{Mg}_{2.06}\text{Sn}_{0.736}\text{Si}_{0.12}\text{Ge}_{0.129}\text{Sb}_{0.015}$	$\text{Mg}_{2.01}\text{Sn}_{0.754}\text{Si}_{0.132}\text{Ge}_{0.148}\text{Sb}_{0.016}$	1.95	67.01	1.10	2.81	1.22	1.75	-141	4.78
$x = 0.6$	$\text{Mg}_{2.06}\text{Sn}_{0.720}\text{Si}_{0.18}\text{Ge}_{0.085}\text{Sb}_{0.015}$	$\text{Mg}_{2.01}\text{Sn}_{0.745}\text{Si}_{0.194}\text{Ge}_{0.091}\text{Sb}_{0.017}$	1.97	66.76	1.10	2.82	1.22	1.75	-141	4.75
$x = 0.8$	$\text{Mg}_{2.06}\text{Sn}_{0.704}\text{Si}_{0.24}\text{Ge}_{0.041}\text{Sb}_{0.015}$	$\text{Mg}_{2.01}\text{Sn}_{0.738}\text{Si}_{0.265}\text{Ge}_{0.034}\text{Sb}_{0.017}$	2.11	60.63	1.10	2.93	1.25	1.76	-140	4.87
$x = 1$	$\text{Mg}_{2.06}\text{Sn}_{0.685}\text{Si}_{0.3}\text{Sb}_{0.015}$	$\text{Mg}_{2.01}\text{Sn}_{0.683}\text{Si}_{0.338}\text{Sb}_{0.018}$	2.20	59.37	1.09	2.77	1.45	1.78	-132	4.78

Graphical Abstract