Thermoelectric power generation is one of the most promising techniques to use the huge amount of waste heat and solar energy. Traditionally, high thermoelectric figure-of-merit, $ZT$, has been the only parameter pursued for high conversion efficiency. Here, we emphasize that a high power factor ($PF$) is equivalently important for high power generation, in addition to high efficiency. A new n-type Mg$_2$Sn-based material, Mg$_2$Sn$_{0.75}$Ge$_{0.25}$, is a good example to meet the dual requirements in efficiency and output power. It was found that Mg$_2$Sn$_{0.75}$Ge$_{0.25}$ has an average $ZT$ of 0.9 and $PF$ of 52 $\mu$W cm$^{-1}$K$^{-2}$ over the temperature range of 25–450 °C, a peak $ZT$ of 1.4 at 450 °C, and peak $PF$ of 55 $\mu$W cm$^{-1}$K$^{-2}$ at 350 °C. By using the energy balance of one-dimensional heat flow equation, leg efficiency and output power were calculated with $T_h = 400 °C$ and $T_c = 50 °C$ to be of 10.5% and 6.6 W cm$^{-1}$ under a temperature gradient of 150 °C mm$^{-1}$, respectively.

The working temperature of thermoelectric materials is limited to 25–600 °C due to its larger Seebeck coefficient, electrical conductivity, and absolute temperature, respectively. Pursuing high $ZT$ has been the focus of the entire thermoelectric community by applying various phonon engineering via nanostructuring approaches to reduce the thermal conductivity ($\sim$7), or by exploring new compounds with intrinsically low thermal conductivity, such as compounds having complex crystalline structure, local rattles, liquid-like sublattice, and highly distorted lattice ($\sim$11). However, for practical applications, efficiency is not the only concern, and high output power density is as important as efficiency when the capacity of the heat source is huge (such as solar heat), or the cost of the heat source is not a big factor (such as waste heat from automobiles, steel industry, etc.). The output power density $\omega$ is defined as the output power $W$ divided by the cross-sectional area $A$ of the leg, i.e., $\omega = W/A$, which is related to power factor $PF = S\sigma$ by the following:

$$\omega = \frac{1}{4} \left( \frac{T_h - T_c}{L} \right)^2 PF,$$

Eq. 2 contains two main parts: square of the temperature difference divided by leg length, and material power factor $PF = S\sigma$. Clearly, to achieve higher power density for a given heat source, we have to either increase the power factor $PF$ or decrease the leg length. However, decreasing the leg length could cause severe consequences such as increase of large heat flux that will increase the cost of the heat management at the cold end, increase of percentage of contact resistance in the device that will increase the parasitic loss and consequently decrease the energy conversion efficiency, increase of the thermal stress due to the larger thermal gradient leading to device failure, etc. Therefore, it is better to increase the power factor $PF$. Because $PF$ is a pure material parameter, we can use it as a criterion in searching for new thermoelectric materials for high output power.

A useful thermoelectric material should possess high $ZT$ value for high efficiency, and also very importantly high $PF$ for high output power. Ideally, temperature-independent $ZT$ and $PF$ over the whole temperature range from cold side to hot side are desired. However, both the $ZT$ and $PF$ of all materials show strong temperature dependency, usually increasing first with temperature and then decreasing when bipolar effect starts to play a role. The working temperature of thermoelectric materials is limited by the band energy gap $E_g$; e.g., Bi$_2$Te$_3$, a well-known thermoelectric material for applications below 200 °C, has an $E_g$ of ~0.13 eV (12). PbTe and associated materials have much higher peak $ZT$ in the temperature range of 400–600 °C due to its larger $E_g$ of 0.32 eV (13). However, the toxicity of lead, poor mechanical properties, and thermal instability above 400 °C seriously limit the application of Pb-based thermoelectric materials. Even though Mg$_2$Si, skutterudites, and half-Heuslers are promising thermoelectrics | magnesium | tin | power factor | output power

Significance

Thermoelectric materials have been extensively studied for applications in conversion of waste heat into electricity. The efficiency is related to the figure-of-merit, $ZT = (S^2\sigma/\kappa)T$, where $S$, $\sigma$, and $\kappa$ are the Seebeck coefficient, electrical conductivity, and thermal conductivity, respectively. Pursuing higher $ZT$ for higher efficiency has been the focus by mainly reducing the thermal conductivity. In this paper, we point out, for a given $ZT$, higher power factor ($S\sigma$) should be pursued for achieving more power because power is determined by ($T_h - T_c$)$^2$($S^2\sigma$)/$L$, where $T_h$, $T_c$, and $L$ are the hot and cold side temperatures, and leg length, respectively. We found a new material, Mg$_2$Sn$_{0.75}$Ge$_{0.25}$, having both high $ZT$ and high power factor.
Mg2Sn material has been investigated less than its analogous important, new n- and p-type materials that can work up to 400 °C, making them unsuitable for power generation applications below 400 °C. Therefore, novel Mg2Sn-based n-type thermoelectric materials that show promise to work below 400 °C for power generation due to the narrow band gap of ~0.26 eV. Historically, MgSn material has been investigated less than its analogous compound MgSi for thermoelectric applications due to its lower ZT (22–25). Most of the research has been focused on the alloy of Mg-Si-MgSn with a peak ZT value of ~1 at 500 °C (26–28). Recently, different groups have improved the peak ZT value to 1.1–1.3 by adjusting the x value in the Mg1-xSn1-x system, solid solution (14, 29, 30). The challenges in preparing and handling these materials were the high vapor pressure and chemical activity of Mg. Methods of directing comelting with subsequent annealing, and solid-state reaction with subsequent annealing and Bridgman method were reported to synthesize MgSi-MgSn alloys (22–30). Powder metallurgy route, e.g., ball milling plus hot pressing, was widely used to fabricate a variety of high-performance thermoelectric bulk materials such as Bi2Te3 (6, 31), PbTe (32), PbSe (33), and skutterudites CoSb3 (16, 34). In fact, ball milling was reported to synthesize MgSi and its alloys MgSi-MgSn (35–38). However, the reported ZT was lower than 0.7 (27, 38), which may be due to the difficulty in avoiding oxidation of Mg. Here, we report a successful synthesis of an Sn-dominated composition MgSn0.75Ge0.25 through ball milling and hot pressing to achieve a ZT of 1.4 at 450 °C and power factor PF of 55 μW cm−1 K−2 at 350 °C. Calculations show that these could yield a leg efficiency η of 10.5%, and output power density ω of 6.6 W cm−2 at Tl = 400 °C and Tc = 50 °C, which will be very useful for the vast amount of waste heat sources at up to 400 °C and concentrated solar energy conversion applications.

**Experiment and Characterization**

**Synthesis.** Elemental powders, including magnesium (Mg, 99.98%; Alfa Aesar), tin (Sn, 99.8%; Alfa Aesar), and germanium (Ge, 99.999%; Alfa Aesar), were weighed according to the stoichiometric MgSn and MgSn0.75Ge0.25. Here, antimony (Sb, 99.99%; Alfa Aesar) and slight extra magnesium was used to adjust the carrier concentration. The element mixtures were then subjected to mechanical ball milling for up to 20 h. The ball-milled powders were then loaded into a graphite die with an inner diameter of 12.7 mm and hot pressed into bulk samples by direct current-induced hot pressing at 600–750 °C for 2 min.

**Crystal Structure.** X-ray diffraction (XRD) measurements were conducted on two systems: PANalytical multipurpose diffractometer with an Xcelerator detector (PANalytical X’Pert Pro) and a Bruker D2 PHASER system. The lattice parameters of MgSn and MgSn0.75Ge0.25 were calculated by the Rietveld refinement method, which was done in Fullprof suite by using a cubic structure and space group (space group: Fm3m, no. 225) as the starting structure. The microstructures of the samples were studied by a JEOl 6340F scanning electron microscope (SEM) and a JEOl 2100F transmission electron microscope (TEM). The composition analysis was conducted by energy-dispersive X-ray spectroscopy (EDS) inside the SEM.

**Thermoelectric Transport Properties.** The electrical resistivity was measured by a reverse dc-current four-point method, whereas the Seebeck coefficient was determined by the slope of the voltage difference versus temperature difference curve based on a static temperature difference method. The simultaneous measurement of electrical resistivity and Seebeck coefficient was conducted on a commercial system (ZEM-3; ULVAC). The thermal conductivity was calculated from the relationship κ = D Cp d, where D, Cp, and d are the thermal diffusivity, specific heat, and volumetric density, respectively. The thermal diffusivity was measured by the laser flash method with a commercial system (LFA457; Netzsch). The specific heat capacity was determined by a differential scanning calorimeter (DSC 404 C; Netzsch). The volumetric density was measured by the Archimedes method. The Hall coefficient, R_h, was carried out on a commercial system (PPMS; Quantum Design) with a magnetic field up to 6 T and an electrical current of 10–20 mA.

**Results and Discussion**

Fig. 1 shows the X-ray diffraction patterns of the ball-milled powder and hot-pressed bulk Mg2Sn samples. The particle size of the starting materials is important to obtain phase-pure samples. Because both the major starting materials Mg and Sn are very soft, they easily stick on the wall of the stainless-steel pot. Luckily, the reacted product MgSn is brittle, which can be ball-milled into nano powders. Even though a structure transition from cubic into hexagonal was reported in MgSn by continuous mechanical ball milling (37), we observed only cubic phase in the ball-milled MgSn nano powders, as shown in Fig. 1. It demonstrates that small stress was left in ball-milled nano powders. The hot-pressed bulk has the same cubic MgSn phase. No oxide impurity was identified, as shown Fig. 1B. To further improve the thermoelectric properties, we explored the partial substitution of Sn with Ge and found the same cubic phase was obtained in hot-pressed MgSn0.75Ge0.25. The Rietveld refinement shows lattice parameter a of 6.7670 Å for MgSn and 6.6786 Å for MgSn0.75Ge0.25, which is in good agreement with the Vegard’s law for the MgSn1-xGe_x system. Fig. 2 shows the microstructures of the as-fabricated MgSn0.75Ge0.25. The SEM image of the freshly fractured surface, as shown in Fig. 2A, shows the grain size distribution ranges from 0.5 to 2 μm. Smaller grains of ~300 nm were also identified in the TEM image, as shown in Fig. 2B. Furthermore, some nano inclusions of ~10 nm were observed in the high-resolution TEM images, as shown in Fig. 2 C and D. Such nano inclusions are most likely due to stress caused by the...
slight composition fluctuation within the single crystalline grain, similar to the Ag/Sb-codoped PbTe (5) and Sn/Te-codoped CoSb3 (34). These nano inclusions are the active phonon-scattering centers. It is noted that the observed nano inclusions have coherent boundaries within the matrix, which should have less impact on the transport of the electrons (7). Currently, we have not yet fully understood the real formation mechanism of these nano inclusions. We speculated that the possible reason would be related to the extra Mg entering the interstitial sites or slight Ge segregation. The measured compositions of Mg_{2.06}Sn_{0.728}Ge_{0.25}Sb_{0.022} by EDS inside SEM are 66.6 at.% for Mg, 21.9 at.% for Sn, 9.9 at.% for Ge, and 1.6 at.% for Sb, as shown in Fig. S1, which are close to the nominal composition.

Fig. 3 shows the thermoelectric properties of the hot-pressed Mg2Sn and Mg2Sn_{0.75}Ge_{0.25}. Antimony is used to further tune the carrier concentration. The carrier concentrations of Mg2Sn and Mg2Sn_{0.75}Ge_{0.25} are 1.8 \times 10^{20} \text{ cm}^{-3} and 3.0 \times 10^{20} \text{ cm}^{-3}, respectively. The net carrier of each Sb atom is estimated to be approximately one carrier per atom, which is independent of Ge content in the Mg2Sn_{1-x}Ge_x system. The electrical resistivity and Seebeck coefficient increase almost linearly below 300 °C, demonstrating degenerate semiconductor behavior, as shown in Fig. 3A and B. The Fermi energy (E_F/k_BT) calculated from the Seebeck coefficient is 0.031–0.049 eV, equal to 1.2–1.9 k_BT. Above 300 °C, the Seebeck coefficient of Mg2Sn tends to saturate, which results from the onset of the bipolar effect due to the narrow band gap. However, Mg2Sn_{0.75}Ge_{0.25} still follows the linear increase above 300 °C, which suggests widening of the band gap. This is consistent with the earlier reported result: Ge continuously increases the band gap from 0.26 eV for x = 0 to 0.41 eV for x = 0.4 in Mg2Sn_{1-x}Ge_x (39). One of the advantages associated with the alloying effect of Ge is the higher power factor of 45 \mu W cm^{-1} K^{-2} near room temperature, as shown in Fig. 3C. This value is even higher than that of the textured Bi2Te2_xSe0.3 polycrystalline sample (39) with 39 \mu W cm^{-1} K^{-2}. The maximum power factor of Mg2Sn_{0.75}Ge_{0.25} has reached 55 \mu W cm^{-1} K^{-2} at 350 °C. Due to the weak temperature-dependent behavior, the Mg2Sn_{0.75}Ge_{0.25} sample also has a higher average power factor of ~52 \mu W cm^{-1} K^{-2} over the temperature range of 25–450 °C, which is 13–16% higher than that of the best Mg2Sn_{1-x}Si_x samples (~46 \mu W cm^{-1} K^{-2} for Mg2Sn_{0.70}Si_{0.3} (29), ~45 \mu W cm^{-1} K^{-2} for Mg2Sn_{0.6}Si_{0.4} (14)]. We have repeated the experiments many times and found fair reproducibility. Fig. 3D shows the power factor of three batches of Mg2Sn_{0.75}Ge_{0.25} samples.

According to the theoretical understanding, Mg2X (X = Si, Ge, Sn) are indirect semiconductors, in which the top of valence band is located at Γ point whereas the bottom of the conduction band is located at X point (39). For Mg2Sn, the lowest conduction band is unoccupied Mg(3s) band (identified as X0-band), followed by a hybridized Mg(3s)-Sn(5p) band (identified as X1-band) that is slightly higher than the lowest band with band edge difference of E_k = 0.16 eV (41). The positions of X0-band and X1-band in Mg2Ge are just reversed (39). A composition-related band convergence was earlier identified. Similar composition-dependent band convergence was observed in PbTe_{1-x}Sb_x (42) and Mg2Sn_{1-x}Si_x (29) systems. In the Mg2Sn_{1-x}Ge_x system, the contribution of the additional band (X1-band) to the total electronic transport significantly increases with the increasing of Ge content. A direct result of the band convergence effect is the increased Seebeck coefficient, which is 13\% higher than that of the best Mg2Sn_{1-x}Si_x from different batches.

$$S = \frac{k_B}{e} \left( \frac{r + 2/3}{r + 3/2} F_{1/2}(\xi) - \frac{2m^*}{r^2} F_{1/2}(\xi) \right)$$  \hspace{1cm} (3)

$$n_H = \frac{2}{n_H} \left( \frac{2m^* k_BT}{h^2} \right)^{3/2} F_{1/2}(\xi)$$  \hspace{1cm} (4)

$$r_H = \frac{3}{4} \frac{F_{1/2}(\xi) F_{-1/2}(\xi)}{F_{1}(\xi)}$$  \hspace{1cm} (5)

where $F_n(\xi)$ is the Fermi integration, $\xi$ is the Fermi energy, and $r$ is the scattering factor in the relaxation time approximation. The increased carrier effective mass $m^*$ could be direct evidence for the increased contribution of the additional X1-band to the main X0-band owing to the shrinkage of the band edge difference $E_k$. 

Fig. 3. Temperature- and composition-dependent electrical transport properties of Mg2Sn_{1-x}Ge_x. (A) Electrical conductivity. (B) Seebeck coefficient. (C) Power factor (PF). (D) PF of Mg2Sn_{0.75}Ge_{0.25} from different batches.
Here, the equivalent two-band model (one conduction band and one valence band) was used to fit the temperature-dependent electrical conductivity and Seebeck coefficient, and then extract the necessary parameters (including carrier mobility, carrier effective mass, band gap, and Fermi energy) for calculating $\sigma_x$, $\sigma_y$, $S_x$, and $S_y$, and finally the $k_{polar}$. A significant reduction in lattice thermal conductivity from 5.13 W m$^{-1}$K$^{-1}$ (Mg$_2$Sn) to 2.27 W m$^{-1}$K$^{-1}$ (Mg$_2$Sn$_{0.75}$Ge$_{0.25}$) at 25 °C was seen due to alloying scattering to phonons. As a combination of the increased power factor and the decreased thermal conductivity, the sample Mg$_2$Sn$_{0.75}$Ge$_{0.25}$ has a peak ZT value of 1.4 at 450 °C, which is 130% higher than that of Mg$_2$Sn. The ZT value of the best n-type Bi$_2$Te$_2$Se$_3$ is presented in Fig. 4D for comparison. Clearly, Mg$_2$Sn$_{0.75}$Ge$_{0.25}$ has higher ZT than Bi$_2$Te$_2$Se$_3$ above 200 °C. Therefore, a segmented leg of Bi$_2$Te$_2$Se$_3$ with Mg$_2$Sn$_{0.75}$Ge$_{0.25}$ could result in a higher efficiency and output power density in the temperature range of 25–450 °C.

To evaluate the thermoelectric performance of Mg$_2$Sn$_{0.75}$Ge$_{0.25}$ in terms of both the conversion efficiency and output power, we compare Mg$_2$Sn$_{0.75}$Ge$_{0.25}$ with some of the reported best Mg$_2$Sn$_{1-x}$Si$_x$ samples in Fig. 5. First, the power factor of Mg$_2$Sn$_{0.75}$Ge$_{0.25}$ is almost three times higher than that of Mg$_2$Sn$_{1-x}$Si$_x$ made by ball milling and hot pressing (38). However, most of the Mg$_2$Sn$_{1-x}$Si$_x$ samples synthesized by melting metallurgy showed ZT higher than 1, e.g., Mg$_2$Sn$_{0.75}$Si$_{0.25}$ showed a ZT of 1.3 near 430 °C but was almost 15% lower in power factor, as shown in Fig. 5A and B. To exemplify the role of $PF$ in the performance of both efficiency and output power, we took the temperature-dependent thermoelectric transport properties into account. The energy balance equation of one-dimensional heat flow is as follows (40, 45–47):

$$\frac{d}{dx}\left[k(x)\frac{dT(x)}{dx}\right] + J^2\rho(x) - JT(x)\frac{dS(x)}{dx} - \sigma_c \frac{w}{A} (T^4(x) - T^4_\infty) = 0,$$

where $\sigma$, $J$, and $T_\infty$ are the emissivity, the Stephan–Boltzmann constant, perimeter of a leg, current density, and the ambient temperature, respectively. The parts on the left-hand side represent the conduction heat, Joule heat, Thomson heat, and radiation heat loss, respectively. Because the temperature is a function of position $x$, we assign $T_b$ at $x = 0$ and $T_c$ at $x = L$ (length of the leg), so that the temperature-dependent thermoelectric properties are also a function of $x$. To solve this differential equation, a finite difference model is developed, where a leg is divided into $n$ nodes, and a central difference method is applied to determine the relationship of adjacent nodes. Here, a conservative temperature boundary of $T_b = 400$ °C and $T_c = 50$ °C that the change of the chemical bond due to Ge is smaller than that due to Si in the Mg$_2$Sn matrix. The most likely reason is that the atomic size of Ge is closer to Sn than that of Si.

Thermal conductivity of as-fabricated Mg$_2$Sn and Mg$_2$Sn$_{0.75}$Ge$_{0.25}$ is calculated from the measured density, thermal diffusivity, and specific heat, and is shown in Fig. 4A and B. The measured specific heat is shown in Fig. 4C with the reference data (44, 45) for comparison. At 450 °C, the specific heat of both samples is ~8% higher than the Dulong–Petit value. The lattice thermal conductivity was calculated by extracting both the contribution of charge carriers and bipolar effect (4):

$$\kappa = \kappa_{car} + \kappa_{polar}.$$

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where $\sigma$, $J$, and $T_\infty$ are the emissivity, the Stephan–Boltzmann constant, perimeter of a leg, current density, and the ambient temperature, respectively. The parts on the left-hand side represent the conduction heat, Joule heat, Thomson heat, and radiation heat loss, respectively. Because the temperature is a function of position $x$, we assign $T_b$ at $x = 0$ and $T_c$ at $x = L$ (length of the leg), so that the temperature-dependent thermoelectric properties are also a function of $x$. To solve this differential equation, a finite difference model is developed, where a leg is divided into $n$ nodes, and a central difference method is applied to determine the relationship of adjacent nodes. Here, a conservative temperature boundary of $T_b = 400$ °C and $T_c = 50$ °C.

Thermal conductivity of as-fabricated Mg$_2$Sn and Mg$_2$Sn$_{0.75}$Ge$_{0.25}$ is calculated from the measured density, thermal diffusivity, and specific heat, and is shown in Fig. 4A and B. The measured specific heat is shown in Fig. 4C with the reference data (44, 45) for comparison. At 450 °C, the specific heat of both samples is ~8% higher than the Dulong–Petit value. The lattice thermal conductivity was calculated by extracting both the contribution of charge carriers and bipolar effect (4):

$$\kappa = \kappa_{car} + \kappa_{polar}.$$
was used considering the potentially thermal instability of Mg$_2$Sn$_{0.75}$Ge$_{0.25}$ above 400 °C. For simplicity, no radiation heat loss was considered here. Fig. 5D shows leg output power under different temperature gradient, i.e., $(T_h - T_c)/L$. Under the same temperature gradient of 150 °C/mm, Mg$_2$Sn$_{0.75}$Ge$_{0.25}$ leg could have an output power density of ~6.6 W cm$^{-2}$ with a leg efficiency of 10.5%, which is better than any of the reported state-of-the-art Mg$_2$Sn$_{1-x}$Si$_x$ materials, as shown in Fig. 5E. Based on the dual index of efficiency and output power, Mg$_2$Sn$_{0.75}$Ge$_{0.25}$ seems to be the best material for power generation in the temperature range of $T_h$ = 400 °C and $T_c$ = 50 °C. It may be arguable that the same output power could also be achieved by using a larger temperature gradient for samples with smaller PF and smaller $\kappa$. However, the main issue is that a larger temperature gradient will result in a larger thermal stress at the contact interface between thermoelectric legs and electrode, which will significantly shorten the lifetime of the device. By comparing Fig. 5 C and F, it is clearly shown that the material with higher power factor is preferred to achieve higher output power for the same ZT values. The figure of “average ZT versus average PF” could be a new criterion for exploring new thermoelectric materials, or for boosting the thermoelectric performance of the known materials. Furthermore, for real applications, the price of the raw materials needs to be taken into consideration. The estimated price of Mg$_2$Sn$_{0.75}$Ge$_{0.25}$ raw material is ~$190/kg according to the US Geological Survey Data Series (2013) (48). It is comparable to the conventional n-type Bi$_2$Te$_2$Se$_0.3$ ($170$/kg) and p-type Bi$_2$xSb$_{1-x}$Te ($209$/kg) but cheaper than Hf$_{0.75}$Zr$_{0.25}$Sn$_{0.99}$Sb$_{0.01}$ ($255$/kg) and In$_4$Se$_3$ ($580$/kg). The cost of Mg$_2$Sn$_{0.75}$Ge$_{0.25}$ can be further reduced from $190/kg to $150/kg without reduction in ZT by partially replacing the 20% germanium with silicon.

Finally, we would like to address a few general rules for exploring novel thermoelectric compounds in terms of the criteria of efficiency (high ZT) plus effectiveness (high PF). First, choose the narrow band gap compounds with high-symmetry crystalline structure for high degenerate energy valley, and hence high PF. Mg$_2$X (X = Si, Ge, Sn) has the cubic structure with narrow band gap. Second, choose heavy atoms for low $\kappa_{dr}$. For the iso-electronic compounds Mg$_2$Sn and Mg$_2$Si, Sn is heavier than Si, so Mg$_2$Sn should have smaller phonon group velocity, and hence lower $\kappa_{lat}$. Third, choose the compounds with smaller electron negativity difference between anions and cations for high carrier mobility. For this rule, Mg$_2$Sn is comparable with Mg$_2$Si. Fourth, balance the effect of alloying element on decreasing $\kappa_{lat}$ and $\mu$. Most of the best thermoelectric materials are compounds with a sublattice filled by two or three isoelectronic atoms, e.g., Te and Se in n-type Bi$_2$Te$_2$Se$_0.3$; Bi and Sb in p-type Bi$_2$Sb$_1$Te$_2$; and Hf, Zr, and Ti in n-type (Hf, Zr, Ti)NiSn. Conventionalnly, Sn is added to Mg$_2$Si to optimize the ZT value, whereas Ge is used in Mg$_2$Sn in our case. The atomic size of Ge is closer to Sn than that of Si, and therefore it has less impact on the carrier mobility, so it should be good for high power factor in Mg$_2$Sn. Fifth, use the compositional band-crossing effect to optimize the weight mobility $\mu (m^*)^{3/2}$, and hence achieve high PF. This is a dominant effect for Mg$_2$Sn$_{0.75}$Ge$_{0.25}$ to have both high PF and ZT. Sixth, apply the nano approaches to selectively scatter the phonons rather than electrons. This effect is also an important factor in our case. Getting to technologically useful materials in thermoelectric power generation could be a slow process, but these guiding rules will be helpful in exploring new promising thermoelectric materials.

Conclusions

We have successfully synthesized Mg$_2$Sn-based materials by ball milling and hot pressing. The composition of Mg$_2$Sn$_{0.75}$Ge$_{0.25}$ shows an average ZT of 0.9 and an average PF of 52 $\mu$W cm$^{-1}$ K$^{-2}$ over the temperature range of 25–450 °C, and also a peak ZT of 1.4 at 450 °C and peak PF of 55 $\mu$W cm$^{-1}$ K$^{-2}$ at 350 °C. Theoretically, Mg$_2$Sn$_{0.75}$Ge$_{0.25}$ leg could have an efficiency $\eta$ of 10.5%, and an output power density $\omega$ of 6.6 W cm$^{-2}$ under a temperature gradient of 150 °C/mm for $T_h$ = 400 °C and $T_c$ = 50 °C. Compared with the reported Mg$_2$Si$_{1-x}$Ge$_x$ system, the higher power factor obtained in Mg$_2$Sn$_{1-x}$Ge$_x$ is associated with the increased $S^2n$ attributable to the band convergence and higher carrier mobility, which in turn are due to the smaller size difference between Sn and Ge than that between Sn and Si. Furthermore, coherent nano inclusions were identified in the Mg$_2$Sn$_{1-x}$Ge$_x$ materials. Recently, 5–10% Ge-doped Mg$_2$Si$_{1-x}$Sn$_x$ have also been reported (49, 50); however, the reported power factor $PF_{max} = 35$ $\mu$W cm$^{-1}$ K$^{-2}$ (ref. 50) is still much lower than what we are reporting in this paper ($PF_{max} = 55$ $\mu$W cm$^{-1}$ K$^{-2}$ in Mg$_2$Sn$_{0.75}$Ge$_{0.25}$).

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49. Tada S, et al. (2013) Preparation and thermoelectric properties of Mg5Sn0.45Sn0.55;Ge; Phys Status Solidi C 10(12):1704–1707.