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High-performance MgAgSb/Mg₃(Sb,Bi)₂-based thermoelectrics with η = 12% at T \leq 583K

Graphical abstract



Highlights

- A peak figure of merit (zT) of 1.6 at 573 K was achieved for p-type α-MgAgSb
- Full-scale Mg-based modules utilizing p-type α-MgAgSb and n-type Mg₃SbBi were fabricated
- High power generation and cooling performance were realized by the Mg-based modules
- The standout advantage of Mg-based modules is the high performance-cost ratio

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In brief

Full-scale thermoelectric modules with high power generation and cooling performance based on p-type α -MgAgSb and n-type Mg₃SbBi have been successfully fabricated in our work. Enhanced thermoelectric performance for both p-type α -MgAgSb and n-type Mg₃SbBi was achieved by controlling point defects and enlarging grain sizes. The superior thermoelectric cooling and power generation performance of our Mg-based module below 583 K enables its broad application at near room temperatures.



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High-performance MgAgSb/Mg₃(Sb,Bi)₂-based thermoelectrics with $\eta = 12\%$ at $T \le 583$ K

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CONTEXT & SCALE For half a century, Bi₂Te₃-based modules have been the only commercially available thermoelectric devices for near-room-temperature applications. However, their performance diminishes above room temperature due to the bipolar effect. In this study, we have fabricated full-scale Mg-based modules using p-type α -MgAgSb and n-type Mg₃SbBi. These modules achieved a power generation efficiency of ~12% and a cooling temperature difference of ~200 K at hot-side temperature of 583 K. Notably, when considering real-world applications, the performance-cost ratio of the full Mg-based module is nearly three times as high as that of Bi₂Te₃-based modules under natural convection cooling conditions. This superior performance is attributed to the enhanced *zT* values of both α -MgAgSb (*zT*_{avg} = 1.4) and Mg₃SbBi (*zT*_{avg} = 1.4) in the temperature range of 300–573 K, along with high durability of the Mg-based materials as well as key advancements in material synthesis and module assembly techniques.

SUMMARY

 α -MgAgSb, as a promising near-room-temperature thermoelectric (TE) material, has suffered from incompetent carrier mobility induced by the scattering of vacancies and grain boundaries. Synthesis of stoichiometric α -MgAgSb with large crystal grains has been challenging. Here, owing to an improved ball-milling process, the phase purity of α -MgAgSb powder precursor was effectively increased during mechanochemical synthesis. After subsequent spark plasma sintering (SPS) and post annealing at 583 K, near-stoichiometric α -MgAgSb exhibiting a mosaic structure was obtained, registering a significantly enhanced μ of 93.3 cm²V⁻¹s⁻¹ and zT_{avg} of 1.4 in 300–573 K. A 7-pair TE module based on α -MgAgSb/Mg₃BiSb was fabricated, which demonstrated a record-high efficiency of 12% at T_h \leq 583 K and a cooling ΔT_{max} of 61 K at 300 K. This work lays the foundation for broad applications of Mg-based TEs.

INTRODUCTION

As one of the indispensable solid-state energy conversion technologies, thermoelectrics (TEs) can directly convert heat to electricity, and vice versa, based on the Seebeck and Peltier effects, respectively. Nowadays, although high-temperature waste heat can be easily harvested and re-used in industry, more than half of that waste heat is, however, classified as low grade (<573 K) and remains difficult to capture using traditional energy conversion technologies.¹ The conversion efficiency ($\eta = \frac{T_h - T_c}{T_h} \frac{\sqrt{1+ZT_{avg}} - 1}{\sqrt{1+ZT_{avg} + T_c/T_h}}$) of a TE module is determined by the hot- and cold-side temperatures of the module (T_h and T_c) and the material's figure of merit ($z = S^2 \sigma / \kappa$), which is calculated

from the electrical transport properties (Seebeck coefficient S and electrical conductivity σ) and thermal conductivity κ of nand p-type TE materials.^{2,3}

Over the past decades, bismuth telluride (Bi₂Te₃) has remained the dominant commercial TE material, exhibiting the highest *z* value of 3.3×10^{-3} K⁻¹ in the near-room-temperature range.^{4,5} However, because the high carrier mobility is often accompanied by the characteristic of narrow bandgaps in high-performance, low-temperature TE materials (e.g., Bi₂Te₃ of ~0.13 eV and BiSb of ~20 meV), the TE performances will rapidly degrade at elevated temperatures due to thermal excitation of the minority carrier and the corresponding detrimental bipolar conduction.⁶ This restrains the utilization of Bi₂Te₃-based materials and modules in emerging TE applications, e.g., thermal

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Figure 1. Thermoelectric performances of α-MgAgSb and the full Mg-based power generation modules

(A) Schematic of strategies to optimize TE properties of α -MgAgSb.

(B) The room-temperature power factor (*PF*) and figure of merit (*zT*) as the function of carrier concentration for MgAg_{0.97}Sb_{0.99}, MgAgSb, and post-annealed MgAgSb (AC, acoustic phonon scattering; I, ionized impurity scattering; GB, grain-boundary scattering; PD, point defect scattering).

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management in high-power electronics and waste heat recovery, which particularly require high performances over a wide temperature range (300-573 K).^{7,8}

In order to minimize the bipolar conduction, new types of TE materials, such as Mg-based Mg₃(Bi,Sb)₂ and α-MgAgSb, have rapidly gained popularity over the past several years owing to their large weighted mobility ratios (A = $\frac{\mu_n(m_n^*)^{3/2}}{\mu_p(m_p^*)^{3/2}}$) as a result of the inherent asymmetric transport properties of charge carriers.^{9–12} The constant high *z* values at elevated temperatures, together with their 40%–90% lower material cost to that of Bi₂Te₃, make them two of the most promising materials in the development of next-generation TE modules for cooling and power generation applications at near room temperatures.^{13–16}

Recent research and development innovations have contributed to rapid advances in n-type Mg₃(Sb,Bi)₂; e.g., it was disclosed that the reduction of grain-boundary scattering in large grains will effectively enhance the zT values of Bi-rich alloys at near room temperatures, peering those of n-type $Bi_2(Te,Se)_3$.¹⁷ However, the development of p-type α -MgAgSb, one of the ideal counterparts of n-type Mg₃(Sb,Bi)₂ in the construction of TE modules, has remained stagnant since we first reported its initial TE performances for the pure α phase with an optimized composition of MgAg_{0.97}Sb_{0.99} and pinned its peak zT at ~ 1.4 .¹⁸ Improvements in the electrical transport properties of *α*-MgAgSb have been hindered by its complex composition segregation and crystallographic structure changes among the α , β , and γ phases in a very narrow temperature range of 588-633 K. These features impose limitations on the maximum temperature values achievable during synthesis and processing steps, thereby constraining efforts to optimize defects and microstructures.¹⁹

In a real crystal, the lattice is not perfect due to the effect of entropy, and these imperfections caused by defects tend to alter the electrical and thermal properties, especially in semiconductor materials. As a result, eliminating imperfections is key to obtaining high-quality crystals and potential high-performance materials. For TEs, the performance can be effectively improved by controlling defects (e.g., GeTe and Mg₃Sb₂).^{20,7} Indeed, the electrical conductivity of MgAgSb at the point of maximum zT value deviates substantially from the ideal electrical conductivity predicted by TE transport theory due to the low mobility caused by the high defect concentrations.²² Notably, due to weak phonon scatterings at near room temperatures (~300 K), the defect scattering is critically detrimental to the carrier transport; thus, the TE performance of α-MgAgSb with intrinsically low lattice thermal conductivity (κ_{lat}) could be further optimized by eliminating the carrier scattering from point defects (PDs) (vacancies of $V_{Ag}{}^-$ and $V_{Sb}{}^{3+}$) and grain boundaries. However, despite the significant amount of effort dedicated to phasepure MgAgSb, such as high-temperature melting, ball milling, hot pressing, annealing, etc.,^{18,23} a defective MgAg_{0.97}Sb_{0.99} phase with additional Ag cationic (and Sb anionic) vacancies has been exclusively obtained to date.

Herein, a unique combined procedure comprised of an improved ball-milling process, spark plasma sintering (SPS), and, particularly, post annealing at the critical phase transition temperature, was developed to synthesize high-performance α -MgAgSb in which the characteristic features of near-stoichiometric crystallographic structures, intrinsic mosaic subgrains, and enlarged grain sizes are achieved (scheme in Figure 1A). Accordingly, the hole transport was facilitated, leading to significant improvements in both electrical transport properties and *zT* values over a wide temperature range (Figures 1B and 1C).

Based on theoretical calculations, the significant increase of hole mobility can be ascribed to the reduction of defect and grain-boundary scattering, which is close to the predicted theoretical limit (Figure S7). A high "B factor" of 0.47 was obtained at 300 K for MgAgSb compared with that of 0.3 for Bi₂Te₃. Meanwhile, in the temperature range of 300–573 K, a *zT* of ~0.97 at 300 K, a peak *zT* of ~1.6 (Figure 1C) at 523 K, and an average *zT* (*zT*_{avg}) of ~1.4 have been achieved (which was verified by a round robin test; Figures 1C, S8,and S9), outperforming all the reported values for the α -MgAgSb system and demonstrating remarkable advantages over p-type commercial Bi₂Te₃.

A full Mg-based TE module, consisting of high-performance p-type α-MgAgSb and n-type Mg_{3,285}Nb_{0,015}SbBi_{0,9975}Te_{0,0035} materials, both with zT_{avg} up to 1.4, was then fabricated and demonstrated superior power generation and TE cooling performances. A power generation efficiency of up to 12% was achieved with respective cold- and hot-side temperatures of 296 and 583 K and the heat flow was measured by a copperbased heat flow meter. A round robin test was conducted to verify the results. This registered efficiency is not only the highest among reported values over the temperature range of 300-583 K but also one of the highest in the temperature range of 300-950 K among single-stage TE power generation modules to date, as shown in Figure 1D. In addition, results also uncovered that the full Mg-based module can outperform that of Bi₂Te₃, especially when passive heat dissipation is required. In this scenario, the output power and efficiency are ${\sim}400\%$ and ${\sim}500\%$ higher than that of the Bi2Te3-based modules, respectively. In terms of the cooling function, the full Mg-based module achieved a ΔT of ~61 K at the hot-end temperature of 300 K, and its cooling performance above 400 K significantly exceeded that of Bi₂Te₃based modules. These findings, together with the substantially reduced material cost, show the great potential of Mg-based TE modules in near-room-temperature applications.

RESULTS AND DISCUSSION

The performance of TE modules is primarily governed by the transport properties of the TE materials used as the device legs; numerous works have been devoted to material design

⁽C) Measured zT as a function of temperature for α -MgAgSb in this work compared with the literature (inset: measured z value between α -MgAgSb prepared in this work and the commercial p-type Bi₂Te₃ from different sources).

⁽D) Measured conversion efficiency for the 7-pair full Mg-based module as a function of temperature difference, in comparison with single-stage modules reported by the literature.^{15,24–32} The purple and blue lines in (C) represent the round robin tests provided by Shanghai Institute of Ceramics, Chinese Academy of Sciences (SIC, CAS) and Beijing Normal University (BNU), respectively.

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and optimization to achieve the optimal performance of TE modules.^{1,14,24} Yet, achieving phase-pure α-MgAgSb products has been challenging in prior state-of-the-art research. Instead, previous high-performance MgAg_{0.97}Sb_{0.99} materials with intrinsic vacancy defects (instead of MgAgSb) have been extensively reported.^{18,33,34} The thermodynamic stability of α -MgAgSb is limited to a narrow compositional range (Figure S1), and any deviation in composition can result in the formation of PDs due to their low formation energies (Figure S2; Table S1). For example, competing phases, such as Ag₃Sb and Ag formed during synthesis, can lead to the generation of Ag vacancies. Significantly, the phase transition of *a*-MgAgSb requires sintering or annealing temperatures lower than \sim 573 K. This constraint on heat treatment temperature makes it difficult to effectively remove vacancies and impurities within a finite period of time. Consequently, selecting appropriate ball-milling conditions to accelerate the reaction rate and obtain a high-purity raw precursor powder of MgAgSb is considered the most effective approach to minimize the defects and impurities.

The synthesis of α -MgAgSb follows a two-step ball-milling process that we developed previously, which has been a broadly used approach to MgAgSb (see also Figure 2A).¹⁸ Figure 2A shows a schematic of the corresponding mechanochemical reaction dynamics, where free energy (G) is presented as a function of reaction progress. The intermetallic MgAg phase was initially synthesized from elemental Mg and Ag, and Sb was ball milled with MgAg in the 2nd step, yielding a powdered product with α -MgAgSb as the main phase (referred to as the raw precursor of MgAgSb herein). Pure MgAgSb can be subsequently

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(A) The illustration of reaction mechanism of the two-step ball-milling synthesis.

(B) Profile plots of Rietveld refinements against powder neutron diffraction (PND) patterns of postannealed α -MgAgSb.

obtained after the final SPS treatment. The advantage of the two-step ball-milling over the conventional all-in-one ball-milling synthesis lies in that it can deactivate the Mg species (which is the most reactive species among Mg, Ag, and Sb) by forming MgAg alloy and effectively avoid the coldwelding issue at the initial milling stage. Notably, by adding Sb at the 2nd step, the energy barriers required for both breaking of metallic Mq-Aq and Sb-Sb bonds and, in turn, the formation of covalent bonds (such as Mg-Sb and Ag-Sb) in MgAgSb significantly increases. Indeed, only a defective α phase with a nominal composition of MgAg_{0.97}Sb_{0.99} (with Ag and Sb vacancies) was available in previous literature studies.

The combined strategies we originally devised in this work, i.e., improving the ho-

modispersion of elements by removing small balls to avoid cold-welding issues, providing stable and enhanced mechanical power through the use of tungsten carbide balls, and the timingbelt operation mode of the ball mill machine (Figure S10), have remarkably accelerated the kinetic process of forming a pure phase of near-stoichiometric a-MgAgSb products, which was observed for the first time. Ex situ powder X-ray diffraction (PXRD) patterns show no peaks from impurity phases of the ball-milled raw MgAgSb precursor powders based on our methods, contrasting markedly with the multi-phase products prepared by previous ball-milling technology (Figure S11). PXRD results reinforce our findings that highly crystalline pure MgAgSb products were obtained after SPS and post-annealing treatments (Figure S12). Rietveld refinements against powder neutron diffraction (PND) patterns further confirm the tetragonal structure (space group $I \overline{4} c2$) of the SPS- and post-annealingtreated products (Figures 2B and S13; Tables S4, S6, and S7); refined sit occupancy factors (SOFs) of the Ag1 and Ag2 consistently approached values slightly lower than unity, with a final stoichiometry of MgAg_{0.992(6)}Sb (the post-annealing product), indicating the near-stoichiometric feature with a less-defective structure. By contrast, Rietveld refinement against PND data of the defective MgAg_{0.97}Sb_{0.99} phase suggests a Ag vacancy concentration of ~2.7(6)% (Table S5). Relatively large anisotropic atomic thermal displacement parameters at the Ag1 and Ag2 sites (for the near-stoichiometric MgAgSb) illustrate the favored Ag dynamics within the lattice (Table S6). These dynamics features are not unreasonable, combined with the refined low concentration of Ag vacancies at these sites. Indeed, the calculated

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low-vacancy formation energy of Ag was 0.17 eV under the Mgpoor condition in our research (Figure S2), which was in good agreement with literature studies for MgAgSb.³⁵

Afterward, an additional post-annealing process at 583 K (i.e., near the α -to- β critical phase transition temperature of 588 K) was designed and adopted to further minimize defects and promote grain growth. The electron backscatter diffraction (EBSD) images show that as-synthesized MgAgSb exhibited an average grain size of 200 nm cf. that of 2-4 µm for the post-annealed MgAgSb sample (Figures 3A, 3B, and S14). The reduced density of the grain boundary accompanied by the grain growth will lead to a significant enhancement of electrical properties as we expected, which we will discuss later. In order to gain more insight into the structural properties of the samples, the MgAgSb samples were analyzed by transmission electron microscopy (TEM) using the ultrathin slices made by the cryo-focused ion beam (cryo-FIB) (Figures 3C and S15). To our surprise, a mosaic subgrain structure was found in the α-MgAgSb samples. As shown in the inset of Figure 3C, a near-perfect single-crystal-type selected-area electron diffraction (SAED) pattern from one single

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Figure 3. Microstructure characterizations of the as-synthesized $MgAg_{0.97}Sb_{0.99}$, as-synthesized MgAgSb, and post-annealed MgAqSb samples

(A and B) Comparison of EBSD images of assynthesized and post-annealed α -MgAgSb samples, respectively.

(C) The TEM image and corresponding SAED of post-annealed α -MgAgSb.

(D) The high-resolution transmission electron microscopy (HRTEM) image of post-annealed α -MgAgSb with its FFT diffractogram, shown in the inset.

(E–H) FFT diffractograms of selected areas within the HRTEM (D).

grain (with a diameter of $\sim 2 \mu m$) was observed. The Bragg-diffracted electrons form arcing short bars rather than traditional sharp dots, suggesting the presence of a fine degree of misorientation, which is believed to be a typical characteristic of mosaic crystals, as reported before.36,37 High-resolution electron microscopy analysis was also performed in order to further identify the degree of misorientation among subgrains within the mosaic structure. The fast Fourier transform (FFT) diffractogram of the high-resolution TEM (HRTEM) image (Figure 3D) shows a single-crystal pattern, although it contains at least four subgrains (outlined in white) with 20-nm sizes. The FFT patterns for subgrains (Figures 3E-3H) are almost identical except for variations in the brightness of diffraction spots and a small rotation or tilting (\sim 5°), affirming the slight misorien-

tation. These low-angle subgrain boundaries (LASGBs) emerge as a result of dislocations undergoing gliding and climbing motions.^{38–40} During heat treatment, a recrystallization process occurs, accompanied by significant grain growth of α-MgAgSb. Concurrently, the high-density dislocations caused by ball milling and the SPS process evolve into a mosaic structure, which is more thermodynamically favorable than dislocation defects in α-MgAgSb. Therefore, the mosaic structure can be observed in various samples subjected to different thermal processing histories, including those SPS-ed, those annealed at 583 K after SPS sintering at 558 K, and those annealed above the phase transition temperature (673 K for 1 day and then 543 K for 3 days), etc. The unique structural characteristics are revealed to impose direct impacts on the TE transport properties of α-MgAgSb, as has been reported in other TE material systems, such as Cu₂Te.^{36,37}

Both electrical and thermal transport properties for as-synthesized α -MgAg_{0.97}Sb_{0.99}, α -MgAgSb, and post-annealed α -MgAgSb have been characterized and analyzed. Results show that the high TE performance mainly originated from Please cite this article in press as: Zhang et al., High-performance MgAgSb/Mg₃(Sb,Bi)₂-based thermoelectrics with η = 12% at T \leq 583K, Joule (2024), https://doi.org/10.1016/j.joule.2024.08.013

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Figure 4. Temperature-dependent TE properties for as-synthesized MgAg_{0.97}Sb_{0.99}, as-synthesized MgAgSb, and post-annealed MgAgSb samples

(A) Electrical conductivity, (B) carrier mobility in comparison with the literature, $^{34,41-43}$ (C) Seebeck coefficient, (D) thermal conductivity and lattice thermal conductivity, (E) carrier mobility and lattice thermal conductivity as a function of grain sizes for α -MgAgSb, (F) zT value, inset shows the average zT in comparison with the value reported in the literature. 14,18,33,41,44,45

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the enhancement of electrical conductivity. In Figure 4A, the room-temperature electrical conductivity increased from 290 S cm⁻¹ for MgAg_{0.97}Sb_{0.99} to 452 S cm⁻¹ for the post-annealed MgAgSb owing to the reduced vacancy defects and the growth of grains. The temperature dependence of electrical conductivity between 300 and 373 K changed from $\sigma \propto T^{-0.9}$ for MgAg_{0.97}Sb_{0.99} to $\sigma \propto T^{-1.5}$ for post-annealed MgAgSb, which demonstrates an acoustic-phonon-dominated scattering behavior due to the reduction of various scattering sources. The inset in Figure 4A shows that the carrier mobility at 300 K increased from 67.8 cm^2 V⁻¹ s⁻¹ for as-synthesized $MgAg_{0.97}Sb_{0.99}$ to 93.3 $cm^2~V^{-1}~s^{-1}$ for the post-annealed MgAgSb, accompanied by an increase in carrier concentration from 2.6 \times 10¹⁹ to 2.9 \times 10¹⁹ cm⁻³. To the best of our knowledge, this ranks as the highest mobility reported for the MgAgSb system so far (Figure 4B).34,41-43 The increase in mobility at room temperature is primarily ascribed to the reduced PD concentration and grain-boundary scattering. As the temperature rose, the electrical conductivity of all three samples first decreased and then increased at 373 K due to the onset of the bipolar effect. The carrier-phonon interaction dominates the scattering of electrons at high temperature, so the MgAgSbbased materials have a similar electrical conductivity value at 573 K. The Seebeck coefficient exhibited the same features of temperature dependence as the electrical resistivity due to the charge carrier excitation in MgAgSb-based materials (Figure 4C). At the same time, the power factor was less affected by the minority carrier and remained constant at an elevated temperature owing to the asymmetric transport properties and low weighted mobility of electrons in the conduction band. The combination of increased electrical conductivity and large Seebeck coefficient gave rise to a power factor of 25 μ W cm⁻¹ K⁻² for post-annealed MgAgSb in the temperature range of 300–573 K (Figure S16).

MgAgSb is a TE material with an inherently low κ_{lat} , which is attributed to the strong Umklapp phonon-phonon scattering from its low sound velocity, large Grüneisen parameter, and complex primitive cell.^{46,47} The contributions of the U-process, vacancies, and boundaries (grain boundaries and LASGBs) to the reduction of κ_{lat} are separately evaluated based on the Debye-Callaway model (see supplemental experimental procedures for more details).^{48,49} The simulated results (green line), which account for the U-process (U), boundaries (B), and PDs, align well with the experimental data (Figure 4D). As illustrated by the spectral κ_{lat} (Figure S16), high-density LASGBs intensively scatter low-frequency phonons due to their frequency-independent nature ($\tau(\omega)_B = d/\nu_g$), while vacancies primarily scatter high-frequency phonons $(\tau_{PD}^{-1} = \frac{V\omega^4}{4\pi v^3}\Gamma)$. However, due to their reduced concentration, vacancies contribute less to the reduction of κ_{lat} .

In addition to the enhanced electrical transport properties realized due to reduced defects and optimized microstructure, as shown in Figures 4E and S17, the κ_{lat} remained almost unchanged after annealing over the entire temperature range. This is mainly attributed to the fact that although the grain boundaries are reduced, the overall density of the boundaries remains unchanged due to the presence of LASGBs, which scatter phonons as effectively as grain boundaries. Meanwhile, the LASGBs are nearly transparent to electrons compared with the grain

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boundaries, allowing for the decoupling of thermal and electronic transport. Compared with the grain boundary, the LASGB has more favorable two-dimensional defects, leading to enhanced TE performance in post-annealed MgAgSb. In MgAgSb, the κ_{lat} is predominantly controlled by U-process scattering and the high density of subgrain boundaries. Consequently, the impact of PDs and grain boundaries is relatively weak.

Enhanced TE performances were further confirmed for the assynthesized and post-annealed α -MgAgSb samples. As shown in Figure 4F, the *zT* of the as-synthesized MgAg_{0.97}Sb_{0.99} sample was consistent with our first reported value,¹⁸ while a room temperature *zT* of 0.85 for as-synthesized MgAgSb and 0.97 for the post-annealed MgAgSb were obtained, which increased by 16% and 30%, respectively, compared with the as-synthesized MgAg_{0.97}Sb_{0.99}. The *zT* values of post-annealed α -MgAgSb increased with temperature and reached a *zT*_{max} of ~1.6 at 523 K, registering a *zT*_{avg} of ~1.4 (as shown in the inset of Figure 4F), which is the highest among all values reported from α -MgAgSb-based materials.^{14,18,33,41,44,45} Furthermore, the excellent thermal stability of post-annealed α -MgAgSb samples was confirmed by the repeated measurement (Figure S18).

In order to fabricate high-performance TE modules, it is equally important to use n-type materials with high *zT* values near room temperature, i.e., ≤ 573 K. By using Nb as the grain-boundary modifier,⁵⁰ we designed the composition of Mg_{3.285}Nb_{0.015}SbBi_{0.9975}Te_{0.0035} in this work. A Mg-vapor-annealing technique was adopted to further improve electrical transport properties,⁵¹ resulting in a remarkable improvement in the *zT* value across the entire temperature range (Figure S19). A*zT*_{avg} value of up to ~1.4 has been achieved in the temperature range of 300–573 K, which is one of the highest values for state-of-the-art Mg₃(Bi,Sb)₂-based materials, as shown in Figure S20.

To be close to real-world applications, we evaluated the power generation performance of our module under three conditions: (1) water cooling in vacuum, (2) water cooling in air, and (3) air cooling, as shown in Figure 5A. When the hot-side temperature of the module is fixed, the cold-side temperature is related to the heat dissipation condition, which can be evaluated by the heat extraction coefficient (h). Due to the intrinsically low thermal conductivity of p-MgAgSb and n-Mg₃(Bi,Sb)₂ materials, the heat flows (Q_b) for the full Mg-based module were only 42% of those in the Bi₂Te₃-based module under the same ΔT , which results in the 75% lower temperature rise at the cold-side and higher ΔT maintained for the Mg-based module under natural convection cooling conditions. As shown in Figure 5B, due to the higher ΔT and power factor of the Mg-based module (Figure S21), the output power of the full Mg-based module was ~400% higher than that of the Bi₂Te₃-based module under natural convection cooling conditions, being more economical and closer to realworld applications. This result was further confirmed under real working conditions, where the Mg-based and Bi₂Te₃-based modules are working on a hot plate of 583 K, with the air fin as the cooling source. The wind-speed-dependent output power of two modules was measured and shown in Figure 5C, which also exhibits the remarkable advantages of the full Mg-based module. Combining the P and Q_h parameters, the measured efficiency (η) of our module is highlighted in Figure 5D. In the case of natural convection cooling and forced water cooling Please cite this article in press as: Zhang et al., High-performance MgAgSb/Mg₃(Sb,Bi)₂-based thermoelectrics with $\eta = 12\%$ at $T \le 583$ K, Joule (2024), https://doi.org/10.1016/j.joule.2024.08.013

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Figure 5. The power generation performance of the full Mg-based TE module

(A) The full Mg-based TE module and measurement setup for various working condition.

(B) Output power and heat flow of modules as a function of heat extraction coefficient h.

(C) Maximal output power of modules as a function of wind speed in air cooling conditions under the hot-side temperature of 583 K.

(D) Efficiency as a function of heat extraction coefficient h.

(E) Maximal output power of the 7-pair module monitored for 250 h under a continuous hot-side temperature of 523 K and water cooling in air conditions.

conditions, owing to the higher *P* and lower Q_h values, the full Mg-based module achieved conversion efficiencies of 6% and 12%, which are ~500% and ~200% higher than those of Bi₂Te₃-based modules, respectively.^{26,28} Indeed, to the best of

our knowledge, the efficiency of 12% is not only the highest among the experimentally measured values in TE modules in the near-room-temperature range (300–583 K) but also one of the highest values among the broader temperature Please cite this article in press as: Zhang et al., High-performance MgAgSb/Mg₃(Sb,Bi)₂-based thermoelectrics with $\eta = 12\%$ at $T \le 583$ K, Joule (2024), https://doi.org/10.1016/j.joule.2024.08.013

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ranges of 300–950 K, as shown in Figure 1D. Thus, the MgAgSb/Mg₃(Bi,Sb)₂ module in this work is probably one of the best choices for electrical power generation from low-grade waste heat at near room temperatures \leq 583 K. Meanwhile, because of the radiation from the heat source, the thermal resistance at the interface, and existence of the contact resistance, the measured η_{max} is slightly lower than the predicted value (Figure S26).

In addition to its high efficiency, the robust durability of the full Mg-based module has been also verified by continuous measurement in vacuum and air conditions. The resistance of the module remained nearly constant under a continuous measurement in vacuum, where the hot-side temperature was set at 573 K for \sim 350 h; the observed increase in the total resistance was within 3%, as shown in Figure S28. Subsequently, the module was monitored for about 5 months in air conditions while the resistance was periodically measured, and the efficiency degraded by only \sim 3%. When working in air, as shown in Figure 5D, to our surprise, the full Mg-based module provided stable output power over 250 h with Th of 523 K, as shown in Figure S29. This can be ascribed to the relatively high thermal and chemical stability of both Mg-based materials at temperatures of <573 K. Meanwhile, the performance of the Bi2Te3-based modules deteriorated quickly at T_h of 523 K, mainly due to degradation of the contact.52

On par with the high power-generation performance mentioned before, we have also investigated the cooling func-



Figure 6. Cooling performance of the full Mg-based TE module

(A) Simulated and measured $\varDelta T_{max}$ as a function of the cold-side temperature for 7-pair full Mg-based and Bi₂Te₃-based cooling modules.

(B) Comparison of the COP between full Mg-based modules and commercial Bi_2Te_3 -based modules as a function of hot-side temperature.

(C) The cost for 7-pair full Mg-based and Bi_2Te_3 -based modules (left), and the comparison of the performance-cost ratio between two modules (right) at the hot-side temperature of 583 K under natural convection cooling conditions.

tionality of the full Mg-based module at near room temperatures ≤573 K. First, as shown in Figures 6A and S30A, a theoretical simulation indicated that the Mg-based modules can generate a series of $\Delta T_{\rm max}$ that will surpass those of commercial Bi2Te3-based modules in a wide temperature range. The solid line with filled circles shows that the measured $\Delta T_{\rm max}$ increases from 83 to 200 K as the cold-side temperature rises from 270 to 390 K for the 7-pair full Mg-based modules. In comparison, the Bi2Te3based modules generated a slightly lower ΔT_{max} of ~80 K at a cold-side T_{c} of 270 K, which then rose to 93 K at a $T_{\rm c}$ of 300 K, followed by degradation to around

72 K at a T_c of 400 K. As the most important indicator of the cooling capability of TE modules, the extraordinary cooling ΔT produced by full Mg-based modules reveals its bright application potential in the fields of TE refrigerators, air conditioners, thermal management of optical communication and high heat-flux chips, etc.^{53,54} In terms of the gaps between the simulated and the measured ΔT values for both modules in Figure 6A, the contact resistance of the p- and n-type legs and the geometry and thermal conductivity of the Al₂O₃ plates were all considered in the calculation to enable the physical description of a real module. However, the deviation between the measured and simulated results could be attributed to a reasonable ignorance of the thermal resistance at multiple interfaces.

The cooling efficiency, COP, which is defined as the ratio between the heat absorbed by the cold side of the module (Q_c) and the energy consumed (P), is another key parameter of thermoelectric cooling (TEC)modules.⁵⁵ As shown in Figure 6B, the maximum COP of the full Mg-based module increased from 2.2 for a T_c of 290 K to 4.3 for a $T_c \sim 400$ K, at a temperature difference of 15 K, while the commercial Bi₂Te₃-based module started with a slightly higher COP of 2.4 for a T_c of 290 K, was overturned by the Mg-based module for a T_c of ~330 K, and then dropped to 2.76 for a T_c of 400 K. When the temperature difference was set at 40 K, which is the typical value in real applications, the COPs of the full Mg-based modules surpassed those of the Bi₂Te₃-based modules over the entire cold-side temperature range of 293–393 K (Figures 6B, S30B, and S31). Moreover, Please cite this article in press as: Zhang et al., High-performance MgAgSb/Mg₃(Sb,Bi)₂-based thermoelectrics with η = 12% at $T \le$ 583K, Joule (2024), https://doi.org/10.1016/j.joule.2024.08.013

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as shown in Figure 6C, the calculated cost of the 7-pair full Mgbased and Bi₂Te₃-based modules is 0.20 and 0.22 \$, respectively, which is close. However, from the point of view of realworld applications, the performance-cost ratio of the full Mgbased module was almost three times higher than that of Bi₂Te₃-based module under natural convection cooling condition at $T_h = 583$ K. This is a direct result of the significantly higher TE performance of the Mg-based materials than those of Bi₂Te₃based module at temperatures ≤ 600 K. In short, the superior TE power generation and cooling functionalities, robust durability, and high cost effectiveness of this full Mg-based module have demonstrated promising prospects for its broad application at near room temperatures.

In conclusion, through a combined strategy of defects engineering and microstructure optimization, near-stoichiometric a-MgAgSb with a mosaic-subgrain-boundary-dominated microstructure, exhibiting extraordinary TE performances, has been successfully synthesized. Besides the intrinsically low κ_{lat} , the hole mobility and electrical transport of the a-MgAgSb were significantly enhanced. The essentially decoupled electronphonon transport led to a record-high zT_{avg} of 1.4 in the temperature range of 300-573 K, which substantially outperformed that of commercial p-type Bi₂Te₃. Given the high compatibilities in terms of the TE performance and mechanical strength between MgAgSb and Mg₃(Bi,Sb)₂, full Mg-based TE modules, composed of 7 pairs of p-type a-MgAgSb and n-type Mg_{3.285}Nb_{0.015}SbBi_{0.9965}Te_{0.0035} TE legs, have been fabricated and evaluated for power generation and cooling. A record-high power generation efficiency of 12% was achieved at temperatures \leq 583 K, and superior cooling performance over traditional Bi₂Te₃-based commercial modules has also been identified. Due to the full Mg-based modules' advantages of cost effectiveness and solid durability, we believe that this work paves the way for the broad application of Mg-based materials in TE power generation and cooling at near room temperatures.

EXPERIMENTAL PROCEDURES

Details regarding the experimental procedures can be found in the supplemental experimental procedures.

RESOURCE AVAILABILITY

Lead contact

Further information and requests for resources and materials should be directed to and will be fulfilled by the lead contact, Huaizhou Zhao (hzhao@ iphy.ac.cn).

Materials availability

The materials in this study will be made available on request.

Data and code availability

The published article includes all data generated or analyzed during this study. Full experimental procedures are provided in the supplemental information.

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AUTHOR CONTRIBUTIONS

H. Zhu and H. Zhao conceived the idea. X.Z. prepared the MgAgSb and Mg₃SbBi-based materials and carried out the thermoelectric transport measurements. X.Z. and H. Zhu constructed the thermoelectric modules and conduced the measurement of the modules. Y.Y., X.Z., and H. Zhu performed the TEM characterization and analyzed the data. Z.F., J.H., and L.H. carried out the high-resolution neutron diffraction studies and Z.F. carried out the Riet-veld refinement of the neutron diffraction patterns. X.D. performed the first-principles calculations. X.Z., N.C., J.Y., K.G., G.L., H. Zhu, and H. Zhao analyzed the data. X.Z., Z.F., H. Zhu, and H. Zhao wrote and edited the paper. All authors contributed helpful discussion to this work.

DECLARATION OF INTERESTS

H. Zhao, X.Z., and H. Zhao have filed one Patent Cooperation Treaty (PCT) patent application (PCT/CN2023/088954) on the work described here.

SUPPLEMENTAL INFORMATION

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Supplemental information

High-performance MgAgSb/Mg₃(Sb,Bi)₂-based

thermoelectrics with η = 12% at *T* \leq 583K

Xiaofan Zhang, Hangtian Zhu, Xuejuan Dong, Zhen Fan, Yuan Yao, Nan Chen, Jiawei Yang, Kaiwei Guo, Jiazheng Hao, Lunhua He, Guodong Li, and Huaizhou Zhao

Supplemental Experimental Procedures

Materials and Methods

Materials synthesis. High-purity Mg tunings (99.8%; Alfa Aesar), Ag particles (99.99; Alfa Aesar), Sb shots (99.999%; Alfa Aesar), Bi pieces (99.999%; Alfa Aesar), Nb pieces (99.99%; Alfa Aesar) and Te pieces (99.999%; Alfa Aesar) were weighed according to the composition of MgAgSb and Mg_{3.2-x}Nb_xSbBi_{1-y}Te_y. For MgAgSb, we first loaded Mg and Ag with an atomic ratio of 1:1 into a stainless-steel jar with carbide balls in the glovebox, followed by ball milling (Hi-Energy/Mill 8000D) for 10 h. Then we added Sb into the jar in the glovebox corresponding to atomic ratio of Mg:Ag:Sb = 1:1:1 with ball milling of 10 h. All the powders were loaded into the graphite die with a diameter of 12.7 mm and sintered by spark plasma sintering (SPS) at 558 K with pressure of 80 MPa for 5 min. The obtained samples were sealed inside an evacuated quartz tube and heated to 583 K at 5 K/min, and then annealed for 24 h to grow grain sizes. For Mg_{3.2-x}Nb_xSbBi_{1-v}Te_v, the elements were loaded into a stainless-steel ball-milling jar in a glovebox and then ball milled for 12 h. The ingot was obtained by sintering using SPS at 1023 K for 5min under a pressure of 50 MPa. The obtained ingot was placed into a magnesium oxide crucible with Magnesium turnings, so that both sides of the pellet were in contact with Mg turnings. The crucible was sealed inside an evacuated quartz tube and annealed at 803 K for 72 h.

Phase and microstructure characterizations. The phase identification of p-MgAgSb and n-Mg_{3,2-x}Nb_xSbBi_{1-v}Te_v were characterized by powder Xray diffraction (Bruker D2 Phaser diffractometer) with Cu K_{α} radiation at room temperature over a 2theta range of 10°-80°. Powder neutron diffraction (PND) measurements were performed against as-synthesized MgAg0.97Sb0.99, as-synthesized MgAgSb, and post-annealed MgAgSb samples (ca. 3 g for each sample) using the high-resolution generalpurpose powder diffractometer (GPPD) (90° bank) at the China spallation neutron source (CSNS). All PND patterns were collected at room temperature for 1 h and Rietveld refinement was performed against PND datasets using GSAS via the EXPGUI interface. The previously published MgAgSb structure was used as the initial model structure for refinement (for the MgAg_{0.97}Sb_{0.99} sample, the structure was slightly modified with SOF(Sb) = 0.99). A minor impurity phase was identified as Fe (space group of Im $\overline{3}$ m) for all samples (0.5 – 0.8 wt%, based on final refinement results) and refined together with the main phase. The minor Fe impurity was most likely introduced into the samples during the ball milling processes; and effects of the trace amount of Fe impurities on thermoelectric property variations can be excluded since they were observed in both MgAgSb and MgAg_{0.97}Sb_{0.99} samples. The following procedures were adopted for Rietveld refinement of the main phase. Typically, background, cell

parameters, peak profile and absorption/reflection coefficients were refined step-by-step at the initial cycles. Atomic coordinates and anisotropic thermal displacement factors were then refined. Prior to the refinement of site occupancy factors (SOF), the absorption/reflection coefficients and thermal displacement factors were unticked initially. The SOF(Ag) factors were firstly refined, where $SOF(Ag_3)$ consistently refined to a value marginally above 1.0 (but within 3 sigma of unity) and then fixed at 1.0. Similarly, the refinement of SOF(Mg) and SOF(Sb) did not suggest vacancies at both sites for the MgAgSb samples. For the MgAg_{0.97}Sb_{0.99} sample, the refinement of SOF(Sb) led to a value of 0.97(2) with a relatively large error *c.f.* that of SOF(Ag) parameters. The refinement of SOF(Sb) for MgAg_{0.97}Sb_{0.99} did not either improve the goodness of fit or affect the final SOF(Ag) parameters; such that the SOF(Sb) was fixed at 0.99. The results indicate that the $MgAg_{0.97}Sb_{0.99}$ is not a line compound and there may exist composition variations in both Ag and Sb sites; however, these are without the research focus of our current study. The refinement profiles plots were exported from GSAS and finally processed and plotted. Rietveld refinement results are included in Fig. 2b, Fig. S13 and Table S4~S7.

The microstructures and grain size investigation were conducted by scanning electron microscopy (SEM, S8100, Hitachi) equipped with electron back-scattering diffraction (EBSD) detector. Scanning transmission electron microscopy (STEM) were conducted using JEOL ARM200F.

Material property characterizations. The electrical resistivity (ρ) and Seebeck coefficient (*S*) were measured by LSR (Linseis LSR-3, Germany) using bar samples with a dimension of 3mm × 3mm × 10mm. The thermal conductivity was calculated by $\kappa = \rho C_P \lambda$, where ρ was mass density, C_p was heat capacity of constant pressure and λ was the thermal diffusivity of the sample. The ρ was measured by the drainage method, and C_p was derived using a differential scanning calorimetry (DSC 404, Netzsch Co. Ltd) and the λ was measured using LFA (Linseis LFA 1000 Laser Flash, Germany). The Hall coefficient (RH) measurement was using PPMS under a reversible magnetic field (\pm 2 T). The Hall carrier concentration (n_H) and the Hall carrier mobility (μ_H) were calculated by $n_H = 1/eR_H$ and $\mu_H = \sigma/(en_H)$, respectively, where e is the electronic charge and σ is the electrical conductivity.

zT measurement uncertainty.

The relative errors can be obtained by the equations:

$$E_{rel}(cA) = E_{rel}A \tag{S1}$$

$$E_{rel}(A \times B) = E_{rel}\left(\frac{A}{B}\right) = \sqrt{(E_{rel}A)^2 + (E_{rel}B)^2}$$
(S2)

$$E_{rel}(A^n) = |n|E_{rel}A \tag{S3}$$

$$E_{rel}\left(\frac{1}{A}\right) = E_{rel}A\tag{S4}$$

Where E_{rel} was the relative error, A and B were the experimental

quantities, c and n were constants. From the equation S1- S4, we can get the equation like:

$$E_{rel}\left(\frac{cA^{n_Bm}}{C^{k_c}}\right) = \sqrt{\left(nE_{rel}(A)\right)^2 + \left(mE_{rel}(B)\right)^2 + \left(kE_{rel}(C)\right)^2}$$
(S5)

The uncertainty of the electrical conductivity is 5% and Seebeck coefficient measurements is 5%. Combining the uncertainties of electrical conductivity and Seebeck coefficient, the measurement uncertainty is about 11% for the power factor. The uncertainty for the total thermal conductivity is about 7% (comprising uncertainties of 5% for the thermal diffusivity, 5% for the specific heat, and 2% for the density). The combined uncertainty for all measurements involved in the calculation of ZT is around 13%.

Analysis of the ball milling progress.

The increased phase purity of precursor powder is mainly due to the homodispersion of elements and enhanced energy of the ball milling, which are keys for the synthesis of high-quality stoichiometric MgAgSb samples. In this work, a series of improvement strategies were adopted for the ball milling process:

1) **Removal of small balls**: The conventional ball milling process for the synthesis of MgAgSb material uses a combination of large (~8g) and small (~1g) stainless steel balls. However, this process has serious cold-welding problems during the mechanical alloying of MgAgSb-based materials,

resulting in an inhomogeneous mixing of the precursor powders and difficulty in obtaining a pure MgAgSb phase. In this work, the coldwelding problem of MgAgSb was successfully avoided by removing the small balls.

2) Use of tungsten carbide balls: The tungsten carbide balls were used instead of the stainless-steel balls. the relative impact velocity V of a sphere which is proportional to the ball mill energy in the ball milling progress can be established by ¹:

$$V^2 = \pi m P_d a^4 / 2R \tag{S6}$$

Where *m* is the ball mass, P_d is the dynamic pressure, *a* is the indentation of radius and *R* is the ball radius. The values used for the calculation can be found in Table S2.

The tungsten carbide balls have larger mass (1.25 times) and smaller size (0.83 times) than the stainless-steel balls, resulting in an approximate 50% increase in grinding energy.

3) **Improved transmission system**: The efficiency of the energy transfer from the motor to the ball mill is closely related to the transmission system. Timing belt is significantly more efficient than comparable flat, wedge or V-ribbed belts because there are no slip or creep losses, and the pre-tension is much lower ². Meanwhile, the efficiency of belt driving mode will be significantly reduced under the conditions of insufficient pretension. Therefore, even with the same speed of motor, the mechanical energy transmitted to the alloying reactions during the ball milling process would be stable and higher through the timing belt mode than other driving belt modes, thus would be favorable for the synthesis of near-stoichiometric MgAgSb.

Combined with the successful avoidance of cold-welding problem and increased ball milling energy, the mechanochemical reaction between the elements is accelerated and completed after the ball milling, resulting in the high purity precursor powder of MgAgSb obtained in this work.

Mobility calculation and the carrier scattering mechanisms.

SPB model provides the expressions as follows³:

$$n_{\rm H} = \frac{4\pi (2m^* k_{\rm B}T)^{3/2}}{h^3} F_{\lambda+1/2}(\eta)$$
(S7)

$$S = -\frac{k_B}{e} \left(\frac{(2+\lambda)F_{\lambda+1}(\eta)}{(1+\lambda)F_{\lambda}(\eta)} - \eta \right)$$
(S8)

$$F_{\rm i}(\eta) = \int_0^\infty \frac{\xi^l d\xi}{1 + \exp\left(\xi - \eta\right)} \tag{S9}$$

Where $k_{\rm B}$ is the Boltzmann constant, *e* the electron charge, *h* the Planck constant, λ the scattering factor, m^* the density of state effective mass, η the reduced Fermi lever, ξ the reduced carrier energy, $F_{\rm i}(\eta)$ the Fermi-Dirac integral. The Lorenz number *L* can be calculated under the SPB approximation:

$$L = -\frac{k_B^2}{e^2} \frac{(1+\lambda)(3+\lambda)F_\lambda(\eta)F_{2+\lambda}(\eta) - (2+\lambda)^2F_{1+\lambda}(\eta)^2}{(1+\lambda)^2F_\lambda(\eta)^2}$$
(S10)

Based on Matthiessen's rule, the total mobility μ can be depicted as:

 $\frac{1}{\mu} = \frac{1}{\mu^{AC}} + \frac{1}{\mu^{Ion}} + \frac{1}{\mu^{GB}} + \frac{1}{\mu^{PD}}$, given the carriers are scattered by acoustic phonons, ionized impurity, grain boundary and point defect. The scattering of different mechanisms is given by^{4,5}:

$$\mu^{AC} = \frac{2^{1/2} \pi e \hbar^4}{3(k_B T)^{3/2}} \frac{\vartheta_l^2 d}{E_{def}^2(m^*)^{3/2} m_l^*} \frac{F_0(\eta)}{F_{\frac{1}{2}}(\eta)}$$
(S11)

$$\mu^{Ion} = \frac{64\sqrt{\pi}\varepsilon_0^2\varepsilon_s^2(2k_BT)^{3/2}}{N_I q^3 m^{*1/2} \ln\left[1 + \left(12\pi\varepsilon_0\varepsilon_s k_BT/q^2 N_I^{1/3}\right)^2\right]}$$
(S12)

$$\mu^{GB} = De(\frac{1}{2\pi m^* k_B T})^{1/2} \exp(-\frac{E_b}{k_B T})$$
(S13)

$$\mu^{PD} = \frac{\pi^2 m^* q^3}{10\varepsilon_0 \varepsilon_s N_N h^3} \tag{S14}$$

Where ϑ_l is the velocity of longitudinal sound waves, *d* the density, E_{def} the deformation potential, ε the dielectric constant, N_I the ionized impurity concentration, *D* the grain size, E_b the potential barrier of the boundary, N_N the neutral impurity concentration.

Calculation Methods.

The calculation of formation energy in our work are performed using density functional theories implemented in VASP ⁶. Generalized-gradient approximations in the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional ⁷ are used. The lattice parameters are relaxed with an energy cutoff of 400 eV and the convergence criteria for energy and stress are less than 10^{-7} eV and 0.01 eV/Å, respectively. A supercell of $2 \times 2 \times 1$ was adopted for the defects formation energy calculation.

Formation energy for α-MgAgSb

The formation energy of α -MgAgSb is calculated based on equation (S15),

 E_{MgAgSb} is the calculated total energy for crystal α -MgAgSb, and E_{Mg} , E_{Ag} , E_{Sb} are the total energies per atom for the bulk magnesium, silver and antimony, respectively.

$$E_f(MgAgSb) = E_{MgAgSb} - E_{Mg} - E_{Ag} - E_{Sb}$$
(S15)

The calculated formation energy of is -0.69 eV for one formula unit.

Stability analysis of α-MgAgSb

When synthesizing MgAgSb from Mg, Ag and Sb element, competing phases such as MgAg, Mg₃Sb₂ and Ag₃Sb are possible to appear in the products. To obtain pure MgAgSb, the chemical potential of Mg, Ag, Sb in MgAgSb must satisfy the equations below:

$$\Delta \mu_{Mg} < 0, \Delta \mu_{Ag} < 0, \Delta \mu_{Sb} < 0 \tag{S16}$$

$$\Delta \mu_{Mg} + \Delta \mu_{Ag} < \Delta H_f(MgAg) \tag{S17}$$

$$3\Delta\mu_{Mg} + 2\Delta\mu_{Sb} < \Delta H_f(Mg_3Sb_2) \tag{S18}$$

$$3\Delta\mu_{Ag} + \Delta\mu_{Sb} < \Delta H_f(Ag_3Sb) \tag{S19}$$

Together with the formation energy of MgAgSb: $\Delta \mu_{Mg} + \Delta \mu_{Ag} + \Delta \mu_{Sb} = \Delta H_f (MgAgSb)$, one can obtain MgAgSb phase if the chemical potential of Mg, Ag, Sb resides in the shaded area shown in Fig. S1.



Fig. S1. The range of chemical potentials for the synthesis of MgAgSb. Defects formation energy of V_{Ag}^{1-} and V_{Sb}^{3+} vacancies in MgAgSb. The defect formation energy is defined by the equation:

 $E_f(defect) = E_{defect}^q - E_{perfect} - \sum_i n_i \mu_i + q(E_F + E_V + \Delta V)$ (S20) in which $E_f(defect)$ is the formation energy of defect which corresponding to V_{Ag}^{1-} and V_{Sb}^{3+} vacancy in our case. And $E_{perfect}$ denotes the total energy the perfect supercell, while E_{defect}^q represents total energy of the defect system, in our case, the energy with one Ag or Sb atom removed for V_{Ag}^{1-} and V_{Sb}^{3+} vacancy, respectively. n_i is the number of atoms being removed or added which is negative if the atom was removed out of the system and positive if the defect was inserted, μ_i denotes the chemical potential of the defect element, E_F is the fermi energy, E_V is the energy with respect to the valence band maximum (VBM), and ΔV is the average difference between the local potentials far from the defect in the defective supercell and the corresponding ones in the perfect supercell, which is very small ^{8,9}. The calculated values of formation energy for V_{Ag}^{1-} and V_{Sb}^{3+} are 0.17 eV and 1.45 eV under Mg-poor condition, and 0.16 eV and 1.25 eV under Mgrich condition, respectively. The value of items in equation S2 are summarized in Table S1.

Table S1. Items in equation S20 expressed in eV, for the calculation of formation energy of V_{Ag}^{1-} and V_{Sb}^{3+} vacancies in MgAgSb.

	Vacancy	E^q_{defect}	E _{perfect}	μ_{Ag}	μ_{Sb}	E _f
Mg-poor	V_{Ag}^{1-}	-576.95	-579.84	-2.72	-4.14	0.17
	V_{Sb}^{3+}	-574.25	-579.84	-2.72	-4.14	1.45
Mg-rich	V_{Ag}^{1-}	-576.95	-579.84	-2.73	-4.34	0.16
	V_{Sb}^{3+}	-574.25	-579.84	-2.73	-4.34	1.25

The relationship between defects formation energy and fermi level was presented in Fig. S2a and S2b for the Mg-poor and Mg-rich conditions, respectively. The formation energy of V_{Ag}^{1-} decreases with the fermi level and turns into negative at the middle of bandgap, illustrating the intrinsic p-type conducting behavior in MgAgSb. These values are consistent with previous report¹⁰, in which the calculated formation energy for V_{Ag}^{1-} and V_{Sb}^{3+} are about 0.25 eV and 1.4 eV under Mg-poor condition, thus conformed our results.



Fig. S2. Defect formation energy of V_{Ag}^{1-} and V_{Sb}^{3+} vacancies in MgAgSb as a function of fermi level, with (a) Mg-poor and (b) Mg-rich environment.

The Debye-Callaway model:

The influence of various defects on lattice thermal conductivity can be evaluated using the Debye-Callaway model:

$$\kappa_{ph} = \frac{k_B}{2\pi^2 \nu} \left(\frac{k_B T}{\hbar}\right)^3 \int_0^{\theta_D/T} \frac{\tau_{tot}(x) x^4 e^x}{(e^x - 1)^2} dx \tag{S21}$$

The integrand term is defined as the spectral lattice thermal conductivity:

$$\kappa_s = \frac{k_B}{2\pi^2 \nu} \left(\frac{k_B T}{\hbar}\right)^3 \frac{\tau_{tot}(x) x^4 e^x}{(e^x - 1)^2} \tag{S22}$$

Here, $x = \hbar \omega / \kappa_B T$ is the reduced phonon frequency, \hbar is the reduced Planck constant, ω is the phonon frequency, κ_B is the Boltzmann constant, vdenotes phonon group velocity, θ_D is the Debye temperature, and $\tau_{tot}(\omega)$ characterizes the frequency-dependent phonon relaxation time. The relaxation time is determined by various scattering processes and can be represented according to Matthiessen's rule:

$$\tau(\omega)^{-1} = \tau(\omega)_U^{-1} + \tau(\omega)_B^{-1} + \tau(\omega)_{PD}^{-1} \dots$$
 (S23)

The complex crystal structure, high elemental weight contrast in MgAgSb, which results in an extremely low sound velocity, and a large Grüneisen parameter γ , collectively contribute to the intrinsic low lattice thermal conductivity. This is primarily attributed to strong Umklapp (U-process) scattering:

$$\tau(\omega)_U^{-1} = A_N \frac{2}{(6\pi^2)^{1/3}} \frac{k_B V^{1/3} \gamma^2 \omega^2 T}{M v^3}$$
(S24)

where V is the atomic volume, M is the average mass. The high-density grain boundaries and mosaic boundaries intensively scatter the phonon. The relaxation time associated with boundary scattering can be expressed as:

$$\tau_{GB}^{-1} = \frac{v}{d} \tag{S25}$$

The contribution of point-defect scattering to the relaxation time can be expressed as:

$$\tau_{PD}^{-1} = \frac{V\omega^4}{4\pi\nu^3}\Gamma\tag{S26}$$

where Γ is point defect scattering parameter and can be expressed as:

$$\Gamma = \left(\frac{m}{M}\right)^2 \left[\sum f_i \left(1 - \frac{m_i}{m}\right)^2 + \varepsilon \sum f_i \left(1 - \frac{r_i}{r}\right)^2\right]$$
(S27)

where, *m* and *r* are the average mass and radius of the substituted site in the host lattice, f_i , m_i , and r_i are the fractional concentration, atomic weight, and atomic radius of the i_{th} substitution atom, and ε is a phenomenological parameter.

Module preparation and characterization.

The procedure of module preparation is shown in the Fig. S3. Thermoelectric legs of p-type MgAgSb and n-type $Mg_{3.2-x}Nb_xSbBi_{1-y}Te_y$ with contact layer were fabricated by the SPS. Ag powder and Mg_2Cu/Cu

were used as contact layers for p- and n-type samples, respectively. The thickness of the obtained pallets was 3 mm and the thickness of contact layers was in the range of 0.1~0.15mm (Fig. S23 and S24). The pellets were diced into legs with a dicing machine (DS830, Heyan technology). The initial side length of the legs after dicing was 1.6 mm, but to remove the contamination layer, they were polished down to the side length of 1.3 \pm 0.1 mm. The legs of n-type Mg_{3.2-x}Nb_xSbBi_{1-y}Te_y were then annealed at 613 K for 2 h as we reported. The p- and n-type legs were placed into a mold and soldered with both sides of patterned metalized Al₂O₃ ceramic plates one after the other. We have tried various kinds of solder materials, such as Sn-Bi, Sn-Sb and Sn-Pb alloys. The welding temperatures of these alloys fall within the range of 523 K to 623 K. Modules can be readily connected using Sn-Bi solder, which resulted in good performance. The Sn-Sb and Sn-Pb solder alloys require higher welding temperatures and offer improved mechanical strength at elevated temperatures. And then a $10 \times 10 \text{ mm}^2$ TE module was successfully fabricated. The fill factor of the Mg-based module is determined to be 23.66%. Bi₂Te₃ legs with dimensions of $1.3 \times 1.3 \times 3$ mm³ were used to make the 7-pair Bi₂Te₃ module with an electroplated Ni based diffusion barrier layer. The p- and n-type Bi₂Te₃ legs were connected in series by a tin-based brazing material to a direct bonded copper (DBC) ceramic substrate. The dimensions of the ceramic substrate were 10×10 mm². Meanwhile, the module is filled with aerogel to minimize the impact of radiation during the measurement of module performance. The cooling and generation performance of the full Mgbased modules were measured by the Mini-PEM (ADVANCE RIKO, Japan) as we reported¹¹.



Fig. S3. The processing diagram of the full Mg-based module fabrication.

Thermoelectric efficiency measurements:

The power output (*P*) and conversion efficiency (η) of the full Mg-based modules under different temperature difference were measured in vacuum (Fig. S4). The cold-side temperature was maintained by cooling water and thermal grease was used to improve the thermal contact of interfaces. The hot-side temperature (T_h) of the module was measured by the thermocouple of the Mini-PEM and the cold-side temperature (T_c) was measured using a K-type thermocouple which was adhered to Al₂O₃ ceramics. A copper column with a cross-section of 10 × 10 mm² was used as heat-flow meter (denoted as Q-meter) with thermal conductivity of 392 W m⁻¹ K⁻¹ for measuring the heat flow through the thermoelectric module. Four K-type thermocouples with a wire-diameter of only 0.3 mm for reducing heat loss were embedded and soldered to the heat-flow meter for determining the temperature difference. The distances between each two adjacent thermocouples are 30 mm for copper-based Q-meter. The whole system is surrounded by quartz cotton.



Fig. S4. Schematic (a) and photograph (b) for the measurement setup for the output power and efficiency of thermoelectric module.

The output power can be measured directly by the instrument and the heat flow can be obtained by:

$$Q_c = \frac{\kappa A}{L} \Delta T \tag{S28}$$

Where Q_c , κ , A, L and $\Delta T = T_1 - T_2$ or $T_2 - T_3$ or $T_3 - T_4$ are the heat flow, thermal conductivity and cross-section of the Q-meter, distance between the two adjacent thermocouples and temperature difference. Therefore, the conversion efficiency (η) can be estimated according to $\eta = \frac{P}{P+Q_c}$. The maximum efficiency can be obtained by varying the load resistance in the circuit and measuring the corresponding output power and heat flow.



Fig. S5. (a) The temperature-dependent thermal conductivity of copper-based and graphite-based Q-meter; (b) temperature-dependent thermal conductivity of Teflon and n-Mg₃SbBi;

In order to verify the accuracy of the copper-based Q-meter, we used Teflon and n-Mg_{3.285}Nb_{0.015}SbBi_{0.9965}Te_{0.0035} sample with cross section of around $10 \times 10 \text{ mm}^2$, which was the same as the full Mg-based module, as the standard sample for heat flow correction. In terms of the quality, we list the following information as shown below: the density, resistivity and Seebeck coefficient of the Mg_{3.285}Nb_{0.015}SbBi_{0.9965}Te_{0.0035} sample at room temperature are 4.78 g cm⁻³, 21.4 $\mu\Omega$ m⁻¹ and -207 μ V K⁻¹, respectively. In addition, the density and degree of polymerization of Teflon is 2.17 g cm⁻³ and 10⁴. The results in Fig. S5 (a) and (b) show that the copper-based Qmeter has an excellent accuracy.

We characterized the power generation performance of our module in a way closer to the real-world applications. When the hot-side temperature of the module is fixed, the cold-side temperature is related to the heat dissipation condition which can be expressed by the heat extraction coefficient (h), which can be obtained by:

$$h = \frac{Q_c}{(T_c - T_0) \times A} \tag{S29}$$

where Q_c , T_c , T_0 and A are the heat-flow, cold-side temperature, ambient temperature and cross-section of the module. The hot-side temperature T_h , ambient temperature T_0 and cross-section A are fixed as 583 K, 283 K and $10 \times 10 \text{ mm}^2$, respectively. The heat extraction coefficient (*h*) can be estimated by measuring the heat flow at different cold-side temperatures using the equipment mentioned above (Fig. S6). Accordingly, the output power, heat flow and conversion efficiency of the module under different heat dissipation conditions are obtained.



Fig. S6. (a) Heat flow of the module under different cold-side temperature (T_c). (b) Estimated heat extraction coefficient (h) using the Equation S29. (c and d) Output power and efficiency of the module as a function of T_c .

The method how we predict the thermoelectric power generation properties of the TEG module^{12,13}.

The TE legs are subdivided along the current direction into n elements, assuming that the temperature T_i is constant in each segment. Thus, we will have constant TE properties in each segment, including thermal conductivity $\kappa(T_i)$, resistivity $\rho(T_i)$, and Seebeck S(T_i). The heat flow from the left side into the segment is:

$$Q(i)_{in} = \kappa(T_i) A_p (T_i - T_{i+1}) / dx$$
(S30)

Where A_p is the cross-section area of the leg, dx is the length of the segment, T_i and T_{i+1} are the temperature of left and right side of the segment, respectively.

The heat flow from the right side into the segment is:

$$Q(i)_{out} = \kappa(T_i)A_p(T_{i+1} - T_{i+2})/dx$$
(S31)

The joule heat generated by the current is:

$$Q(i)_{joule} = I^2 \rho(T_i) dx / A_p \tag{S32}$$

The Thomson heat can be calculated as:

$$Q(i)_{Thomson} = -IT_i(S_{i+1} - S_i)$$
(S33)

The thermal radiation emitted from the segment surface to the environment:

$$Q(i)_{radiation} = -\varepsilon\sigma(T_i^4 - T_r^4)wdx$$
(S34)

where ε is the emissivity of the TE material, σ is the Stefan-Boltzmann

constant, T_r is the environment temperature, w is the perimeter of the crosssection area.

The following formula can be derived from energy balance in steady state:

$$Q(i)_{out} = Q(i)_{in} + Q(i)_{joule} + Q(i)_{Thomson} + Q(i)_{radiation}$$
(S35)

Though solving this finite element problem, we will get the temperature distribution function T_i along the leg, which enable us to obtain the basic parameters and performance of the device. The total heat flow transfer into the legs is:

$$Q_{in} = \kappa(T_1)A_p(T_1 - T_2)/dx + T_1IS_1 - \frac{1}{2}(I^2\rho(T_1)dx/A_p - IT_1(S_2 - S_1) - \varepsilon\sigma(T_1^4 - T_r^4)wdx)$$
(S36)

Open circuit voltage of the device:

$$V_{oc} = \sum_{1}^{n} S_{i} (T_{i} - T_{i+1})$$
(S37)

Dependence of voltage on current:

$$V = V_{oc} - I \sum_{1}^{n} \rho(T_i) dx / A_p$$
(S38)

The output power of the device:

$$P_{out} = IV \tag{S39}$$

The energy conversion efficiency of device:

$$\eta = P_{out} / Q_{in} \tag{S40}$$

The COP of cooling device:

$$\eta = Q_{in} / P_{out} \tag{S41}$$



Fig. S7. The predicted and measured carrier concentration dependent thermoelectric transport properties of MgAgSb with different defect type. (a) Electric conductivity (σ) and carrier mobility (μ); (b) power factor (*PF*); (c) thermal conductivity (κ) and (d) figure of merit (*zT*).



Fig. S8. The round robin test of thermoelectric properties for MgAgSb. (a) electrical conductivity σ ; (b) Seebeck coefficient *S*; (c) thermal conductivity κ ; (d) figure of merit *zT*. The purple and blue lines are the round robin tests provided by Shanghai Institute of Ceramics, Chinese Academy of Sciences (SIC, CAS) and Beijing Normal University (BNU), respectively. Electrical conductivity and Seebeck coefficient were measured by ZEM-3 at BNU and SIC, CAS, and by LSR-3 in this work (IOP, CAS). The thermal conductivity was measured by LFA 457 at BNU and SIC, CAS, and by LFA1000 in this work.



Fig. S9. Temperature-dependent thermal diffusivity (a) and specific heat (b) for assynthesized MgAg_{0.97}Sb_{0.99}, as-synthesized MgAgSb and post-annealed MgAgSb in this work and round robin test measurements provided by Shanghai Institute of Ceramics, Chinese Academy of Sciences (SIC, CAS) and Beijing Normal University (BNU), respectively.



Fig. S10. The ball mill equipment with timing belt mode (a) and belt drive mode (b).



Fig. S11. XRD patterns (a) and (b) of Ball-milling powder precursor and zT value (c) of the as-synthesized MgAgSb under different ball milling condition.



Fig. S12. XRD patterns of as-synthesized MgAgSb and post-annealed MgAgSb.



Fig. S13. Profile plots of the Rietveld refinement against experimental powder neutron diffraction patterns for as-synthesized MgAg_{0.97}Sb_{0.99} (a) and as-synthesized MgAgSb (b) measured at 300 K.



Fig. S14. Fresh fracture morphologies and corresponding grain size distributions of assynthesized (a) and post-annealed (b) MgAgSb samples.



Fig. S15. The mosaic subgrain microstructure of as-synthesized MgAg_{0.97}Sb_{0.99} (a), assynthesized MgAgSb (b) and post-annealed MgAgSb (c).



Fig. S16. Frequency-dependent spectral lattice thermal conductivity of post-annealed MgAgSb sample.



Fig. S17. The power factor of as-synthesized MgAg_{0.97}Sb_{0.99}, as-synthesized MgAgSb and post-annealed MgAgSb samples.



Fig. S18. Thermal cycling test of the α -MgAgSb materials. (a) Electrical conductivity σ ; (b) Seebeck coefficient *S*; (c) thermal conductivity κ ; (d) figure of merit *zT*.



Fig. S19. Thermoelectrical properties of n-type Mg₃(Bi,Sb)₂. (a) electrical conductivity σ ; (b) Seebeck coefficient *S*; (c) thermal conductivity κ ; (d) figure of merit *zT*.



Fig. S20. Measured zT as a function of temperature for Mg_{3.285}Nb_{0.015}SbBi_{0.9975}Te_{0.0035} (a) and α -MgAgSb (b) in this work compared to literatures (inset shows the average zT) ¹⁴⁻²³.



Fig. S21. Thermoelectric properties of p-MgAgSb, n-Mg₃(Bi,Sb)₂, p-Bi₂Te₃ and n-Bi₂Te₃. (a) electrical conductivity; (b) Seebeck coefficient; (c) power factor; (d) thermal conductivity.



Fig. S22. Contact resistivity of p-type MgAgSb (a) and n-type Mg₃(Bi,Sb)₂ (b).



Fig. S23. SEM images and EDS mapping results for (a) p-type MgAgSb and (b) n-type Mg3(Bi,Sb)₂ junctions.



Fig. S24. SEM images and EDS mapping for the contact layers of the (a) p-type MgAgSb and (b) n-type $Mg_3(Bi,Sb)_2$ legs at the hot side of module, which have been monitoring for 250 h under a continuous hot-side temperature of 523 K in air condition.



Fig. S25. The current-dependent power generation properties under different hot-side temperature of 7-pair full Mg-based TEG module based on copper Q-meter. (a) Voltage (V); (b) Output power (*P*); (c) Heat-flow from hot-side (Q_h); (d) Conversion efficiency (η).



Fig. S26. The predicted and measured temperature-dependent power generation properties of 7-pair full Mg-based TEG module based on copper Q-meter. (a) Opencircuit voltage (V_{oc}) and internal resistivity (R_{in}); (b) Output power (P); (c) Heat-flow from hot-side (Q_h); (d) Conversion efficiency (η).



Fig. S27. The round robin test current-dependent power generation properties under different hot-side temperature of full Mg-based TEG module at Harbin Institute of Technology (Shenzhen). (a) Voltage (V); (b) Output power (*P*); (c) Heat-flow from hot-side (Q_h); (d) Conversion efficiency (η).



Fig. S28. Resistance and efficiency of the 7-pair module was monitored for 230 h under a continuous hot-side temperature of 573 K.



Fig. S29. Time dependence of voltage (a) resistivity (b) and of the full Mg-based module during durability test with T_h of 523 K under air.



Fig. S30. (a) Maximum temperature difference as a function of hot-side temperature T_h of full Mg-based module, MBST/SBTS module and commercial Bi₂Te₃-based modules. (b) Coefficient of performance (COP) for the full Mg-based module and Bi₂Te₃-based module working at $\Delta T = 40$ K, $T_h = 373$ K.



Fig. S31. The equipment for measuring the COP of the module.

Parameters	Hi-Energy/Mill 8000D	SPEX 8000D Mixer/Mill	
Drive mode	Timing belt mode	Belt driving mode	
Motor speed	1425 RPM	1425 RPM	
Clamp speed	875 RPM	875 RPM	
Voltage	230V/50Hz	230V/50Hz	
Type of grinding ball	Carbide ball	Steel ball	
Diameter of each grinding ball	10.5 mm	12.6 mm	
Mass of each grinding ball	10 g	8 g	

 Table S2. Parameters for the calculation of ball-milling reaction.

Table S3. Density for the MgAg_{0.97}Sb_{0.99}, MgAgSb and post-annealed MgAgSb material in this work and round robin test measurements provided by Shanghai Institute of Ceramics, Chinese Academy of Sciences (SIC, CAS) and Beijing Normal University (BNU), respectively.

Sample	Density (g cm ⁻¹)
MgAg0.97Sb0.99	6.053
MgAgSb	6.115
Post-annealed MgAgSb	6.095
Round-robin test at BNU	6.103
Round-robin test at SIC, CAS	6.096

Sample MgAg _{0.97} Sb _{0.99}		MgAgSb	Post-annealed MgAgSb
Chemical Formula (Refined)	MgAg _{0.973(6)} Sb _{0.99}	MgAg _{0.993(7)} Sb	MgAg _{0.992(6)} Sb
Crystal System	Tetragonal	Tetragonal	Tetragonal
Space Group	<i>I</i> -4c2	<i>I</i> -4c2	<i>I</i> -4c2
Lattice parameters ($\alpha = \beta = \gamma = 90^\circ$) / Å a = b	9.16698(14)	9.16388(12)	9.16430(11)
С	12.70911(30)	12.70812(25)	12.71061(23)
Cell volume / Å ³	1067.991(32)	1067.185(27)	1067.494(24)
Formula weight / g mol ⁻¹	999.34	1013.28	1012.32
Formula units, Z	16	16	16
No. of observations	2588	2593	2554
χ^2	1.860	1.093	1.451
Rp	<i>Rp</i> 0.0467		0.0458
<i>wRp</i> 0.0501		0.0493	0.0494

Table S4. Crystallographic data obtained from the Rietveld refinement for the assynthesized MgAg_{0.97}Sb_{0.99}, as-synthesized MgAgSb and post-annealed MgAgSb against PND data.

Table S5. Atomic parameters of MgAg0.97Sb0.99	from the Rietveld refinement
against PND data.	

Atom	Wyckoff symbol	x	у	Z	100×U _{iso} /Å ² (Equivalent)	Occupancy
Mg	16;	0.02517	0.28234	0.11048	1 547	1.0
	101	(24)	(28)	(26)	1.547	1.0
Sh	16;	0.26428	0.02327	0.11756	1 427	0.00
30	101	(29)	(28)	(22)	1.437	0.99
Δ α1	8e	0.27580	0.27580	0.25	1.409	0.974(7)
Agi		(25)	(25)	0.23		
Ag2	4b	0	0	0.25	1.369	0.946(9)
Ag3	4a	0	0	0	1.175	1.0
Atom	U_{11}	U_{12}	U_{13}	U_{22}	U_{23}	U_{33}
A a 1	0.01342	0.00122	0.01739	0.01342	-0.01739	0.01543
Agi	(140)	(190)	(171)	(140)	(171)	(210)
Ag2	0.01654	0.01287	0.0	0.01654	0.0	0.0083
	(300)	(205)		(300)	0.0	(30)
Ag3	0.01226	0.0	0.0	0.01226	0.0	0.01074
	(202)	0.0	0.0	(202)	0.0	(265)

Atom	Wyckoff symbol	x	у	Z	100×U _{iso} /Å ² (Equivalent)	Occupancy
Mg	10	0.02472	0.28252	0.11051	1.171	1.0
	101	(23)	(24)	(21)		1.0
Sh	16;	0.26394	0.02318	0.1174	1.020	1.0
30	101	(23)	(22)	(19)	1.029	1.0
A a 1	8.0	0.27559	0.27559	0.25	0.25 1.46	0.998
Agi	80	(24)	(24)	0.25		(8)
Ag2	4b	0	0	0.25	1.906	0.982(10)
Ag3	4a	0	0	0	0.724	1.0
Atom	U_{11}	U_{12}	U_{13}	U_{22}	U_{23}	U 33
A g1	0.01289	0.00207	0.01842	0.01289	-0.01842	0.01802
Agi	(133)	(192)	(205)	(133)	(205)	(224)
Ag2	0.02402	0.01915	0.0	0.02402	0.0	0.00914
	(231)	(264)		(231)	0.0	(306)
Ag3	0.00577	0.0	0.0	0.00577	0.0	0.01017
	(236)	0.0		(236)		(267)

Table S6. Atomic parameters of MgAgSb from the Rietveld refinement againstXRD data.

Table S7. Atomic parameters of post-annealed MgAgSb from the Rietveldrefinement against XRD data.

Atom	Wyckoff symbol	x	У	Z	100×U _{iso} /Å ² (Equivalent)	Occupancy
Mg	16;	0.02482	0.28249	0.11027	1.053	1.0
	101	(20)	(21)	(18)	1.055	
Sh	16;	0.26439	0.02374	0.11786	1 1 2 1	1.0
30	101	(20)	(20)	(17)	1.121	1.0
A ~1	9 a	0.27597	0.27597	0.25	1.192	0.993(7)
Agi	80	(21)	(21)	0.25		
Ag2	4b	0	0	0.25	2.037	0.983(9)
Ag3	4a	0	0	0	0.55	1.0
Atom	U_{11}	U_{12}	U_{13}	U_{22}	U_{23}	U_{33}
A a 1	0.01022	0.00077	0.01253	0.01022	-0.01253	0.01532
Agi	(110)	(161)	(126)	(110)	(126)	(186)
Ag2	0.02422	0.0092	0.0	0.02422	0.0	0.01268
	(201)	(127)		(201)	0.0	(272)
Ag3	0.00330	0.0	0.0	0.00330	0.00330 (178) 0.0	0.00989
	(178)	0.0	0.0	(178)		(251)

Material	Price			
Mg	2.21\$/kg			
Ag	520\$/kg			
Sb	5.61\$/kg			
Bi	6.16\$/kg			
Te	72\$/kg			
Nb	61.4\$/kg			
Al ₂ O ₃ ceramic plate	0.42\$ per set			

Table S8. Components of TE modules and corresponding market prices from *Wikipedia*.

Table S9. Parameters for the carrier scatter mechanism calculation.

Parameters	Values		
Longitudinal sound speed	3357		
Transverse sound speed	1780		
Grüneisen parameter	2.138		
Density	6.1		
Poisson's ratio	0.35		
Average atomic volume	2.23×10 ⁻²⁹ m ³ /atom		
Average atomic mass	1.05×10 ⁻²² g/atom		
Subgrain average radius	20 nm		

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