Towards tellurium-free thermoelectric modules for power generation from low-grade heat

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Thermoelectric technology converts heat into electricity directly and is a promising source of clean electricity. Commercial thermoelectric modules have relied on Bi2Te3-based compounds because of their unparalleled thermoelectric properties at temperatures associated with low-grade heat (<550 K). However, the scarcity of elemental Te greatly limits the applicability of such modules. Here we report the performance of thermoelectric modules assembled from Bi2Te3-substitute compounds, including p-type MgAgSb and n-type Mg3(Sb, Bi)2, by using a simple, versatile, and thus scalable processing routine. For a temperature difference of ~250 K, whereas a single-stage module displayed a conversion efficiency of ~6.5%, a module using segmented n-type legs displayed a record efficiency of ~7.0% that is comparable to the state-of-the-art Bi2Te3-based thermoelectric modules. Our work demonstrates the feasibility and scalability of high-performance thermoelectric modules based on sustainable elements for recovering low-grade heat.

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More than 60% of the energy generated by burning fossil fuels is dissipated as waste heat, of which more than half is low-grade heat with temperatures <550 K. Effective harnessing this “cooler” heat to generate electricity is vital for alleviating the burden on the energy supply and reducing the emission of greenhouse gases. Although potential technologies, such as the organic Rankine cycle, thermogalvanic cells, and thermo-osmotic are being explored, these are limited by their low efficiencies, short lifetimes, and difficulty in system integration. In comparison, thermoelectric (TE) technology stands out owing to its solid-state nature, which guarantees ultra-long operational lifetime, and is particularly attractive for heat-to-electricity conversion. The broader applicability of TE technology relies on the availability of high-performance materials and modules that operate efficiently below 550 K.

The energy conversion efficiency of a TE material is governed by the dimensionless figure of merit $zT$, defined as $zT = S^2\sigma T/\kappa T$, where $S$, $\sigma$, $T$, and $\kappa$ are the Seebeck coefficient, the electrical conductivity, the absolute temperature, and the total thermal conductivity, respectively. Among various materials tested to date, Bi$_2$Te$_3$-based materials have unparalleled TE properties and have thus been the focus of laboratory-scale demonstrations and commercial devices that operate below 550 K with typical conversion efficiencies of about 3–6%. However, the wider applicability of Bi$_2$Te$_3$-based commercial modules is severely limited by the scarcity of Te with a concentration of <0.001 ppm in the Earth’s crust and an annual production of less than 500 metric tons. Therefore, it is imperative to develop TE modules from other, more abundant materials while retaining high performance at temperatures below 550 K.

In recent years, Mg-based materials, including n-type Mg$_3$(Sb, Bi)$_2$ and p-type MgAgSb have attracted great attention from the TE community because of the nontoxic nature, abundance of their constituent elements, and their high $zT$ of ~1.0 at temperatures <550 K. Moreover, these materials exhibit excellent mechanical robustness and compatible TE properties between the n-type and p-type TE materials. Previous reports showed excellent performances of these materials at the device level. For example, Kraemer, et al. reported a ~8.5% efficiency of single-leg MgAgSb operating between 293 K and 518 K. Mao, et al. improved the cooling performance by using Mg$_3$(Sb, Bi)$_2$ to replace the Bi$_2$(Te,Se)$_3$ for n-type legs. These work merit the great potential of these materials in replacing the Bi$_2$Te$_3$ for low-grade heat recovery applications. However, for successful delivery, it is essential to employ synthesis routines that are potentially scalable for these Te-free TE modules, as well as to address their device-level issues such as geometry optimization, brazing process, and contact optimization, etc. Till now, despite their promise, the assembly of these substitute compounds into power-generation modules has not been reported.

Herein, we synthesized p-type MgAgSb and n-type Mg$_3$(Sb,Bi)$_2$ compounds using direct mechanical alloying followed by rapid current-assisted sintering. Note that for n-type Mg$_3$(Sb,Bi)$_2$, we used less than 0.2% Te as the dopant in this work to secure the material properties since its performance was widely validated, so that the module is not completely free of Te. However, Te is not an essential dopant with available alternatives, such as Sc, Nd, Y, etc., yielded similar TE performances according to several recent studies. We reproduced these high-performance materials with a synthesis routine that is potentially scalable. Such ups-scaling potential is critically important for heat-recovery applications. Subsequently, these high-$zT$ compounds were translated into high-performance TE modules. We realized a high conversion efficiency of ~6.5% and ~7.0% under a temperature difference of ~250 K in a single-stage module and a segmented module, respectively. Our efficiency is comparable to those reported for Bi$_2$Te$_3$-based modules. This work marks a feasible, sustainable alternative to Bi$_2$Te$_3$-based TE modules and will spur the application of TE technology in converting low-grade heat to electricity.

**Results**

**Scalable preparation of thermoelectric materials and modules.** High-performance TE materials with simple synthesis are favored for module fabrication. However, the synthesis of Mg-based compounds usually involves procedures that are either complicated, expensive, or time-consuming. For example, the synthesis of Mg$_3$(Sb,Bi)$_2$ compounds usually involves complicated processing routines including melting (such as arc melting, induction melting, or traditional melting), pre-annealing, powerization, sintering (such as spark plasma sintering, hot pressing, or induction pressing), and post-annealing. In another example, MgAgSb, being in a phase at room temperature, changes to the β phase at ~573 K, and to the γ phase at ~633 K. Whereas only the α phase has the requisite high $zT$, phase-pure α-MgAgSb is difficult to obtain using traditional melting techniques unless a time-consuming annealing process is followed.

An alternative synthesis routine were reported to overcome such limitations for synthesizing the n- and p-type legs using only three steps: weighing, mechanical alloying, and rapid sintering (Fig. 1a, b; “Methods”). Following these reports, we here...

![Fig. 1 Fabrication of Te-free TE materials and modules.](image)
employed mechanical alloying not only because it is a lower-cost way to realize large-scale production, but also because it allows for accurate stoichiometry that ensures high reproducibility, which is necessary to scale up production. This is especially essential for this work since the compounds studied here are rich in Mg, Bi, and Sb, which would otherwise largely evaporate if traditional melting techniques were used. The phases of the TE materials were characterized by X-ray diffraction (XRD). The XRD patterns (Supplementary Fig. 1a, b) indicated high purity for the n-type $\text{Mg}_3.3\text{Bi}_{1.498}\text{Sb}_{0.5}\text{Te}_{0.002}$ (denoted as n-Sb0.5) and $\text{Mg}_3.3\text{Bi}_{1.298}\text{Sb}_{0.7}\text{Te}_{0.002}$ (denoted as n-Sb0.7), and the p-type $\text{MgAg}_{0.97}\text{Sb}_{0.99}$ (abbreviated as “p-MgAgSb”). We then undertook scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) elemental mapping of n- and p-type legs with contact layers. The elemental distribution was nearly uniform (Supplementary Fig. 1c, d) and we could find no obvious interaction between the TE materials and the contact layers.

Using the mechanically-alloyed powder samples, we then fabricated the TE legs for module assembly by sintering in one step the TE powder together with contact-layer powder on both sides. Note that such one-step sintering was also applied for segmented n-type legs. Herein, based on the previous reports, we selected Fe and Ag as the contact layers for the n- and p-type segments, respectively. The selected contact resistivity at the n-type/Fe and p-type/Ag junctions, which was found to be $26.6 \, \Omega\cdot \text{cm}^2$ and $6 \, \Omega\cdot \text{cm}^2$, respectively (Fig. 3b). Although these values remain higher than those for the benchmark Bi$_2$Te$_3$/Ni (1 – 5 $\mu\Omega\cdot \text{cm}^2$) that was realized upon optimizations for more than half a century, the overall interfacial

Thermoelectric properties and module optimization. We measured the transport properties of the TE materials, including the electrical conductivity, the Seebeck coefficient, and the thermal conductivity. The compounds synthesized in this work, including n-Sb0.5, n-Sb0.7, and p-MgAgSb, possess similar properties when compared to previous reports (Fig. 2) despite the straightforward synthesis procedure. For p-MgAgSb, we obtained a peak $zT$ of ~1.0 at 423 K and an average $zT$ of ~0.9 at temperatures ranging from room temperature to 548 K (Fig. 2d). For the n-type materials, whereas n-Sb0.5 showed a higher $zT$ up to 423 K, n-Sb0.7 exhibited better performance at higher temperatures (423 K to 548 K). The peak $zT$ values reach 0.9 (at 423 K) and 1.2 (at 548 K) in n-Sb0.5 and n-Sb0.7, respectively.

Based on the $zT$ profiles of n-Sb0.5 and n-Sb0.7, we postulated that a segmented leg could maximize the average $zT$ of the n-type materials. According to the transport properties these compounds, we employed finite element simulation to assist in designing the geometrical configuration of the TE modules. With a hot-side temperature ($T_{\text{hot}}$) of 548 K and a cold-side temperature ($T_{\text{cold}}$) of 293 K, we evaluated the maximum conversion efficiency as a function of the working current ($I$), the ratio of the cross-sectional areas between the p- and n-type legs ($A_p/A_n$), and the height ratio of the two n-type materials ($H_{n, \text{Sb0.7}}/H_{n, \text{Sb0.5}}$) in a segmented leg (Fig. 3a and Supplementary Fig. 2). We found that the ratio of $H_{n, \text{Sb0.7}}/H_{n, \text{Sb0.5}}$ was optimal over a large range from 0.75 to 1.75 (Supplementary Fig. 2). In addition, the ratio of $A_p/A_n$ was found to have a limited impact on efficiency (Fig. 3a). These results suggest that the module performance is not sensitive to the geometric factors, which is beneficial since it tolerates certain deviations in the TE-leg fabrication process without degrading the efficiency. Accordingly, we fabricated TE modules with segmented n-type legs with the ratio of $A_p/A_n$ being unity to facilitate the device assembling.

To further evaluate the module quality, we characterized the contact resistivity at the n-type/Fe and p-type/Ag junctions, which was found to be $26.6 \, \mu\Omega\cdot \text{cm}^2$ and $6 \, \mu\Omega\cdot \text{cm}^2$, respectively (Fig. 3b). Although these values remain higher than those for the benchmark Bi$_2$Te$_3$/Ni (1 – 5 $\mu\Omega\cdot \text{cm}^2$) that was realized upon optimizations for more than half a century, the overall interfacial

Fig. 2 Temperature-dependent thermoelectric properties of the fabricated materials. a Absolute Seebeck coefficient $|\alpha|$, b electrical conductivity $\sigma$, c total thermal conductivity $k_{\text{tot}}$, and d figure of merit $zT$. n-Sb0.5: $\text{Mg}_3.3\text{Bi}_{1.498}\text{Sb}_{0.5}\text{Te}_{0.002}$ (green triangles); n-Sb0.7: $\text{Mg}_3.3\text{Bi}_{1.298}\text{Sb}_{0.7}\text{Te}_{0.002}$ (blue diamonds); p-MgAgSb: $\text{MgAg}_{0.97}\text{Sb}_{0.99}$ (red rings). The error bars represent the corresponding measurement uncertainties from the commercial devices.
Free modules in this work under a series of temperature differences (ΔT) of 250 K. The uncertainties from the commercial device. The error bars represent the measurement errors. Moreover, the module with segmented legs boosted the performance of a segmented Te-free module. The error bars represent the measurement uncertainties from the commercial device.

Fig. 3 Module optimization. a Simulated efficiency (η) with respect to the A/An ratio and the working current (I) for the single-stage module (n-Sb0.7) under T_hot = 543 K and T_cold = 293 K. b Measured electrical contact resistivity at the n-type/Fe and p-type/Ag junctions. The red circles and blue diamonds represent the scattering resistance across the junctions, the solid horizontal lines indicate the contact resistivity.

Fig. 4 Performance of the Te-free segmented modules. Comparison of the measured conversion efficiency (η_max lines with symbols) among the Te-free modules in this work under a series of temperature difference (ΔT). The η_max of the Bi2Te3-based modules from the literature (dashed lines) were also plotted for comparison. The inset shows the photograph of a segmented Te-free module. The error bars represent the measurement uncertainties from the commercial device.

Resistance impacts the efficiency of our module inconsiderably. This was demonstrated by comparing the measured internal resistance, open-circuit voltage, output powers, and conversion efficiency with and without the contact resistance of the single-stage module (Supplementary Fig. 3) and segmented module (Supplementary Fig. 4).

Discussion

Te-free TE modules could provide a clean and effective way of converting low-temperature waste heat to electricity. However, their practical applicability has been hindered by difficulties in synthesizing these Te-free materials on large scale, and high-performance TE modules based on such materials have not been successfully fabricated. We were able to synthesize Bi2Te3 (BiSb)2 and p-type MgAgSb by using a scalable routine that combined mechanical alloying and current-assisted sintering. By allowing a much simpler synthesis of such TE materials, our approach presents a substantial advance in shortening the synthesis period and reducing the elemental loss, which is especially essential for large-scale synthesis. The synthesized Te materials were subsequently translated into single-stage and segmented TE modules with conversion efficiency reaching ~6.5% and ~7.0%, respectively, for a temperature difference of ~250 K.

On the other hand, numerous challenges have to be overcome before realizing the ultimate substitution of Bi2Te3 module by a Te-free one, since the former has been investigated for more than half a century yet the latter is in its infancy. The required studies include but are not restricted to (1) upscale to the level of kilogram without degrading the TE properties, possibly by using planetary ball milling; (2) thermal cycle test to examine the device reliability at elevated temperatures; (3) long-term stability (in years) under actual operating conditions and different atmospheres such as current load and temperature gradient; (4) techniques for packaging and sealing to overcome potential instabilities under atmosphere at elevated temperatures.

Despite the aforementioned challenges, this work thus realizes high-performance TE modules free from Bi2Te3 that are capable of harvesting low-grade (<550 K) waste heat. The efficiency demonstrated in this work exceeds that of the best Bi2Te3-based modules. Subsequent enhancements are possible upon further advances in the material properties and optimize the filling factor of flow, whereas the output power (Supplementary Figs. 3-4) were almost identical between simulations and measurements. The larger output heat flow in measurement suggests the potential existence of a thermal bypass, possibly due to the insufficient vacuum level or because of the direct thermal radiation from the hot side to the cold side in the Mini-PEM measurement setup since the small filling factor in our module (~16%). Our state-of-the-art modules are comparable to the Bi2Te3-based ones, and could potentially be improved by a better thermal management. In principle, our work demonstrated the feasibility of an Te-free TE module for extended applications due to their remarkable sustainability.
the modules. The use of abundantly available elements and the ease of fabrication render our modules a notable substitute for the Bi₂Te₃-based modules in low-grade heat recovery. This will potentially spur the application of thermoelectric technology for power generation from low-grade heat.

**Methods**

**Synthesis of n- and p-type materials.** High-purity powder Bi (99.9%), Sb (99.9%), Te (99.99%), Mg (99.8%), and Ag (99.9%) were weighed out in the atomic ratios of Sb₉₋ₓBiₓTe₃₋ₓO₂₋ₓ (denoted as n-Sbₐ), MgₓBi₉₋ₓSbₓTe₃₋ₓO₂₋ₓ (denoted as n-SbₐOₓ), and MgₙAgₓSb₉Te₃₋ₓO₂₋ₓ (denoted as p-MgAgSb). For each sample, the weighed elements were loaded into a hardened steel ball-milling jar in a glove box under an argon atmosphere with an oxygen and water level below 1.0 ppm and then ball-milled for 20 hours in a SPEX 8000D machine. The ball-milled powders were subject to field-assisted sintering (FAST, FCT System GmbH) together with the contact powders. Powders of iron (Fe, purity 99.8%) and silver (Ag, purity 99.9%) were selected as the contact layers for n-type and p-type materials, respectively. The n-type materials were sintered in a graphite die under a pressure of 50 MPa at 1023 K for 3 minutes and the p-type materials were sintered in a tungsten carbide (WC) die under a pressure of 120 MPa at 553 K for 3 min. The phase purity and crystal structure of the samples were examined by X-ray diffraction (XRD, Bruker D8, Co radiation) and their microstructures were analyzed by scanning electron microscopy (SEM). The sample homogeneity was characterized by energy-dispersive X-ray spectroscopy (EDX). The temperature-dependent Seebeck coefficient (S) and electrical conductivity (σ) were measured by the standard four-probe method (LSR-3, Linseis). The temperature-dependent thermal diffusivity (λ) was measured by a laser flash method under a helium atmosphere (LFA 1000, Linseis). The density (ρ) of the samples was measured by the Archimedes method, and the heat capacity (C_p) was obtained from previous reports [17–20]. The thermal conductivity (κ = λ / ρ · C_p). The measurement uncertainties are 2%, 5%, and 7% for σ, S, and κ, respectively, which yield an error in T/ε of ~18%.

**Thermoelectric module fabrication and characterization.** The sintered n- and p-type bulk samples with contact layers were cut into legs using a diamond wire saw in the dimension of 2.0 × 2.0 × 6.5 mm³. The TE legs (with the contacts), electrodes, and the ceramic substrates were bonded in a single step. The bonding was enabled by curing the silver paste at 548 K for 30 minutes in a high-vacuum tube furnace. To reduce the thermal contact loss, a graphite sheet (0.1 mm thick) was used as an interlayer. To perform the three-dimensional finite element simulation, a commercial software was used to model with the same dimensions as the experimental thermoelectric element was used to calculate the electric power and heat flow outputs. Fourth-order polynomial was used to calculate the electric power and heat flow outputs. Fourth-order polynomial was used to fit the temperature-dependent Seebeck coefficient, electrical conductivity, and thermal conductivity for both n- and p-type materials were used as material properties in the simulations.

**Data availability**

All data generated or analyzed during this study are included in the published article and its Supplementary Information. The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Author contributions
P.Y., R.H., Z.R., K.N., and G.S. designed the work. P.Y. and H.R. assembled the modules and characterized the module performance. R.H. and P.Y. prepared the TE materials and measured the transport properties. J.M. measured the contact resistance. J.S. assembled the ceramic substrate with electrodes. P.Y. and Q.Z performed simulations. P.Y., R.H., K.N., and G.S. wrote the manuscript. All authors edited the manuscript.

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