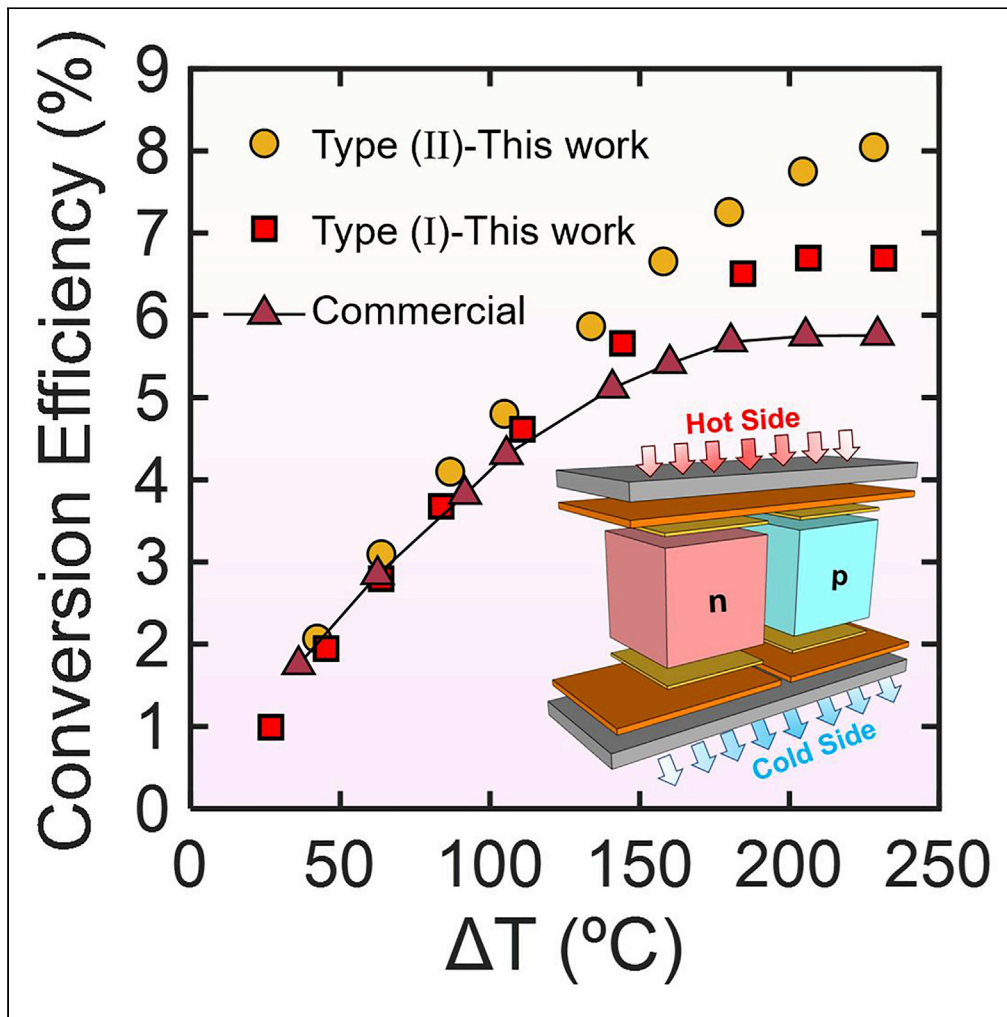


Article

Bismuth Telluride Thermoelectrics with 8% Module Efficiency for Waste Heat Recovery Application



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HIGHLIGHTS

Significant improvement
in design of bismuth
telluride alloys is
demonstrated

High peak and average zT
are obtained in both p-
and n-type bismuth
telluride alloys

Thermoelectric generator
with conversion efficiency
of 8% is fabricated

High efficiency
accelerates the transition
of TEGs for waste heat
recovery

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Article

Bismuth Telluride Thermoelectrics
with 8% Module Efficiency
for Waste Heat Recovery ApplicationAmin Nozariasbmarz,^{1,2,*} Bed Poudel,¹ Wenjie Li,¹ Han Byul Kang,¹ Hangtian Zhu,¹ and Shashank Priya^{1,*}

SUMMARY

Thermoelectric generators (TEGs) offer cost-effective and sustainable solid-state energy conversion mechanism from wasted heat into useful electrical power. Thermoelectric (TE) materials based upon bismuth telluride (BiTe) systems are widely utilized in applications ranging from energy generation to sensing to cooling. There is demand for BiTe materials with high figure of merit (zT) and TEG modules with high conversion efficiency over intermediate temperatures (25°C–250°C). Here we provide fundamental breakthrough in design of BiTe-based TE materials and utilize them to demonstrate modules with outstanding conversion efficiency of 8%, which is 40% higher compared with state-of-the-art commercial modules. The average zT of 1.08 for p-type and 0.84 for n-type bismuth telluride alloys is obtained between 25 and 250°C. The significant enhancement in zT is achieved through compositional and defect engineering in both p- and n-type materials. The high conversion efficiency accelerates the transition of TEGs for waste heat recovery.

INTRODUCTION

It is estimated that ~70% of the energy produced worldwide is rejected into the environment mostly in the form of waste heat (Forman et al., 2016). A sustainable, cost-effective, and efficient way to recover some fraction of the wasted heat would have great impact on overall renewable energy production and in reducing carbon footprint. One of the promising ways to recover thermal energy is through thermoelectric generators (TEGs). TEGs are silent solid-state devices with no moving parts and utilize environmentally sustainable materials (Bell, 2008; Snyder and Toberer, 2008). The challenge with TEGs has been their low conversion efficiency, which is one of the main obstacles in their widespread application. The theoretical conversion efficiency (η_{\max}) of TEGs is expressed by Equation (1) (Goldsmid, 1995):

$$\eta_{\max} = \left(\frac{T_H - T_C}{T_H} \right) \frac{\sqrt{1 + (zT)_{\text{avg}}} - 1}{\sqrt{1 + (zT)_{\text{avg}}} + \left(\frac{T_C}{T_H} \right)} \quad (\text{Equation 1})$$

where T_C and T_H are cold and hot side temperatures, respectively, and $(zT)_{\text{avg}}$ is the average thermoelectric (TE) materials figure-of-merit. zT is a dimensionless materials-dependent component that is defined by Equation (2):

$$zT = \frac{\sigma S^2}{\kappa} T \quad (\text{Equation 2})$$

where σ , S , κ , and T are electrical conductivity, Seebeck coefficient, total thermal conductivity (including electronic [$\kappa_{\text{Electronic}}$], lattice [κ_{Lattice}], and bipolar [κ_{Bipolar}] thermal conductivities), and absolute temperature, respectively (Snyder and Toberer, 2008). The term σS^2 is known as power factor (PF). It is known that high PF is an important factor toward enhancing the output power of a TEG (Liu et al., 2016; He et al., 2016); however, it is not sufficient to improve TEG's conversion efficiency, which is mainly dependent on zT .

In the literature, the primary research focus has been on improving the peak zT , i.e., $(zT)_{\text{peak}}$, by manipulating electron and phonon transport properties through different techniques such as nano-inclusions (Nozariasbmarz et al., 2016; Kang et al., 2020), band gap engineering (Pei et al., 2012; Zhu et al., 2018),

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formation of resonant dopant states (Chen et al., 2017; Tan et al., 2015), energy filtering effect (Liang et al., 2017), all-scale hierarchical architectures (Biswas et al., 2012), and mitigation of lattice strain (Chen et al., 2015). These techniques do not assure high conversion efficiency of TEGs mainly due to the low $(zT)_{avg}$ or high device contact resistance. In general, the efficiency of a TEG can be improved by (1) high $(zT)_{avg}$ of TE materials (Equation 1), (2) large temperature gradient (Equation 1), (3) appropriate TEG design to minimize the heat loss (Rowe and Min, 1996; Kishore et al., 2020), and (4) small electrical and thermal contact resistances at the junction of TE materials and substrate mainly controlled by the quality of contact metallization of the TE materials, device fabrication process, soldering/brazing material, and interconnect electrodes (Bjørk, 2015; Nozariasbmarz et al., 2019a). All these factors should be considered in the design and fabrication of the TEGs with high efficiency. Fabrication of reliable low-resistance electrical contacts between TE legs and headers has been difficult to accomplish in TE device fabrication (Joshi and Poudel, 2016; Feng et al., 2013). At the device level, thermal contact resistance at the TE leg/metal interconnect junction and metal interconnect/ceramic substrate, as well as the thermal conductivity of the ceramic substrate affects the temperature distribution and drop across the TEG (Liu and Bai, 2019). Thus, a comprehensive strategy is required for designing high-efficiency TEGs that comprises materials for TE legs, soldering/brazing, metallization, interconnects, and headers (Kishore et al., 2020). This article addresses these aspects ranging from materials to TE modules. We demonstrate p- and n-type bismuth telluride (BiTe) alloys with high $(zT)_{avg}$ leading to efficient module performance for waste heat recovery application in the temperature range of 25 to 250°C.

RESULTS

Theoretically, the conversion efficiency of TEGs is enhanced by augmented temperature difference (ΔT) and $(zT)_{avg}$ (Figure 1A). In ideal conditions, at a ΔT of 230°C, the η_{max} of a module with $(zT)_{avg}$ equal to 0.8, 1, 1.2, and 1.4 is 7.9%, 9.3%, 10.4%, and 11.5%, respectively. However, there is a deviation between the theoretical and experimental values of the efficiency mainly due to the parasitic losses through the TE legs and junctions. Also, the deviation arises because the actual TE leg temperature is lower than the measured external temperature of hot and cold side headers. Figure 1B shows the schematic of a single couple TEG module investigated in this study. Top and bottom headers are made of aluminum nitride (AlN), which has high thermal conductivity but low electrical conductivity, to efficiently conduct the heat from heater to TEG. The copper (Cu) interconnects provide the series electrical connection. The joining material makes electrical and thermal conduction between legs and headers; and finally, there are p- and n-type TE legs. The sample IDs, compositions, and synthesis process of the TE legs are defined in Table S1 (see Transparent Methods). Type (I) module is constructed using Type (I)-p ($Bi_{0.5}Sb_{1.5}Te_3$) and Type (I)-n ($Bi_2Te_{2.7}Se_{0.3}S_{0.01}$) materials, and Type (II) module is constructed using Type (II)-p ($Bi_{0.4}Sb_{1.6}Te_3$) and Type (II)-n ($Bi_2Te_{2.7}Se_{0.3}S_{0.01}Cu_{0.01}$) materials.

To validate the performance of synthesized materials, single couple modules were fabricated using Type (I) and Type (II) materials (inset of Figure 1C). The performance of our modules is compared with a single couple fabricated using commercial p- and n-type materials acquired from Crystal Ltd. Type (II) module demonstrates 8% efficiency and 2.1 W/cm² power density at $\Delta T = 230^\circ C$, which is among the highest values reported in the literature for BiTe modules (Figures 1C and 1D). The efficiency and power of Type (I) module is found to be 6.7% and 0.92 W/cm², respectively. The efficiency of both modules is ~15% less than theoretical estimation (Figure 1A). Type (II) TEG module (inset of Figures 1C, S1, and S4) demonstrates 40% and 15% higher conversion efficiency compared with the commercial crystalline materials and the best literature value, respectively. A full TEG module comprises 18 couples, i.e., 36 p- and n- TE legs, thus it will exhibit 18× higher power compared with the single couple made using similar p- and n-type legs. Results in Figure 1E clearly demonstrate the quality of the module fabrication process where output power for full TEG module is found to be close to ~18× that of single couple over the wide temperature range.

Figure 2 compares the TE properties of Type (I)-p, Type (II)-p, and commercial p-type BiTe alloys as function of temperature. The TE properties of commercial alloy are shown as a reference (Poudel et al., 2008). The electrical conductivity of all samples (Figure 2A) decreases with temperature due to the reduction of Hall mobility as a result of the electron-phonon scattering at high temperature. The electrical conductivity of Type (II)-p is higher than that of Type (I)-p in all temperature ranges, which is due to the higher carrier concentration (Figures 2B and S2A). The difference between two samples compensates at higher temperatures. Carrier concentration in BiTe alloys is controlled through vacancies and antisite defects, wherein

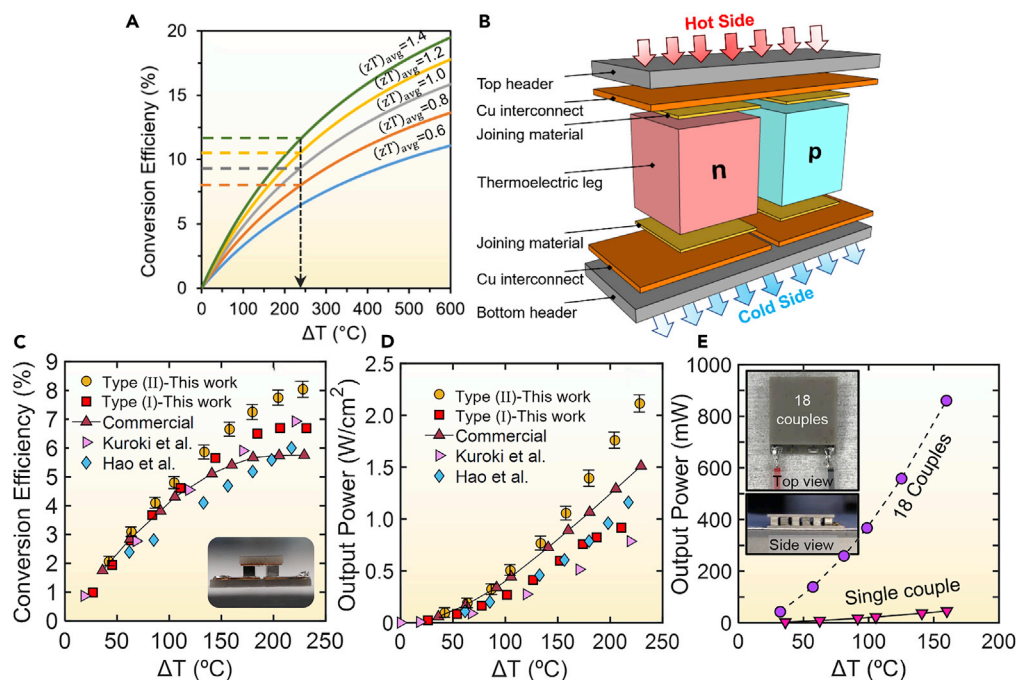


Figure 1. Conversion Efficiency, Output Power, and Components of Customized Single Couple TEG Module

(A) Theoretical conversion efficiency (η_{\max}) of TEGs versus temperature difference (ΔT) for different $(zT)_{\text{avg}}$ values. The black dashed arrow shows $\Delta T = 230^\circ\text{C}$.

(B) Schematic drawing of different components of customized single couple TEG module.

(C) Conversion efficiency of the fabricated BiTe modules compared with commercial and state-of-the-art modules (Kuroki et al., 2014; Hao et al., 2016). The error bar indicates uncertainty of the conversion efficiency measurement. The inset is the actual fabricated single couple TEG module.

(D) Output power density of the fabricated BiTe modules compared with commercial and state-of-the-art modules (Kuroki et al., 2014; Hao et al., 2016). The error bar indicates uncertainty of the output power measurement.

(E) Comparison of the output power of single couple and full module (18 couples). The inset shows top and side views of the full module.

See also Figures S1 and S4 and Table S1.

Bi and Sb vacancies donate 3 holes and Te contributes 2 electrons, Bi on Te-site antisite defect donates one hole, and Te on Bi-site contributes one electron (Stterthwaite and Ure, 1957; Horak et al., 1986).

The Seebeck coefficient of Type (I)-p is higher up to $\sim 200^\circ\text{C}$; after that it converges to similar values as that of Type (II)-p (Figure 2B). At lower temperatures, due to lower carrier concentration in Type (I)-p, the electrical conductivity is lower as well. Higher carrier concentration generally results in lower absolute value of Seebeck coefficient and higher electrical conductivity. Carrier concentration of Type (II)-p is higher than that of Type (I)-p up to 175°C as Type (II)-p has higher doping. This explains why the Seebeck coefficient of Type (II)-p is lower than that of Type (I)-p in this temperature range (Figures 2B and S2A). The PF of Type (II)-p is larger than Type (I)-p over all temperature ranges, which is due to its significantly larger electrical conductivity (Figure 2C). This difference is constant at all temperature ranges. Type (II)-p and Type (I)-p samples have the maximum PF of $47 \mu\text{W}/\text{cmK}^2$ and $34 \mu\text{W}/\text{cmK}^2$, respectively. As shown in Figure 1D, the module fabricated from high-PF materials results in high output power.

The combination of lattice and bipolar thermal conductivity ($\kappa_{\text{Lattice}} + \kappa_{\text{Bipolar}}$) of the samples is approximately similar up to 200°C , and then it deviates at high temperature (Figure 2D). The overall reduction of the total thermal conductivity of Type (II)-p up to 150°C is due to the phonon scattering (Tritt, 2004), and it increases at higher temperatures due to the bipolar thermal conduction (Figure 2E). However, in Type (I)-p, the bipolar effect has shifted to room temperature and the total thermal conductivity monotonically increases with temperature. The notable drop in thermal conductivity of Type (I)-p is due to the reduction in electronic part of thermal conductivity. This agrees with higher Seebeck coefficient, i.e., reduced

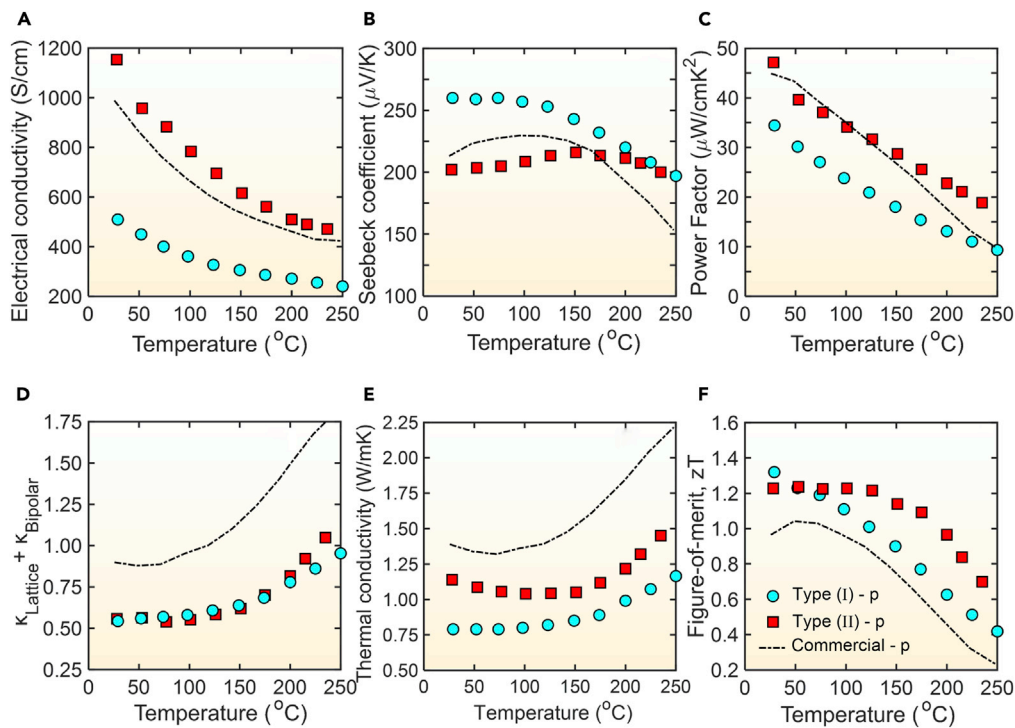


Figure 2. Temperature-Dependent Thermoelectric Properties of the Synthesized p-Type Materials

(A) Electrical conductivity.

(B) Seebeck coefficient.

(C) Power factor (PF).

(D) Lattice + bipolar thermal conductivity.

(E) Total thermal conductivity.

(F) zT for Type (I)-p, Type (II)-p, and commercial p-type BiTe alloys. The TE properties of commercial p-type alloy are shown for comparison.

See also [Figure S2A](#).

dopant concentration in Type (I)-p. The thermal conductivity of both samples is less than that of commercial p-type alloy in all temperature ranges.

[Figure 2F](#) shows the comparison of the zT values versus temperature. Above 50°C, zT of Type (II)-p is higher than that of Type (I)-p, and only at room temperature, Type (I)-p has higher zT. The $(zT)_{\text{peak}}$ of Type (I)-p and Type (II)-p is 1.3 and 1.25, respectively. The magnitude of $zT \sim 1.2$ is maintained in a broad temperature range up to 150°C in Type (II)-p resulting in high $(zT)_{\text{avg}}$. Better TE properties above room temperature make this material suitable for low-grade waste heat recovery application, such as energy harvesting from hot-water pipes ([Kishore et al., 2020](#)). Type (I)-p with higher $(zT)_{\text{peak}}$ and lower thermal conductivity at room temperature is appropriate for specific applications that involve high heat sink/source contact resistance such as body heat harvesting ([Nozariasbmarz et al., 2019a; 2020a, 2020b; Suarez et al., 2016](#)) and body cooling ([Kishore et al., 2019](#)).

[Figure 3](#) compares the TE properties of the synthesized Type (I)-n and Type (II)-n BiTe alloys as function of temperature. The TE properties of a commercial n-type alloy are also shown for comparison ([Hu et al., 2016](#)). Similar to p-type samples, the electrical conductivity of both n-type samples ([Figure 3A](#)) decreases with temperature due to the reduction of Hall mobility as a result of the electron-phonon scattering at high temperatures. The electrical conductivity of Type (II)-n is higher than that of Type (I)-n in all temperature ranges ([Figure 3A](#)) due to the higher carrier concentration in Type (II)-n as shown in [Figure S2B](#). This confirms the donor behavior of Cu dopant. In n-type BiTe alloys, Se enhances Te vacancies, resulting in higher electronic contribution. Cu atoms can also enter the interstitial sites among four Te atoms, resulting in lattice expansion along $\langle 001 \rangle$ direction ([Liu et al., 2011](#)). Below 200°C, Type (I)-n has higher absolute value of Seebeck coefficient than Type (II)-n. Beyond 200°C, their values converge ([Figure 3B](#)). The Seebeck

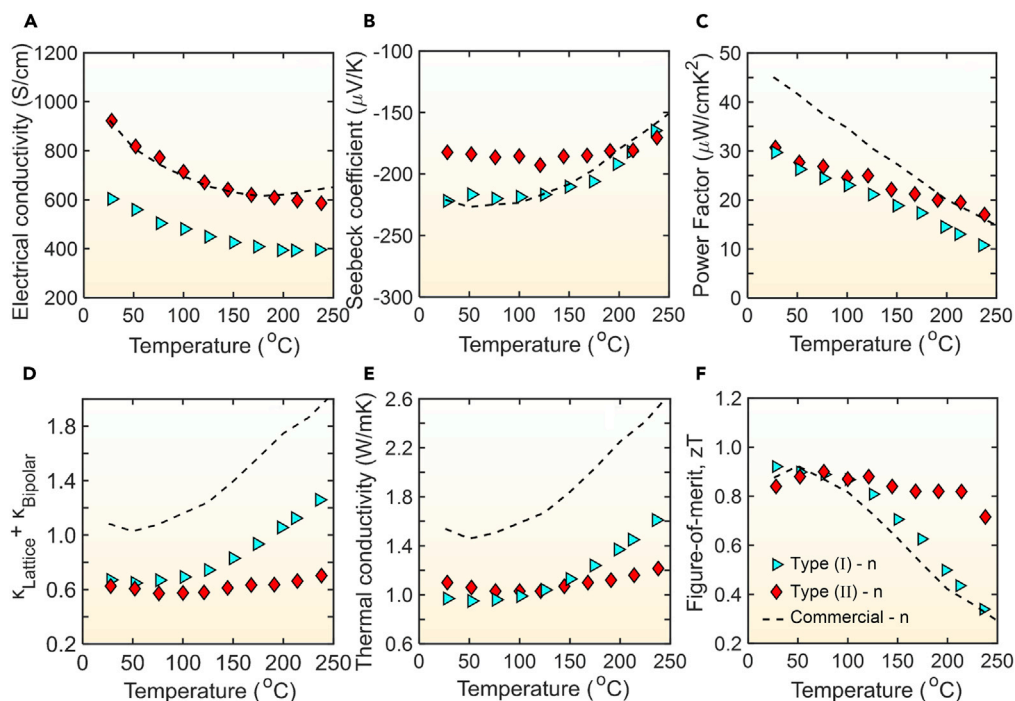


Figure 3. Temperature-Dependent Thermoelectric Properties of the Synthesized n-Type Materials

(A) Electrical conductivity.

(B) Seebeck coefficient.

(C) Power factor (PF).

(D) Lattice + bipolar thermal conductivity.

(E) Total thermal conductivity.

(F) zT for Type (I)-n, Type (II)-n, and commercial n-type BiTe alloys. The TE properties of commercial n-type alloy are shown for comparison.

See also [Figure S2B](#).

coefficient of Type (II)-n barely changes with temperature. Carrier concentration of Type (II)-n is higher than Type (I)-n up to 175°C. Type (II)-n has higher dopant concentration, which results in lower absolute value of Seebeck coefficient compared to Type (I)-n in the temperature range considered here ([Figures 3B](#) and [S2B](#)).

Both n-type samples have almost similar PF up to 100°C. Above 100°C, Type (II)-n has larger PF, mainly due to the higher electrical conductivity at elevated temperatures ([Figure 3C](#)). The maximum PF of both n-type samples is $\sim 30 \mu\text{W}/\text{cmK}^2$, which is smaller than those of commercial n-type and all p-type samples. The magnitude of $\kappa_{\text{Lattice}} + \kappa_{\text{Bipolar}}$ for the synthesized samples is similar at room temperature, and then it deviates at higher temperatures due to the shifting of bipolar conduction to lower temperatures in Type (I)-n ([Figure 3D](#)). Addition of dopants shifts the onset temperature for bipolar effect to higher temperature by preventing the generation of minority carriers. The low κ_{Lattice} of Type (II)-n is mainly due to the solid solution alloying with sulfur and copper, which results in thermal conductivity reduction through point defect mechanism that induces localized strains and mass fluctuations ([Liu et al., 2013](#); [Hu et al., 2014](#)). As shown in [Figure 3E](#), the total thermal conductivity of the synthesized samples is lower than that of commercial n-type alloy in all temperature ranges. The thermal conductivity of Type (I)-n is smaller than that of Type (II)-n up to 125°C, after which it rapidly increases due to the strong bipolar effect. Although dopants are mainly used to tune the Fermi level by optimizing the carrier concentration, the alloying elements in Type (II)-n provide atomic mass and size contrast compared with Bi-Te-Se matrix alloy, resulting in smaller thermal conductivity at high temperature.

[Figure 3F](#) demonstrates zT comparison of n-type samples versus temperature. Type (I)-n has higher zT up to 75°C due to the smaller thermal conductivity in this temperature range. Above 100°C, zT of Type (II)-n is higher due to the high PF and low thermal conductivity. The $(zT)_{\text{peak}}$ of Type (I)-n and Type (II)-n is 0.92 and 0.9, respectively. In Type (II)-n, $zT \sim 0.9$ is maintained in a broad temperature range from 50°C to

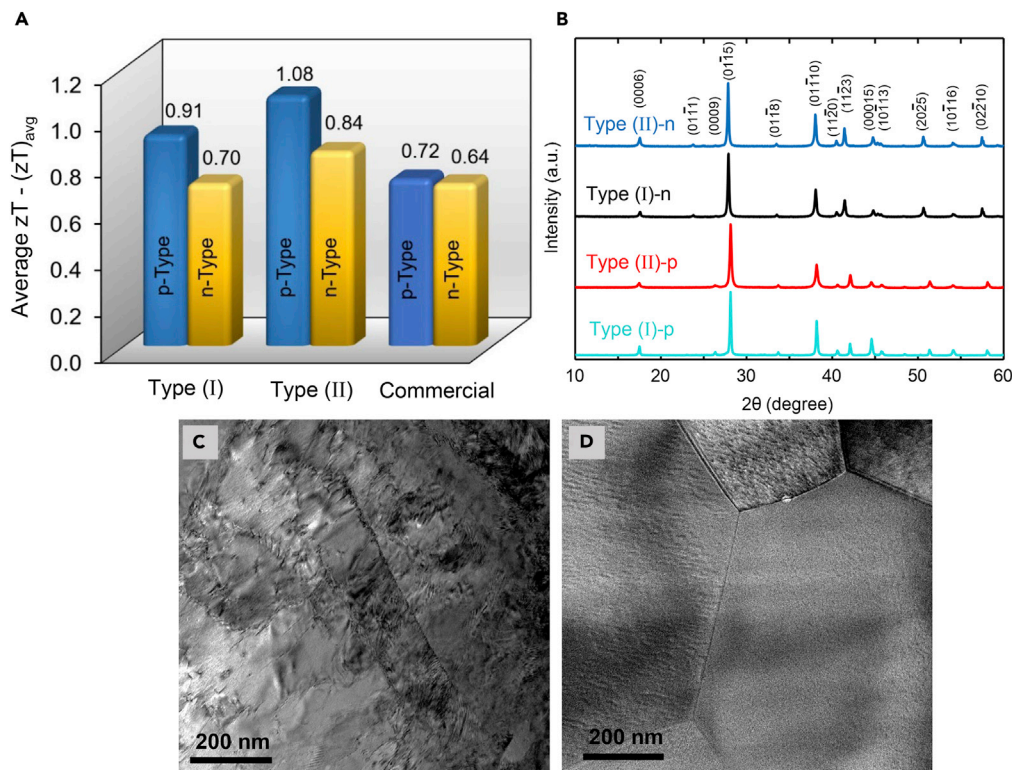


Figure 4. $(zT)_{avg}$, Phase Identification, and Microstructure of the Synthesized Materials

(A) Comparison of the $(zT)_{avg}$ of the synthesized Type (I) and Type (II) materials along with commercial materials. (B) XRD patterns of Type (I)-p, Type (II)-p, Type (I)-n, and Type (II)-n materials. (C) TEM image of Type (II)-p material. (D) TEM image of Type (II)-n material. Enlarged view of TEM images are shown in Figure S3.

150°C, which results in high $(zT)_{avg}$ in this material. Type (I)-n has lower thermal conductivity and higher Seebeck coefficient and zT at room temperature, which makes this material appropriate for applications that require large contact resistance between TE and heat source/sink at room temperature such as wearable electronics (Nozariasbmarz et al., 2019a, 2019b; 2020a, 2020b). However, comparatively Type (I)-n is not the best candidate for power generation at high temperature due to its zT degradation. Instead, Type (II)-n is a more suitable candidate for TE power generation due to its high performance over the entire temperature range.

The magnitude of $(zT)_{avg}$ for Type (II)-p and Type (II)-n materials is found to be 1.08 and 0.84, respectively (Figure 4A), which is 50% and 30% higher than that of commercial materials and among the best reported $(zT)_{avg}$ values for BiTe alloys. It should be noted that compared with Type (I) materials that have higher $(zT)_{peak}$, Type (II) materials have ~20% higher $(zT)_{avg}$, which results in 20% improvement in device conversion efficiency. These results confirm the importance of search for TE materials with high $(zT)_{avg}$ to achieve elevated efficiencies in TEGs. Figure 4B shows the comparison of the X-ray diffraction (XRD) patterns of Type (I)-p, Type (II)-p, Type (I)-n, and Type (II)-n materials. All materials are pure, and the XRD patterns are approximately similar except for minor peak shifting due to the p- or n-type doping. Transmission electron microscopic (TEM) image of Type (II)-p reveals microstructure consisting of high dislocation density (Figures 4C and S3A). The arrays of dislocations are shown by yellow arrows in Figure S3A. In p-type BiTe alloys, in addition to point defects, dislocations also contribute to transport properties by suppressing thermal conductivity (Poudel et al., 2008; Kim et al., 2015). TEM image of Type (II)-n shows a dislocation-free microstructure with sharp grain boundaries (Figures 4D and S3B). As mentioned earlier, one of the mechanisms for zT enhancement in n-type BiTe is through increase of point defect density, which is created through alloying elements, i.e., sulfur and copper. For example, Cu atom increases the distance between two BiTe layers that are weakly bonded by van der Waals force (Liu et al., 2011; Bludaska et al., 2004). The fringes on the surface of the grains in Type (II)-n are due to the lattice distortion and strain (Liu et al., 2011).

DISCUSSION

We report synthesis of p- and n-type BiTe materials and utilize them to demonstrate high-performance TEG modules for waste heat recovery application. Both p- and n-type BiTe alloys with high average and peak zT were synthesized via a combination of defect engineering and substitutional alloying. A record 8% conversion efficiency and 2.1 W/cm² power density in BiTe alloy-based modules was achieved. The TEG modules with high average zT-based BiTe alloys exhibit 40% higher efficiency compared with the commercial crystalline materials and 15% higher efficiency than the values reported in literature. This study reveals that high average zT and module design variables are critical factors in enhancing the efficiency of TEGs.

Limitations of the Study

As literature and commercial thermoelectric generators have used different sizes of TE modules and TE leg sizes, accurate comparison of all different modules is limited. In addition, whereas efficiency measurement of a single couple module is relatively simple and can be standardized, measuring the efficiency of large-size modules is challenging mostly due to the inaccurate heat flow measurement.

Resource Availability

Lead Contact

Further information and requests for resources should be directed to and will be fulfilled by the Lead Contact, Amin Nozariasbmarz (aln192@psu.edu).

Materials Availability

This study did not generate new unique materials.

Data and Code Availability

Data in this study will be provided upon request from the corresponding author.

METHODS

All methods can be found in the accompanying [Transparent Methods supplemental file](#).

SUPPLEMENTAL INFORMATION

Supplemental Information can be found online at <https://doi.org/10.1016/j.isci.2020.101340>.

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AUTHOR CONTRIBUTIONS

A.N. and B.P. conceived the idea; A.N. and B.P. designed and conducted the experiments; H.Z. performed the XRD measurements; S.P. supervised the research; All authors contributed to the discussions and writing of the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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Supplemental Information

Bismuth Telluride Thermoelectrics with 8% Module Efficiency for Waste Heat Recovery Application

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SUPPLEMENTAL DATA ITEMS

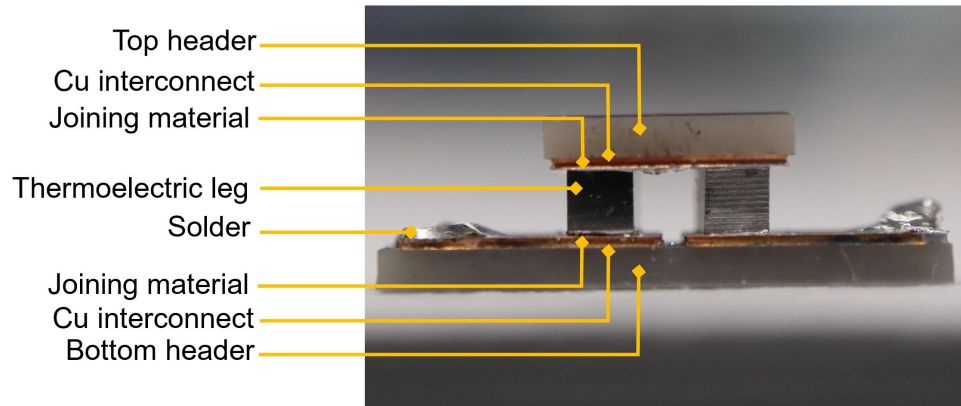


Figure S1. Customized Single Couple TEG Module with Its Components. Related to Figure 1.

Fabricated single couple TEG module. The module consists of top and bottom AlN headers, copper interconnects, joining material and thermoelectric legs.

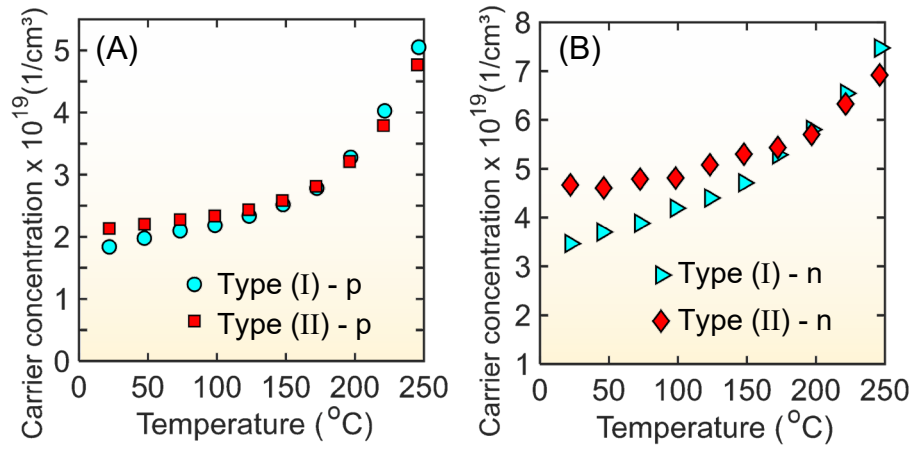


Figure S2. Carrier Concentration of P- and N-type Materials. Related to Figure 2 and Figure 3.

Temperature dependent carrier concentration of synthesized (A) p-type and (B) n-type BiTe alloys.

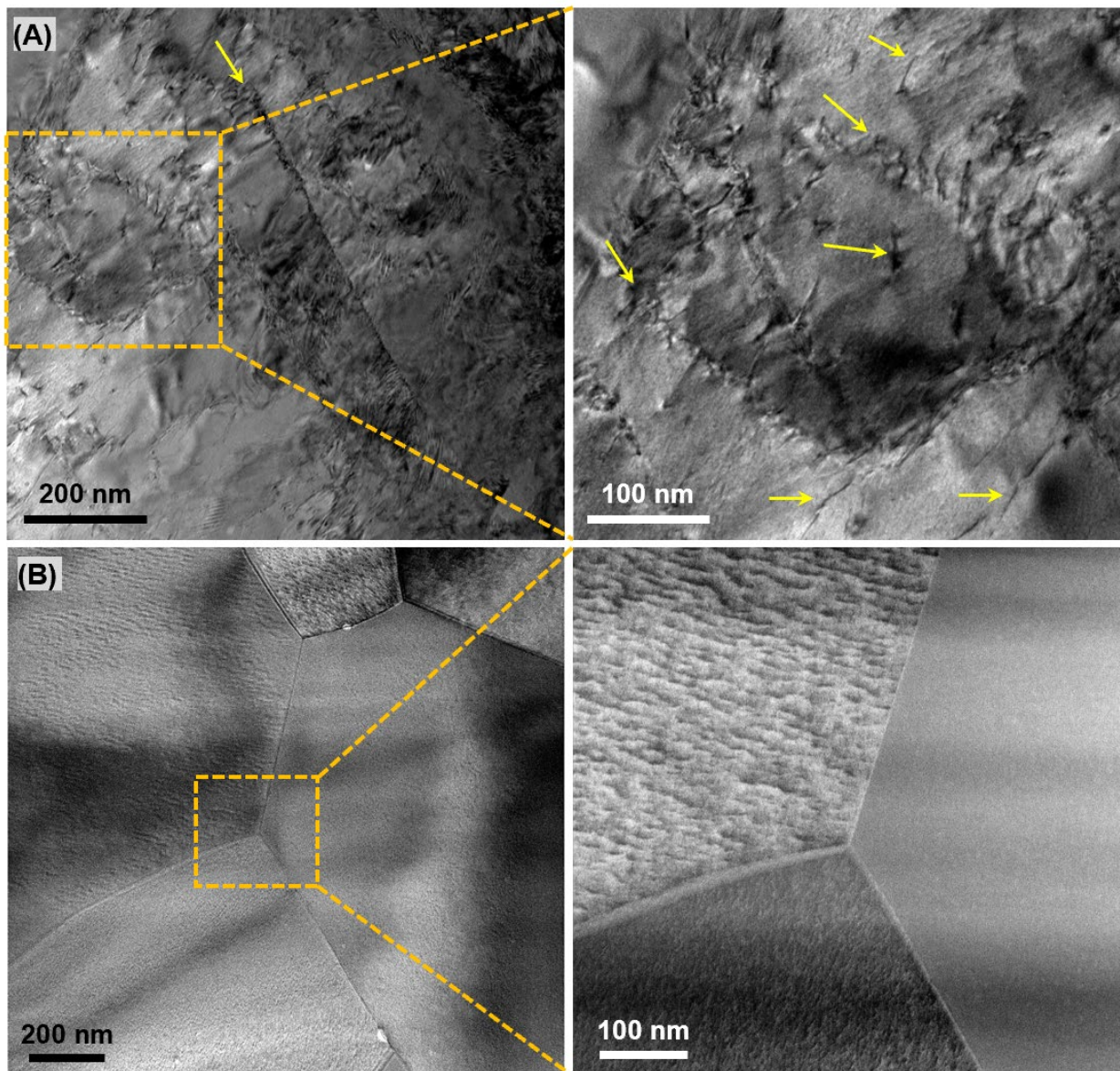


Figure S3. Transmission Electron Microscopy (TEM) Images. Related to Figure 4.

TEM image of (A) Type (II)-p, and (B) Type (II)-n materials. The enlarged view of p-type material includes numerous single and arrays of dislocations dispersed all over the sample indicated by yellow arrows. n-type material is dislocation free and the surface fringes are due to the lattice distortion as a result of Cu doping.

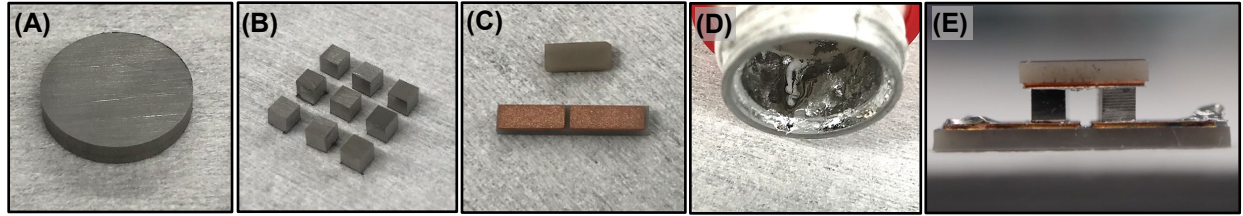


Figure S4. Module Fabrication Process. Related to Figure 1.

(A) Synthesized bismuth telluride disk by SPS, (B) diced legs from p- and n-type disks, (C) top and bottom DBC headers with copper interconnect, (D) liquid metal, and (E) fabricated single couple TEG module.

Table S1. List of sample ID, compositions, synthesis process and SPS condition of synthesized materials, Related to Figure 1, Figure 2, and Figure 3

Sample ID	Type	Composition	Powder Synthesis Process	SPS Temperature (°C) / Soaking Time (min)
Type (I)-p	p-type	$\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3 + 10\% \text{Extra Te}$	Melting + Ball Milling	520 / 2
Type (II)-p	p-type	$\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$	Ingot + Ball Milling	520 / 2
Type (I)-n	n-type	$\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}\text{S}_{0.01}$	Ball Milling	450 / 2
Type (II)-n	n-type	$\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}\text{S}_{0.01}\text{Cu}_{0.01}$	Ball Milling	450 / 2

TRANSPARENT METHODS

Materials Synthesis

High-purity elements of Bi (99.9%, pieces), Sb (99.9%, shots), Te (99.9%, lumps), Se (99.9%, pellets), S (99.9%, flakes), and Cu (99.999%, powder) were used to fabricate BiTe alloys. p- and n-type nanostructured BiTe alloys were separately synthesized in powder form according to the stoichiometric ratio of the raw elements listed in Table S1. The ingot of Type (I)-p was prepared by melting the raw elements in a sealed quartz tube for 24 hours at 1000°C inside a conventional furnace and subsequent quenching. The ingot was then loaded into a hardened steel vial along with steel balls with ball to powder ratio of 1:1 and ball milled for 3 hours using SPEX mixer/mill (Model 8000D, SPEX SamplePrep) and clamp speed of 1060 cycles per minute to obtain homogeneous powder. Nanostructured powder of Type (II)-p was prepared by pulverizing and ball milling a commercial p-type ingot for 3 hours using the same equipment. In order to prepare n-type powders, the elements for each composition were weighted and loaded into a hardened steel vial along with steel balls, with ball to powder ratio of 1:1. The vial was sealed inside an argon filled glovebox and the loads were subsequently milled for 13 hours using the same equipment.

The synthesized p- and n-type alloys were then collected and consolidated in a cylindrical graphite die with an inner diameter of 12.7 mm at different temperatures using spark plasma sintering (SPS) at 520°C (for p-type) and 450°C (for n-type) under constant 30 MPa pressure for 2 minutes, to obtain the samples with 12.7 mm diameter and ~2 mm height. Two graphite foils were put on top and bottom of powder to protect samples from sticking to graphite rods. The temperature was monitored using a K-type thermocouple placed at the center of the die, close to the middle of the sample. The sample IDs, compositions, powder synthesis process, SPS temperature and soaking time of the synthesized alloys are listed in Table S1. Type (I) module is made using Type (I)-p and Type (I)-n materials, and Type (II) module is made using Type (II)-p and Type (II)-n materials. It should be noted that the reason of naming the samples as Type (I) and Type (II) is due to the similar application temperature range of each type.

Structural Characterization

The phase identification and purity of the synthesized samples were characterized by X-ray diffraction (XRD) using PANalytical Empyrean with Cu-K α radiation in 2 θ angle range of 10-60°. The microstructure of the samples was investigated by transmission electron microscope (TEM) using a Talos F200X at 200 kV. The samples for TEM were prepared by focused-ion beam (FIB) technique.

Transport Properties Characterization

The thermal diffusivity (D) of the synthesized disks with 12.7 mm diameter and 2 mm thickness was measured using an LFA-467 HT HyperFlash[®] instrument from room temperature to 250°C. Specific heat capacity (C_p) was measured using differential scanning calorimeter (Netzsch DSC 214 Polyma). The thermal conductivity (κ) of the samples was then calculated from the relationship $\kappa = \rho DC_p$, where ρ is the mass density of the samples measured using Archimedes' principle. After thermal conductivity measurement, the sintered disks were then cut into rectangular 2 mm \times 2 mm \times 12.4 mm bars for electrical conductivity and Seebeck coefficient measurement. The electrical conductivity and Seebeck coefficient were simultaneously measured from room temperature to 250°C using a commercially available ULVAC-RIKO ZEM-3 system. In order to check the anisotropy of the transport properties, a sample with 12.7 mm diameter and 12.7 mm height was synthesized and measured in both perpendicular and parallel to the pressing direction. The properties differ less than 5% in two directions. Carrier concentration was measured using a Lakeshore-8400 series system from room temperature to 250°C. Data was obtained over magnetic fields up to 1.0 T, with a sample current excitation of 200 mA rms.

Thermoelectric Generator (TEG) Module Fabrication

The unicouple fabrication process is shown in Figure S4. The sintered n- and p-type BiTe disks were diced into 1.8 mm \times 1.8 mm \times 1.92 mm legs using a wire saw (Figure S4-B). The legs were connected to top and bottom substrates (Figure S4-C) using GaSn eutectic liquid metal to provide electrical and thermal contact at the junction of thermoelectric leg/header (Figure S4-D).

Module Characterization and Testing

The output power and conversion efficiency of the single couple TEGs were simultaneously measured under vacuum condition from room temperature to 260°C using a customized efficiency measurement system (Nozariasbmarz et al., 2019). The hot side temperature was precisely controlled by a heater that provides constant heat flow (Q_{in}) to the top side of the module. TEG converts a portion of this heat into output power (P_{out}) and rejects the rest (Q_{out}) into the Q-meter which is connected to a water-cooled heatsink (cold side) with constant temperature of ~20°C. The open circuit voltage (V_{oc}) and device voltage (V_d) were recorded at a certain current using a voltmeter (KEITHLEY) and a power supply (KEITHLEY 2200-20-5). Using this information, internal resistance (R_i) and P_{out} were then calculated. The temperatures of Q-meter, hot and cold side were monitored using K-type thermocouples. The system was calibrated thoroughly to minimize the heat loss. The efficiency (η) of the TEG is obtained by equation (S1):

$$\eta = \frac{P_{out}}{Q_{in}} = \frac{P_{out}}{P_{out} + Q_{out}} \quad (S1)$$

where $P_{out} = \frac{V_{oc}^2}{4R_i}$, and according to Fourier's law of heat conduction (Sobota, 2014), $Q_{out} = \kappa A \left(\frac{dT}{dx} \right)$, where κ is the thermal conductivity of the Q-meter (here is brass), A is the cross-section area of the Q-meter, and $\frac{dT}{dx}$ is the temperature gradient along the Q-meter which is measured by several thermocouples at specific distances. The uncertainty of the power and efficiency measurement is $\pm 5\%$. The output power of the full module was measured in air from room temperature to 180°C using a customized system with similar V_{oc} , V_d and R_i measurement setup. The hot side temperature was controlled by a heater and the cold side temperature was maintained at 20°C using house water cooling circulation. The hot and cold side temperatures were precisely monitored using K-type thermocouples.

Supplemental References

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