# Thermoelectric energy conversion using nanostructured materials

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## **ABSTRACT**

High performance thermoelectric materials in a wide range of temperatures are essential to broaden the application spectrum of thermoelectric devices. This paper presents experiments on the power and efficiency characteristics of low-and mid-temperature thermoelectric materials. We show that as long as an appreciable temperature difference can be created over a short thermoelectric leg, good power output can be achieved. For a mid-temperature n-type doped skutterudite material an efficiency of over 11% at a temperature difference of 600 °C could be achieved. Besides the improvement of thermoelectric materials, device optimization is a crucial factor for efficient heat-to-electric power conversion and one of the key challenges is how to create a large temperature across a thermoelectric generator especially in the case of a dilute incident heat flux. For the solar application of thermoelectrics we investigated the concept of large thermal heat flux concentration to optimize the operating temperature for highest solar thermoelectric generator efficiency. A solar-to-electric power conversion efficiency of ~5% could be demonstrated. Solar thermoelectric generators with a large thermal concentration which minimizes the amount of thermoelectric nanostrucutured bulk material shows great potential to enable cost-effective electrical power generation from the sun.

#### INTRODUCTION

The Seebeck effect can be exploited to generate power from a temperature difference. The efficiency of thermoelectric power generation systems depends on the material-specific thermoelectric figure of merit, the heat source and sink temperatures, and the heat transfer into and out of the devices. The efficiency of ideal thermoelectric devices  $(\eta_{te})$  is determined by the operating temperatures and the materials' dimensionless figure of merit (ZT), defined as  $ZT = (S^2\sigma/k)T$ , where S,  $\sigma$ , k, and T are the Seebeck coefficient, electrical conductivity, thermal conductivity, and absolute temperature, respectively<sup>1,2</sup>. The device efficiency can be expressed as

$$\eta_{te} = \frac{T_h - T_c}{T_h} \frac{\sqrt{1 + (ZT)_M} - 1}{\sqrt{1 + (ZT)_M} + \frac{T_c}{T_h}} \tag{1}$$

where  $T_c$  is the cold-side temperature,  $T_h$  the hot-side temperature, and  $(ZT)_M$  the effective ZT of the thermoelectric materials between  $T_c$  and  $T_h$ . According to Eq. (1), an efficiency of approximately 8.6% can be reached by imposing a temperature difference of 200 °C across an ideal thermoelectric device with  $(ZT)_M = 1$  and  $T_c = 20$  °C. In recent years, significant progress has been made on improving thermoelectric materials.<sup>3-8</sup>

## 2. EXPERIMENTAL PERFORMANCE DEMONSTRATION OF MATERIALS

The determination of materials' figure merit requires the characterization of their properties including the Seebeck coefficient, electrical and thermal conductivity as a function of temperature. Measurements of these properties usually have uncertainties and hence it is desirable to test device performance as a cross-check for materials property characterization and a pathway for real world application. Actual device performance, however, depends not only on the

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Proc. of SPIE Vol. 8031 80311J-1

figure of merit, but also has various parasitic losses such as thermal and electrical contact resistances. In this section we discuss some experimental results on devices using low- and mid-temperature nanostructured materials we have developed<sup>5</sup>.

#### 2.1 LOW-TEMPERATURE MATERIALS

As long as a temperature difference can be established across a thermoelectric device, some of the transported heat is converted to electric power. Figure 1(a) shows a thermoelectric power testing rig for one pair of p-type (positive Seebeck coefficient) and n-type (negative Seebeck coefficient) thermoelectric legs with dimensions of  $\sim 1.5 \times 1.5 \times 1.5$  mm³. With a temperature difference of 180 K across the thermoelectric unicouple, a power of 80 mW is generated (Fig. 1(b)). Figure 1(b) also shows that thermoelectric generators with typical leg sizes limited by bulk manufacturing processes are high current and low voltage devices because the Seebeck coefficient of typical thermoelectric materials is  $\sim 200 \ \mu\text{V/K}$ . Imposing a temperature difference of 180 K across one thermoelectric unicouple yields an open-circuit voltage of  $\sim 70 \ \text{mV}$ . Hence, in a practical device, many p-type and n-type legs are connected electrically in series and thermally in parallel, as shown in Fig. 1(c). A significantly larger number density (per unit area) of thermoelectric unicouples can be incorporated in a microfabricated device, leading to a higher voltage output and lower device current that is more easily matched to an external load.

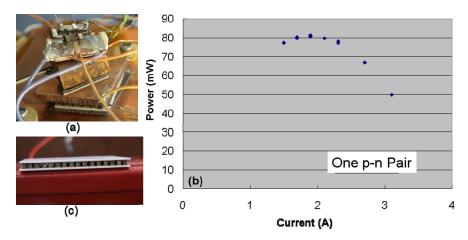


Figure 1: (a) Platform for testing one pair of p- and n-type legs, (b) power output from the unicouple, and (c) a thermoelectric device with many unicouples connected electrically in series and thermally in parallel.

## 2.2 MID-TEMPEATURE MATERIALS

Thermoelectric devices are all-solid state heat engines, and hence, are subjected to the Carnot limit (Eq. 1). Various heat sources at different temperatures, call for thermoelectric materials spanning over a wide temperature ranges. Figure 2 shows experimentally measured efficiencies of skutterudite-based materials. Such materials have potential applications in mid-temperature waste heat recovery, such as from vehicle exhaust gas streams. Our skutterudite materials have demonstrated conversion efficiencies of 11% at 600 °C with the cold side maintained at a temperature close to 50 °C (Fig. 2). Modeling based on measured thermoelectric properties suggests that even higher efficiencies are possible. In practice, electrical and thermal contact resistances, and the thermal expansion coefficient mismatch between materials can cause a reduction in device performance below the ideal efficiency expressed by Eq. (1).

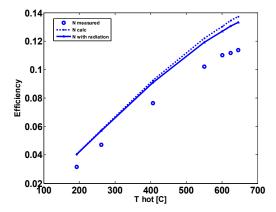


Figure 2: Experimentally measured single-leg efficiency of an n-type skutterudite material with a cold-side temperature at 50°C.

## 3. SOLAR APPLICATION OF THERMOELECTRICS

Besides the importance of the properties of thermoelectric materials for the device performance, the key for the application of thermoelectric generators is to establish a temperature difference across the device. Considering heat conduction only, the heat flux across a thermoelectric element with a length L and temperature difference  $\Delta T$  is given by  $q = k\Delta T/L$ . For L = 1 mm and thermal conductivity, k = 1 Wm<sup>-1</sup>K<sup>-1</sup>, and  $\Delta T = 100$  K, the heat flux is  $10^5$  W/m<sup>2</sup>. Such high heat fluxes may result in large temperature drops outside the actual thermoelectric generator leading to a significant difference between the heat source/sink and thermoelectric junction temperatures. Additionally, creating large heat fluxes from a heat source only providing small heat fluxes can also be a very challenging task. Recently, we have exploited the idea of thermal concentration to develop a flat-panel solar thermoelectric generator with ~5% solar to electric power conversion efficiency (Fig. 3(a)&(b)). Thermal concentration uses heat conduction to concentrate the dilute heat flux from the sun (~1000 W/m<sup>2</sup>) to match the heat flux of thermoelectric devices, leading to a significant reduction in the materials required to fabricate solar thermoelectric generators.

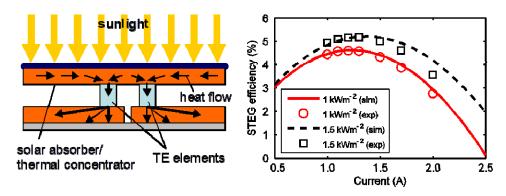


Figure 3: Performance of a solar thermoelectric generator (a) illustration of the concept of using thermal concentration to match heat flux through the device, and (b) efficiency measured at two different solar fluxes.

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## References

[1] Goldsmid, H. J., Thermoelectric Refrigeration. Plenum, New York, (1964).

- [8] Minnich, A., Dresselhaus, M. S., Ren, Z. F., Chen, G., "Bulk nanostructured thermoelectric materials: current research and future prospects", Energy & Environmental Science, 2, 466-479, (2009).
- [9] Boettner, H., "Micropelt Miniaturised Thermoelectric Devices: Small Size, High Cooling Power Densities, Short Response Time", Proceedings of 24th ICT, (2005).
- [10] Yang, J., Hao, Q., Wang, H., Lan, Y. C., He, Q. Y., et al., "Solubility Study of Yb in n-type Skutterudites Yb<sub>x</sub>Co<sub>4</sub>Sb<sub>12</sub> and Their Enhanced Thermoelectric Properties", Phys. Rev. B, 80, 115329 (2009).
- [11] Kraemer, D., Poudel, B., Feng, H.-P., Caylor, J. C., Yu, B., et al., "High-performance flat-panel solar thermoelectric generators with large thermal concentration", Nature Materials (2011).

Proc. of SPIE Vol. 8031 80311J-4

<sup>[2]</sup> Rowe, D. M. Thermoelectrics Handbook Nano to Macro, CRC Taylor & Francis, Boca Raton, (2006).

<sup>[3]</sup> Hsu, K. F., Loo, S., Guo, F., Chen, W., Dyck, J. S., et al., "Cubic AgPb(m)SbTe(2+m): bulk thermoelectric materials with high figure of merit", Science, 303, 818-821 (2004).

<sup>[4]</sup> Dresselhaus, M. S., Chen, G., Tang, M. Y., Yang, R. G., Lee, H., et al., "New Directions for Low-Dimensional Thermoelectric Materials", Advanced Materials, 19, 1043-1053, (2007).

<sup>[5]</sup> Poudel, B., Hao, Q., Ma, Y., Lan, Y., Minnich, A., et al., "High-Thermoelectric Performance of Nanostructured Bismuth Antimony Telluride Bulk Alloys", Science, 320, 634-638 (2008).

<sup>[6]</sup> Heremans, J. P., Jovovic, V., Toberer, E. S., Saramat, A., Kurosaki, K., et al., "Enhancement of Thermoelectric Efficiency in PbTe by Distortion of the Electronic Density of States", Science, 321, 554-557, (2008).

<sup>[7]</sup> Tritt, T. M., Subramanian, M. A., "Thermoelectric Materials, Phenomena, and Applications: A Bird's Eye View", MRS Bulletin, 31, 188-198, (2006).