Beating the maximum cooling limit with graded thermoelectric materials

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The maximum cooling temperature of a uniform thermoelectric material is limited by its nondimensional figure of merit $ZT$. Conventionally cascaded stages or materials with a larger figure of merit are needed to obtain a higher cooling temperature. In this letter, the authors prove that the maximum cooling in an optimally graded single-stage device could be much larger than the value predicted based on the highest local $ZT$ of the material. The cooling enhancement is attributed to the redistribution of the Joule heating and Peltier cooling profiles along the current and heat flow directions. © 2006 American Institute of Physics. [DOI: 10.1063/1.2396895]

The maximum cooling temperature is one of the performance parameters for a thermoelectric module. Excluding nonideal parasitic effects such as electrical and thermal contact resistances, the maximum cooling is equal to $\frac{1}{2} ZT^2$, where $T$ is the absolute temperature at the cold side and $Z$ is the material thermoelectric figure of merit. The nondimensional figure of merit is defined as $ZT = (S^2 \sigma / k) T$, where $S$ is the Seebeck coefficient, and $\sigma$ and $k$ are the electrical and thermal conductivities, respectively. Since a large electrical conductivity for a solid state material is usually accompanied with a small Seebeck coefficient and a large electronic contribution to thermal conductivity, it is very difficult to find a thermoelectric material with a large $ZT$ value. The largest $ZT$ value for commercial bulk materials, based on Bi$_2$Te$_3$ alloys, is around 1 at room temperature. Thus the highest theoretical cooling is ~72 K. To achieve higher cooling temperatures, one needs to use cascaded stages. Heat spreaders should be applied between adjacent stages to reduce the heat load density of the subsequent stage. Each stage can be optimized separately to its optimal working current. However, the extra thermal resistance of the packaging and heat spreading materials in between cascaded stages will reduce the total cooling temperature.

Efforts have been made to increase the maximum cooling temperature by engineering the Peltier cooling and Joule heating profiles in a single-stage three-dimensional thermoelectric device. The cooling enhancement by ~25% was predicted. This is due to three-dimensional heat and current spreading. But it could only be achieved with an array of coolers to control local current at each location. Most generally, it has been proved that the maximum cooling of a single element thermoelectric material cannot be improved by changing its geometry. In this letter, we increase the maximum cooling of a single thermoelectric element by using graded thermoelectric materials in a one-dimensional current and heat flux configuration. It should be noted that the grading of the thermoelectric properties here is different from the conventional “functionally graded thermoelectric material (FGM).” FGM is based on the fact that the material properties change with temperature and thus one should try to maximize the local $ZT$ values by changing the material type or composition based on the local temperature. This is most useful when the device is under a very large temperature gradient. The numerical simulation of an inhomoge-
cooling temperatures in the following study. In this way, we
can neglect the temperature variation in the materials and its
effects on the local Peltier cooling power and physical
properties of the material.

We first tested two staircase Seebeck profiles plotted in
Fig. 1. The left-hand side of the first section is thermally
insulated and the right-hand side of the second section is
connected to a heat sink. In case 1, the first section of the
staircase material has the Seebeck coefficient $S_1$, the
electrical conductivity $\sigma_1$, and the section length $L_1$. The optimal
current density to achieve the largest cooling temperature for
this section is $I_{\text{opt}} = S_1 T \sigma_1 / L_1$, in which half of the Joule
heating produced in the first section cancels half of the
Peltier cooling at the left junction. If we put a second section
at the heating side and if we want to have half of the Joule
heating of the first section to be canceled by half of the
Peltier cooling at each interface, we have

$$\Delta T = \frac{1}{2} ZT^2 \sum_{n=1}^{N} \frac{1}{n^2}.$$  

which is larger than the maximum cooling temperature of a
single section. It asymptotically becomes $\frac{1}{2} ZT^2 (\pi^2/6 - 1/N
+ 1/2N^2)$ at large $N$ and has an upper limit when $N$ goes
to infinity. $I_{\text{opt}}$ is not actually optimized for the multiple-section
device, which has a slightly higher maximum cooling
temperature at smaller current values than $I_{\text{opt}}$. However, it is
obvious that we can surpass the maximum cooling limit of $\frac{1}{2}
ZT^2$ for a uniform single section thermoelectric material by
using multiple cascaded sections with the same $ZT$. The
above calculation of the maximum cooling temperature tries
to motivate the rational for choosing the Seebeck profile
and the length of each section. Given that the Peltier effect is an
interface source of cooling or heating and Joule heating is a
volumetric source of heating, one can solve the differential
heat equation directly and obtain Eq. (2) without the need to
use the equivalent circuit analogy.

In a different realization of the staircase Seebeck profile
(case 2), we want half of the Peltier cooling power at the
interfaces of adjacent sections to be canceled by half of the
Joule heating in the adjacent two sections at $I_{\text{opt}}$, the optimal
current for the first section. The net equivalent effects are
that half of the Peltier cooling at each interface remains,
and the entire Joule heating in the body is compensated for.
This requires that the Seebeck coefficient of the $n$th section is
$(n+1/2)S_1$, the electrical conductivity is $\sigma_1/(2n-1)^2$, and
the section length is $L_1/(2n-1)^2$. From the thermal circuit
analysis, it is easy to conclude that the optimal current for an
$N$-section material is the same as $I_{\text{opt}}$ and the maximum cool-
ing temperature is

$$\Delta T = \frac{1}{2} ZT^2 \sum_{n=1}^{N} \frac{1}{2n - 1},$$  

which is larger than $\frac{1}{2} ZT^2$ and has no upper limit when $N$
goes to infinity. This increases even faster with the number
of sections $N$ compared to case 1. One could ask if the cool-
ing efficiency is lower when the cooling temperature is in-
creased. Conventionally, the thermoelectric efficiency is
given by the coefficient of performance (COP),

$$\phi = \frac{Q_{\text{TE}}}{W} = \frac{I S T_{\text{opt}} - \Delta T/R_{\text{sh}} - 0.5 I^2 R}{I(S\Delta T + IR)},$$

which is the ratio of the net cooling power and the electrical
work. However, the COP depends on the heat load and other
thermal boundary conditions. Furthermore, it is zero when
we evaluate the maximum cooling temperature without any
heat load. Thus, to compare efficiencies of the uniform and
graded materials, we formulate a new term that is indepen-
dent of the boundary conditions,

$$\eta = \frac{Q_{\text{TE}}}{W_{\text{TE}}} = \frac{\Delta T/R_{\text{sh}}}{I(R + \Delta T)}.$$  

The term $\eta$ is the ratio of the equivalent net cooling power
and the consumed electrical power. In Fig. 2, we plot the
cooling temperature and the efficiency for case 2 of the stair-
case materials with one or two sections, respectively.

![Fig. 1. Staircase Seebeck profiles as a function of distance in case 1 (with
Seebeck step $S_1$) and in case 2 (with Seebeck step $2S_1$). Distance and See-
beck coefficients are normalized with respect to the length and Seebeck
coefficient of the first section, respectively.

![Fig. 2. Cooling temperature and the efficiency for the staircase material in
case 2 with one or two sections, respectively.](http://apl.aip.org/apl/copyright.jsp)
two section graded material compared to a 1-section uniform material at its maximum cooling point. If a conventional definition of a COP is used, the two-section material will have a larger advantage compared to the one-section case.

The reason that we can get a larger cooling temperature with staircase thermoelectric materials is that the Joule heating and Peltier cooling are redistributed through the material body. One could suppose that a continuously graded material should be able to achieve better results. For a one-dimensional thermoelectric transport, the heat equation at steady state can be written as

$$\frac{d}{dx} \left( K(x) \frac{dT(x)}{dx} \right) = -\frac{J^2}{\sigma(x)} + J T(x) \frac{dS(x)}{dx}. \quad (6)$$

Again, to simplify the proof of concept and obtain an analytical solution, we assume that the thermal conductivity $K$ and the power factor $S(x)^2/\sigma(x) = A$ are constant in a material of length $L$. The Seebeck coefficients at the starting and ending positions are represented by $S_0$ and $S_L$, respectively. The variation of Peltier cooling power due to small temperature change is always negligible since it is only a small fraction of the total Peltier cooling power at room temperature ($\Delta T \ll T$). Then, the cooling temperature of the continuously graded material is

$$\Delta T = \frac{1}{K} \left( \int_0^L dx \int_0^x dx' \left( -\frac{J^2 S^2(x')}{A} \right) + \int_0^L J T S(x) dx \right). \quad (7)$$

The differential gives the optimal current density as

$$J_{\text{opt}} = \frac{T \int_0^L dx S(x) dx}{(2A) \int_0^L dx \int_0^x S^2(x') dx'}. \quad (8)$$

The resulting maximum cooling temperature is

$$\Delta T_{\text{max}} = \frac{1}{2} ZT^2 \int_0^L dx \int_0^x S(x) dx \int_0^x S(x') dx'. \quad (9)$$

It can be observed that the maximum cooling temperature is larger than $\frac{1}{2} ZT^2$, if the Seebeck coefficient increases with position monotonically. It is interesting to note that the maximum cooling temperature is independent of the absolute magnitudes of the Seebeck coefficient, as long as the ratio $S_L/S_0$ is fixed. It is also independent of the length $L$ and the absolute gradient of the Seebeck profile, as long as its shape is scaled as $S(ax)$ where $a$ is a constant. This means that the grading optimization is not limited to a specific range of material properties or dimensions of the device. In Fig. 3, we plot the maximum cooling temperature with respect to the Seebeck coefficient ratio $S_L/S_0$ for three different Seebeck profile functions. The maximum cooling temperatures of all these three functions increase with the ratio $S_L/S_0$. The exponential function performs better than linear function. Of the three functions, the third one, $1/S_0 - 1/S(x) = x$, performs the best. It is the continuously graded version of case 2 from the staircase configuration and it is well above that of the staircase, as expected.

In a very nice publication, Bergman and Levy found that ZT of an arbitrary composite material is always less than the best ZT of its constituents. Here we found that the maximum cooling of an optimally designed segmented thermoelectric material can be larger than the $0.5 ZT^2$ limit given by best ZT of its constituents. These two results do not contradict each other. Since Peltier cooling is an interface heat exchange and Joule heating is a volume heat generation, in a segmented material, one cannot use the average Z (Z_{av}) of the composite to find maximum cooling using the equation $0.5 Z_{av} T^2$.

In conclusion we can overcome the maximum cooling limit of the uniform thermoelectric material set by its figure of merit ZT with the use of graded materials. More than twice maximum cooling temperature of the uniform material with the same ZT can be achieved. For practical applications, one should take into account the exact dependences of the electrical conductivity, the Seebeck coefficient, and the thermal conductivity of real materials. The temperature dependences of these material properties need to be considered for a large temperature gradient. Even though analytical solutions could be quite challenging to find, one can solve this problem with a self-consistent numerical method and expect a similar cooling enhancement by redistributing the Peltier cooling and Joule heating with graded thermoelectric materials.

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