Beating the maximum cooling limit with graded thermoelectric materials

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(Received 20 April 2006; accepted 10 October 2006; published online 20 November 2006)

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 σ and k are the electrical and thermal conductivities, respectively.[1] 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 BiTe 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.[2] Most generally, it has been proved that the maximum cooling of a single element thermoelectric material cannot be improved by changing its geometry.[3] 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.[4–6] The numerical simulation of an inhomogeneous Bi_2Te_3 material showed very little improvement in the efficiencies of power generators and refrigerators.[7] We focus on answering the following question: Is it possible to exceed the limit of the maximum cooling temperature set by the ZT value by changing material's local Seebeck coefficient and electrical conductivity without increasing its ZT? The answer is yes.

In a uniform thermoelectric cooling material, the maximum cooling temperature is limited by the Joule heating accompanying the Peltier cooling. If a constant heat load is applied to the cold side and the hot side is connected to a heat sink, the temperature difference across a uniform thermoelectric material is given by

$$\Delta T = R_{\text{th}}\left(SIT_c - \frac{1}{2}I^2R - Q_c\right), \quad (1)$$

where I is the current, T_c is the temperature at the cooling side, ΔT is the temperature difference across the material, and R and R_{th} are the electrical and thermal resistances of the element, respectively. The Peltier cooling is localized near the interface with the metal contact. The $1/2$ factor in front of the total Joule heating comes from the integral of the distributed Joule heating which flows to the heat sink. If we want to use a thermal circuit to analyze cooling, the distributed Joule heating can be represented by two localized heat sources at the two ends of the uniform material each with a value of $1/2$ of the total Joule heating. When the cooling power is zero, it is easy to find that the maximum cooling temperature is $\frac{1}{2}ZT^2$ by optimizing ΔT with respect to I. It is logical to wonder if the maximum cooling temperature can be increased by redistributing the Joule heating and Peltier cooling using graded materials while not taking higher ZT value as a target. Just for simplicity, we study the maximum cooling of several graded thermoelectric profiles with a constant ZT along the graded direction. The graded thermoelectric profile can be manufactured by varying the doping density and/or the material composition in the growth direction. Thermal conductivity is usually dominated by the lattice contribution. If the doping density changes with position, the electrical conductivity changes much faster than the Seebeck coefficient and when one increases, the other one decreases and vice versa. Thus, it is a good approximation that the thermoelectric power factor ($S^2\sigma$) and thermal conductivity are constant in a finite range of carrier density around the maximum ZT value. Furthermore, to simplify the analysis for the proof of concept, we use low ZT materials and small

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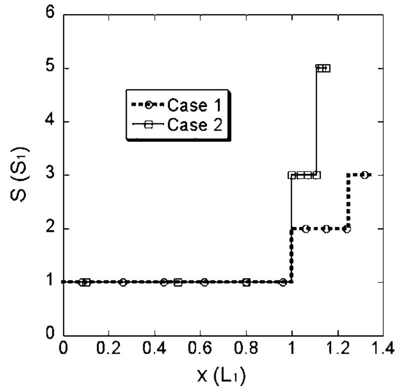

FIG. 1. Staircase Seebeck profiles as a function of distance in case 1 (with Seebeck step S_1) and in case 2 (with Seebeck step $2S_1$). Distance and Seebeck coefficients are normalized with respect to the length and Seebeck coefficient of the first section, respectively.

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 σ_1, and the section length L_1. The optimal current density to achieve the largest cooling temperature for this section is $J_{\text{opt}}=S_1T\sigma_1/L_1$, 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 generated at that interface, the second section should have a Seebeck coefficient of $2S_1$. At this point we would want the remaining half of the Peltier cooling at the interface between the two sections to be canceled by the half of the Joule heating of the second section. The resulting length of the second section should be $L_1/4$, since the electrical conductivity of the second section would be $\sigma_1/4$ if the power factor was the same for all the sections. If the same procedure is continued, we can cascade N sections. In the nth section, the Seebeck coefficient is nS_1, the electrical conductivity is σ_1/n^2, and the section length is L_1/n^2. When the thermal conductivity is constant in all the sections, the total cooling temperature at J_{opt} is

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

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. J_{opt} is not actually optimized for the multiple-section device, which has a slightly higher maximum cooling temperature at smaller current values than J_{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.

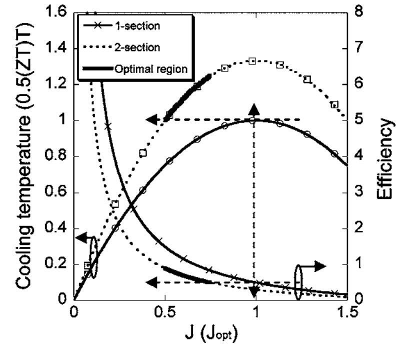

FIG. 2. Cooling temperature and the efficiency for the staircase material in case 2 with one or two sections, respectively.

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 J_{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 nth section is $(2n-1)S_1$, 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 J_{opt} and the maximum cooling temperature is

$$\Delta T=\frac{1}{2}ZT^2\sum_{n=1}^{N}\frac{1}{2n-1}, \tag{3}$$

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 cooling efficiency is lower when the cooling temperature is increased. Conventionally, the thermoelectric efficiency is given by the coefficient of performance (COP),

$$\phi=\frac{Q_c}{W}=\frac{IST_c-\Delta T/R_{\text{th}}-0.5I^2R}{I(S\Delta T+IR)}, \tag{4}$$

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 independent of the boundary conditions,

$$\eta=\frac{Q_{\text{TE}}}{W_{\text{TE}}}=\frac{\Delta T/R_{\text{th}}}{I(IR+S\Delta T)}. \tag{5}$$

The term η 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 staircase materials with one or two sections, respectively. Compared to the one section, the two section achieves a higher cooling temperature but a lower efficiency for all currents. But one can obtain both a higher cooling temperature and a larger cooling efficiency in the thick solid line region with a 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

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

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

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

The differential gives the optimal current density as

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

The resulting maximum cooling temperature is

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

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.

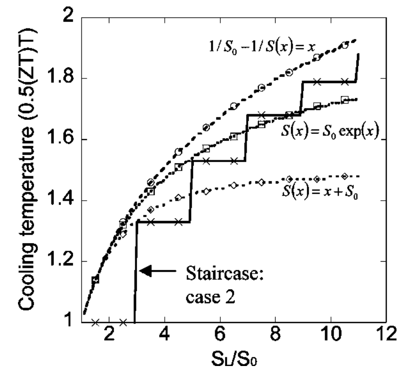

FIG. 3. Maximum cooling temperature as a function of the Seebeck coefficient ratio S_L/S_0 for three different Seebeck coefficient profiles.

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.[8] Here we found that the maximum cooling of an optimally designed segmented thermoelectric material can be larger than the $0.5ZT^2$ 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 $0.5Z_{\text{av}}T^2$.

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.

This work was supported by ONR MURI Thermionic Energy Conversion Center.

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