Do we really need high thermoelectric figures of merit? A critical appraisal to the power conversion efficiency of thermoelectric materials

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This paper will show that, while *ZT* is an appropriate performance index when optimizing the heat conversion rate, it may mislead research in view of applications aiming at large electric power production. This is of special relevance when related to the surge of research in the area of low-dimensionality semiconductors where *ZT* is increased by lowering the thermal conductivity κ. It will be shown that, when operating between sources at fixed temperature, the highest power output can be obtained by increasing κ, not decreasing it, the larger electric power output economically enabling thermoelectric generators for massive electric power production. © *2011 American Institute of Physics*. [doi:10.1063/1.3634018]

The increasing demand of power resources along with the availability of relatively cheap materials (such as nanostructured silicon[1–3] and composites[4]) for thermoelectric (TE) conversion may make sensible to reconsider the possible uses of TE materials in the energy arena. Currently, TE generation is mostly considered appealing when electricity has to be made available in situations where electric power has a high added value, e.g., in outer space probes, for rural or offshore generation, or wherever wiring from main supplies is either unsuitable or impossible. We will refer to this type of applications as *primary* energy conversion. However, the availability of low-cost, relatively highly efficient materials can make thermoelectricity a player also in large scale power recovery, assuming a major role in electric power generation. Actually, almost half of the power nominally available worldwide is wasted as low enthalpy heat during its conversion into electricity,[5] while heat dissipation from industrial plants not only leads to power waste but also negatively impacts on the environment. We will refer to this type of applications as *secondary* energy conversion. It can be verified[6] that, even at present, TE materials meet manufacturing cost requirements to qualify as electric power sources based on the recovery of waste heat. This is actually economically sustainable even for TE efficiencies ≤1% with lifetimes ≥5 yr at the current thermoelectric generator (TEG) prices *provided that TEG maximizes its heat input*.

The main aim of this paper is to show that, while TE materials with low thermal conductivities κ are excellent candidates for local, high added value electric power generation, the major improvements already achieved and sensibly further achievable in the near future by nanostructuring,[7] alloying,[8] or heavy doping[9–11] should lead to rethink the current use of TE figures of merit, shifting the current predominant attention from the figure of merit Z ($= \alpha^2\sigma/\kappa$, where α is the Seebeck coefficient and σ is the electrical conductivity) to the power factor $\mathscr{P}$ ($= \alpha^2\sigma$).

As any device capable of (partially) converting heat into a different form of energy, TEGs are characterized by their conversion efficiency. It can be easily computed if one assumes the material to be uniform, the device to be operated under steady state conditions, and the temperature difference being small enough for σ, α, and κ to be independent of T. More sophisticated evaluations are available in the literature.[12–16] Following Ioffe,[17] in a two-leg circuit made of two thermoelectric materials 1 and 2 operating between two thermostats at T_H and T_C ($T_H > T_C$) and neglecting the heat generated by the Thomson effect, the yield at which the thermal power $\dot{Q}$ is converted into electrical power W, $\phi \equiv W/\dot{Q}$, can be maximized with respect to its geometric parameters, giving

$$\phi = \eta_C \frac{m/(m+1)}{1 + \dfrac{m+1}{Z_{12}T_H} - \dfrac{1}{2}\dfrac{\Delta T}{T_H(m+1)}}, \qquad (1)$$

where $m \equiv R/r_{12}$, R is the (external) electric load, r_{12} is the sum of the electrical resistances of the two legs, $\eta_C = (T_H - T_C)/T_H$ and

$$Z_{12} := \frac{\alpha_{12}^2}{k_{12}r_{12}} = \frac{\alpha_{12}^2}{\left(\sqrt{\kappa_1\rho_1} + \sqrt{\kappa_2\rho_2}\right)^2} \qquad (2)$$

is the figure of merit of the paired legs, with the single subscripts labeling the pertinent leg, $k_{12} = k_1 + k_2$ is the sum of the leg thermal conductances, and $\alpha_{12} = |\alpha_1| + |\alpha_2|$.

A second optimization of ϕ (over m) is needed to obtain the actual efficiency. As for any circuit, also in the case of a TEG, the maximum output power is delivered when the load is matched to the generator, i.e., for $m = 1$, leading to

$$\eta_w = \frac{1}{2}\eta_C\left(1 + \frac{2}{Z_{12}T_H} - \frac{\Delta T}{4T_H}\right)^{-1}. \qquad (3)$$

Instead, optimizing ϕ as of its efficiency, namely choosing m so that $\partial\phi/\partial m = 0$, leads to $m = \sqrt{1 + Z_{12}\bar{T}}$ (where $\bar{T} = (T_H + T_C)/2$) so that

$$\eta_{TE} = \eta_C \frac{\sqrt{1 + Z_{12}\bar{T}} - 1}{\sqrt{1 + Z_{12}\bar{T}} + T_C/T_H}. \qquad (4)$$

It is worthwhile to remark that for any given temperature difference, the highest electric power output for a given TEG is

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obtained when $r = R$ with an efficiency η_w while the best conversion efficiency η_{TE} is reached for a load $R = r\sqrt{1 + Z_{12}\bar{T}}$. Although it can be easily proved that $\eta_w \leq \eta_{TE}$, η_w and η_{TE} significantly differ only at high temperatures and for high Z_{12} values.

Use of Eq. (4) often leads to the conclusion that Z_{12} is a proper criterion of comparison among TE materials. This may be actually true when TE devices operate between two reservoirs at fixed temperatures and with small power inputs. A different yet important setting is whenever heat is actually *recovered* wherever a given thermal power $\dot{Q}$ must be anyway dissipated for the primary application to be sustained (e.g., chemical reactors, nuclear or thermal plants, and refuse incinerators). This sets an optimal thermal conductance k_{opt} for the TE device. Disregarding the amount of heat actually converted into electric power (of order of a few percents of the input power[6]), one gets

$$\dot{Q}/S = -\kappa_{opt}\partial T/\partial z, \qquad (5)$$

where z is the coordinate normal to the dissipating surface of area S. It is easy to verify that

$$\kappa_{opt} = (d/S)\dot{Q}/(T_H - T_C), \qquad (6)$$

where d is the thickness of the TE layer. Taking as an example the autothermal step of the ammonia industrial synthesis,[18] in a chemical reactor dissipating 10^4 kcal/min over an area of 10 m^2 with $T_H = 350$ K, one computes an ideal thermal conductivity for $d = 1$ cm of about 25 W K^{-1} m^{-1}, namely a figure close to that of stainless steel (from 12 to 45 W K^{-1} m^{-1}). Guaranteeing the proper thermal flow makes the choice of the optimal TE material less trivial, since both η_w and η_{TE} depend anyway on Z_{12} (and therefore on κ), not only on $\mathscr{P}$. In principle, one might consider the possibility of keeping low κ values to raise Z_{12} while dissipating part of the heat flow through separated, non-TE walls. Thus, a construction (Fig. 1, inset) might be considered wherein two different materials are used, namely a poor thermal conductor A capable of eff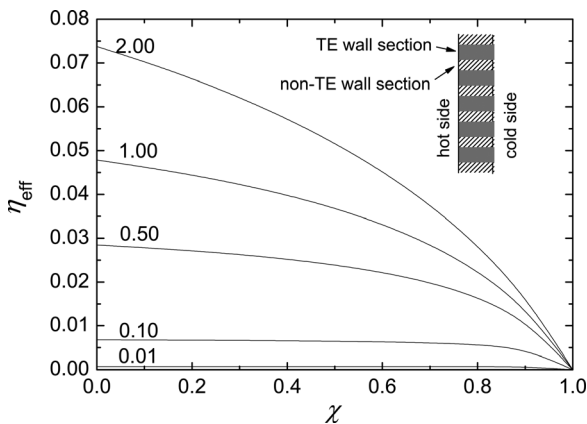icient TE conversion and a good non-TE thermal conductor B compensating for the inefficient heat dissipation of A. If x is the fraction of the thermal exchanger area capable of TE generation, Kirchhoff theorem imposes a relation between the heat flows through A and B, so that the thermal conductivities κ_A and κ_B of the two materials relate to κ_{opt} as

$$\kappa_{opt}(S/d) = \kappa_A(xS/d_A) + \kappa_B((1-x)S/d_B). \qquad (7)$$

Since only heat flowing through A gets converted into electric power, the effective efficiency accounts to

$$\eta_{eff} = \eta_C \frac{\kappa_A}{\kappa_{opt}} \frac{d}{d_A} x \frac{\sqrt{1 + \mathscr{P}\bar{T}/\kappa_A} - 1}{\sqrt{1 + \mathscr{P}\bar{T}/\kappa_A} + T_C/T_H}. \qquad (8)$$

Manifestly enough, since $\kappa_A < \kappa_{opt}$, $x < 1$, and taking hereafter $d = d_A = d_B$, the construction may turn out to be convenient only if the decrease of κ_A results in a relevant increase of the TE efficiency. Replacing κ_A from Eq. (7) into Eq. (8) one can write

$$\eta_{eff} = \eta_C(1-\chi) \frac{\sqrt{1 + Z_{opt}\bar{T}(1-\chi)^{-1}} - 1}{\sqrt{1 + Z_{opt}\bar{T}(1-\chi)^{-1}} + T_C/T_H}, \qquad (9)$$

where $Z_{opt} := \mathscr{P}/\kappa_{opt}$ and $\chi := (1-x)(\kappa_B/\kappa_{opt})$ measures the fraction of heat not converted into electricity. Since $0 < \chi < 1$ (with $\chi = 0$ for $x = 1$), plotting η_{eff} as a function of χ (Fig. 1) clearly shows that thermal shunting never leads to an improvement of the effective efficiency, η_{eff} steadily decreasing with χ for any given $Z_{opt}\bar{T}$. Thus, one can conclude that when operating with constrained heat flows, TE materials must be optimized for their $\mathscr{P}$ (not for their $Z_{12}T$). Thermal conductivity is set by the need of ensuring proper heat dissipation, this usually implying high κ.[6] Unless critically thin devices are built ($d \ll 1$mm), low-κ materials have little chance to be deployed to recover waste heat.

Consider now systems where the endpoint temperatures are fixed while κ can be freely set (i.e., we have no constraint due to the need of dissipating a given thermal power). The electrical power output computes to

$$W = \eta_{TE}\dot{Q} = \eta_{TE}(\kappa S/d)\Delta T. \qquad (10)$$

Since $ZT \propto \kappa^{-1}$, the largest electrical power output that can be obtained is reached not for the highest figure of merit (largest η_{TE}) but when maximizing $\kappa\eta_{TE}(\kappa)$. Note that this does not oppose Eq. (4). What is claimed here is that, when operating between two heat reservoirs, the highest achievable efficiency not necessarily guarantees the largest electrical power output—it only guarantees that the thermal power is converted at the highest rate. Instead, a higher electrical power can be obtained if one accepts to convert the thermal energy with suboptimal conversion efficiency, since this allows for a larger thermal flow to run through the TEG. Manifestly enough, maximizing $\kappa\eta_{TE}$ does not correspond to maximizing η_w either. What is considered here is to trim the TEG specifications looking for the highest power output that can be extracted when operating between two endpoints at fixed temperatures. Fig. 2 shows W and $\eta_{TE}(\kappa)$ vs. κ for different $\mathscr{P}$ values. It is immediate to realize how the largest
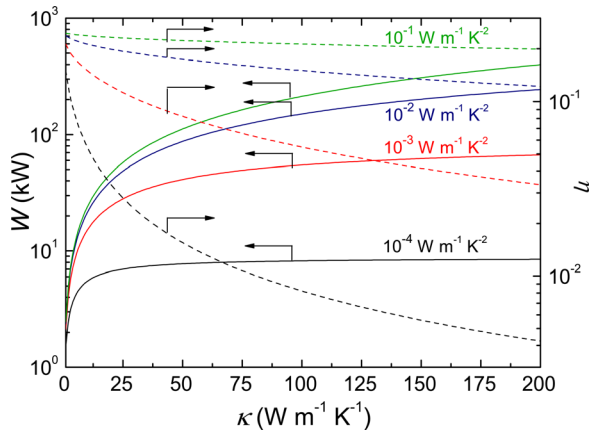

FIG. 1. Effective efficiency of a shunted thermoelectric wall (inset) dissipating a fixed thermal power between 300 K and 400 K vs. the fraction of heat dissipated by non-TE walls for different $Z_{opt}\bar{T}$ values. Although heat dissipation through non-TE wall sections allows for lower κ (higher Z) for TE ones, the overall conversion efficiency decreases with χ.

FIG. 2. (Color online) Plot of $W = \kappa\eta_{TE}S\Delta T/d$ (solid lines) vs. κ for different $\mathscr{P}$ values. In the graphs, we set $T_H = 400$ K, $T_C = 300$ K, $d = 1$ cm and $S = 1$ m^2. Note how W increases with κ.

power output can be obtained for high, not for low, thermal conductivities. Actually, Eq. (10) returns

$$W = \frac{\mathscr{P}(\Delta T)^2 S/(2d)}{(1 + \mathscr{P}T_H/2\kappa) + \sqrt{1 + \mathscr{P}\bar{T}/\kappa}}, \quad (11)$$

with $W = \mathscr{P}(\Delta T)^2 S/4d$ in the $\kappa \to \infty$ limit. Obviously enough, this result is strictly correct if the two endpoints act as thermal reservoirs. In a more realistic situation of finite thermal capacities, it is anyway appropriate to conclude that the electric power output increases with κ provided that neither the heat flowing through the TEG or the Joule heating originated at lead contacts for high current densities is so large to perturb T_H and T_C.

In summary, it has been shown that while ZT is an appropriate performance parameter when TEGs have to optimize the rate of heat conversion, it may be strongly misleading in a number of actual applications. Specifically, when operating under fixed heat flow conditions, low-κ materials are unsuitable to maximize the electric power output as thermal shunts may be required to sustain the needed heat dissipation. Maybe

more surprisingly, high ZT may be also unsuitable when generating electric power between thermal reservoirs at fixed temperatures. Also in such a case, while high figures of merit guarantee the highest thermodynamic efficiency, still at any given value of power factor, the highest output can be obtained by increasing κ, not decreasing it. Low-κ TE materials have nonetheless an important application niche when used to convert heat into electric power from low temperature sources sustaining limited energy flows (e.g., nuclear generators based upon radioisotopic decay).

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