ⓘD **Byungki Ryu,** ⓘD **Jaywan Chung, Eun-Ae Choi,** ⓘD **Pawel Ziolkowski, Eckhard Müller,** and **SuDong Park**

COLLECTIONS

ⓕ   This paper was selected as Featured

View Online   Export Citation   CrossMark

ARTICLES YOU MAY BE INTERESTED IN

Counterintuitive example on relation between *ZT* and thermoelectric efficiency Ⓕ

Byungki Ryu,[1,a] ⓘ Jaywan Chung,[1,a] ⓘ Eun-Ae Choi,[2] Pawel Ziolkowski,[3] ⓘ Eckhard Müller,[3,4] and SuDong Park[1]

AFFILIATIONS

[1]Energy Conversion Research Center, Electrical Materials Research Division, Korea Electrotechnology Research Institute (KERI), Changwon 51543, South Korea

[2]Department of Computational Materials Science, Materials Processing Innovation Research Division, Korea Institute of Materials Science (KIMS), Changwon 51508, South Korea

[3]German Aerospace Center (DLR), Institute of Materials Research, Cologne 51170, Germany

[4]Institute of Inorganic and Analytical Chemistry, Justus Liebig University, Giessen 35392, Germany

[a]Authors to whom correspondence should be addressed: byungkiryu@keri.re.kr and jchung@keri.re.kr

ABSTRACT

The thermoelectric figure of merit *ZT*, which is defined using electrical conductivity, Seebeck coefficient, thermal conductivity, and absolute temperature *T*, has been widely used as a simple estimator of the conversion efficiency of a thermoelectric heat engine. When material properties are constant or slowly varying with *T*, a higher *ZT* ensures a higher maximum conversion efficiency of thermoelectric materials. However, as material properties can vary strongly with *T*, efficiency predictions based on *ZT* can be inaccurate, especially for wide-temperature applications. Moreover, although *ZT* values continue to increase, there has been no investigation of the relationship between *ZT* and the efficiency in the higher *ZT* regime. In this paper, we report a counterintuitive situation by comparing two materials: although one material has a higher *ZT* value over the whole operating temperature range, its maximum conversion efficiency is smaller than that of the other. This indicates that, for material comparisons, the evaluation of exact efficiencies as opposed to a simple comparison of *ZT*s is necessary in certain cases.

Thermoelectric technology has attracted much attention because of the strong demand for eco-friendly energy harvesting.[1] As a thermoelectric heat engine does not contain any moving parts and has a small volume, it can be highly applicable for energy harvesting if the conversion efficiency is sufficient. Over the past decades, the dimensionless thermoelectric figure of merit $ZT = (\alpha^2 / \rho\kappa) T$ has been considered as a good estimator for maximum thermoelectric conversion efficiency, where α, ρ, κ, and T are the Seebeck coefficient, electrical resistivity, thermal conductivity, and absolute temperature, respectively.[2–4] Consequently, the discovery of high-*ZT* thermoelectric materials has been central to the achievement of high-performance thermoelectric devices.

The *ZT*-based efficiency theory follows from the constant property model (CPM), in which all thermoelectric properties (TEPs: α, ρ, and κ) are considered to be *T*-independent.[4] In this model, the temperature distribution inside a one-dimensional ideal thermoelectric engine is uniquely determined as a quadratic polynomial.[5] As a result,

the hot-side heat flux and the generated power are analytically determined. Finally, the thermoelectric efficiency (η) under the operating temperature between the hot-side temperature T_h and the cold-side temperature T_c is bounded above by $\eta_{\max} = \frac{\Delta T}{T_h} \cdot \frac{\sqrt{1+ZT_m}-1}{\sqrt{1+ZT_m}+T_c/T_h}$ where $\Delta T = T_h - T_c$ and $T_m = (T_h + T_c)/2$.[1–4] Note that in CPM, there is a monotonically increasing relationship between *ZT* and the maximum thermoelectric efficiency.

However, in reality, charge and heat transports are strongly temperature-dependent.[6] Within the degenerate limit, the electrical resistivity and Seebeck coefficient of materials are roughly proportional to T.[3,6,7] In non-degenerate semiconductors, ρ decreases as T increases. The lattice thermal conductivity of crystalline materials is roughly proportional to T^{-1} above room temperature owing to anharmonic three phonon processes.[6–8] Therefore, for wide-temperature applications, single parameter *ZT* estimation could give non-negligible errors in the prediction of the efficiency of thermoelectric heat engines.[9–11]

Although *nonlinearity* in thermoelectric equations indicates that there is *no analytical expression* for thermoelectric efficiency,[5,10,12] there have been several efforts to generalize the relations in non-CPM conditions. Several average ZT schemes have been proposed and their proportionality on efficiency is tested in conditions when the peak or average ZT is smaller than 2.6.[13–16] However, it is unclear *whether average ZT schemes work as well in a higher ZT regime as they do in the low ZT regime.*

In this Letter, we report a counterintuitive example of relations between ZT and thermoelectric efficiency. We find two distinct sets of thermoelectric property (TEP) curves, where one set of TEPs has higher ZT curves over the whole operating temperature range, but its maximum conversion efficiency is smaller than that of the other set. Our finding highlights the mathematical inexactness of ZT in efficiency prediction, especially for high ZT (>10). For a low ZT, we also find additional examples that the efficiency is lower although the average or peak ZT is higher.

We consider an ideal thermoelectric heat engine containing a one-dimensional single thermoelectric leg sandwiched by hot and cold sides.[4,11] The thermoelectric leg has a length of L and cross-sectional area of A. The Dirichlet thermal boundary condition is adopted with hot-side temperature T_h at $x = 0$ and cold-side temperature T_c at $x = L$. In this heat engine, the thermal and electrical currents flow along the leg. In this ideal engine, only thermal diffusion and Peltier heat through solids are allowed; radiative and convective heat is neglected. For simplicity, we assume a time-independent steady-state condition and positive Seebeck coefficient in the operating temperature range. The heat engine forms a closed circuit with a load resistance R_L. Therefore, by applying a non-zero temperature difference, voltage (V_{gen}) is generated and current (I) flows from the hot to the cold side. With the internal resistance of thermoelectric material denoted by R, the induced current is written[3,5] as follows:

$$ I = \frac{V_{gen}}{(R + R_L)} = \frac{V_{gen}}{R(1 + \gamma)}, \tag{1} $$

where $V_{gen} \equiv \int_0^L \left(-\alpha \frac{dT}{dx} \right) dx = \int_{T_c}^{T_h} \alpha(T) dT$, $R = \int_0^L \rho(T) \frac{dx}{A}$, and $\gamma \equiv \frac{R_L}{R}$.

The thermoelectric efficiency is defined as the ratio of the external power delivered (P) to the hot-side heat flux (Q_h). Thus, the efficiency (η), at a given relative resistance $\gamma = \frac{R_L}{R}$, is computed using the exact temperature distribution $T(x)$ as follows:[3,4]

$$ \eta\left(\gamma = \frac{R_L}{R} \right) = \eta(I) = \frac{P}{Q_h} = \frac{I\,(V_{gen} - IR)}{-\kappa A \left(\dfrac{dT}{dx} \right)_{T_h} + I\,\alpha(T_h)\,T_h}. \tag{2} $$

Then, the maximum efficiency η_{max}, which satisfies the relation $\eta(\gamma) \le \eta_{max}$ for all $\gamma \ge 0$, is searched using the Brent-Dekker optimization method. Note that a positive γ indicates that the heat engine is in power generation mode. To determine $T(x)$, we solve the second order differential equation for a one-dimensional leg given as follows:[5]

$$ \frac{d}{dx}\left(\kappa(T) \frac{dT}{dx} \right) + \rho(T) J^2 - T \frac{d\alpha}{dT} \frac{dT}{dx} J = 0, \tag{3} $$

where $J = I/A$. Here, the temperature satisfies the boundary conditions of $T(x=0) = T_h$ and $T(x=L) = T_c$.

The analysis considers a one-dimensional thermoelectric heat engine with a leg length of 1 mm and a leg cross-sectional area of 1 mm^2, operating at $T_h = 900$ K and $T_c = 300$ K. When the electrical circuit of the heat engine is open, only thermal current flows from the hot to the cold side. If the material has a non-zero Seebeck coefficient, it generates electrical voltage. When the circuit is closed, the induced voltage generates an electrical current and the power is delivered to the outside load resistance.

Two *imaginary* thermoelectric materials, *mat1* and *mat2*, are considered for the thermoelectric leg. We assume that the materials have linear TEP curves for the Seebeck coefficient, electrical resistivity, and thermal conductivity (see Table I and Fig. 1). The two materials have the same linear resistivity and constant thermal conductivity: the resistivity is 1×10^{-5} $\Omega \cdot$m at 300 K and 3×10^{-5} $\Omega \cdot$m at 900 K, and thermal conductivity is set to 1 W/m/K. However, the Seebeck coefficients are different for the two materials. In *mat1*, the Seebeck coefficient is constant and set to 816 μV/K. Thus, its ZT is 20 at 300 K and 900 K. In *mat2*, the Seebeck coefficient is a linear function of

TABLE I. Thermoelectric properties and engine performances of imaginary materials: *mat1* and *mat2* for absolute ZT inversion and *mat3* to *mat5* for average ZT inversion and peak ZT inversion. The engine performances are computed within an operating temperature range from $T_c = 300$ K to $T_h = 900$ K.

| Example Material		Absolute ZT inversion		Average ZT inversion and peak ZT inversion			
		mat1	mat2	mat3	mat4	mat5	
ρ ($\Omega \cdot$m)	300 K	1×10^{-5}	1×10^{-5}	1×10^{-5}	1×10^{-5}	1×10^{-5}	Linear on T
	900 K	3×10^{-5}	3×10^{-5}	3×10^{-5}	3×10^{-5}	3×10^{-5}	
α (V/K)	300 K	816×10^{-6}	816×10^{-6}	327×10^{-6}	173×10^{-6}	0	Constant or linear on T
	900 K		1155×10^{-6}	0		365×10^{-6}	
κ (W/m/K)	300 K	1	1	1	1	1	Constant
	900 K						
ZT	300 K	20	20	3.2 (peak)	0.9	0	
	900 K		40 (peak)	0		4 (peak)	
$[ZT]_{eng}$		20.0000	29.1421	0.8	0.9	1	
$(\alpha_h - \alpha_c)/(\alpha_h + \alpha_c)$		0	0.1716	-1	0	1	
γ_{opt}		4.59 184	6.79 592	1.25 749	1.58 136	1.97 241	
η_{max} (%)		48.585	47.422	15.089	14.675	13.448	
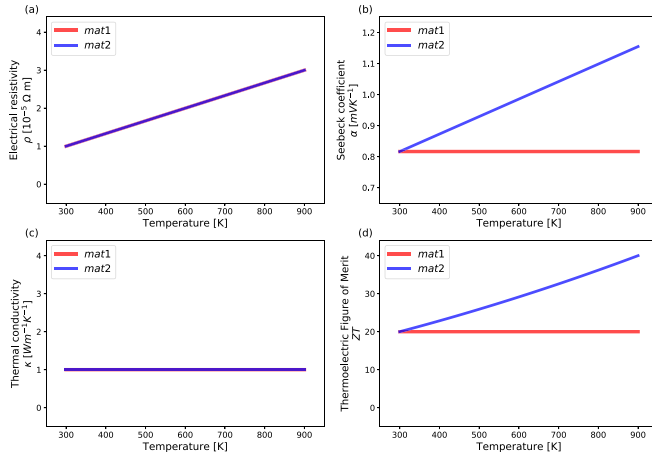
FIG. 1. Thermoelectric properties of two imaginary materials, *mat1* (red line) and *mat2* (blue line).

temperature: 816 μV/K at 300 K and 1155 μV/K at 900 K. Thus, the ZT of *mat2* is 20 at 300 K and 40 at 900 K. The ZT of *mat1* is clearly smaller than the ZT of *mat2* over the whole operating temperature range from 300 to 900 K.

We compute the maximum thermoelectric efficiency by solving the thermoelectric differential equation for temperature distribution as previously described. Table II and Fig. 2 show the computed ideal thermoelectric efficiency as a function of $\gamma = \frac{R_L}{R}$. Each TEP curve set has a single maximum value. The maximum efficiencies of *mat1* and *mat2* are computed as 48.585% and 47.422%, respectively.

Therefore, *mat1* and *mat2* have counterintuitive outcomes: the maximum efficiency of *mat1* is definitely larger than the maximum efficiency of *mat2* ($\eta_{\max}^{mat1} = 48.585\% > \eta_{\max}^{mat2} = 47.422\%$), whereas the ZT of *mat1* is definitely smaller than the ZT of *mat2* ($ZT^{mat1} = 20 \leq ZT^{mat2}$). This is the first type of *the ZT paradox*, the *absolute ZT inversion*, that the higher efficiency appears with smaller ZT values over the whole operating temperature range.

We investigate a TEP condition where the *absolute ZT inversion* occurs by performing a parametric study for $\eta_{\max}$ and ZT. Figures 3(a) and 3(b) show the relation between $\eta_{\max}$ and ZT space for a wide ZT range from 0.2 to 44. In each figure, we consider a 31×31 uniform ZT mesh for the cold side ZT (ZT_c) and hot side ZT (ZT_h). At this moment, for the TEP parameter space, we consider the linear Seebeck coefficient on T ($d\alpha/dT = $ const.), linear electrical resistivity ($\rho/T = $ const.), and constant thermal conductivity. Note that the highly asymmetric behavior of $\eta_{\max}$ can be observed in the higher ZT regime. The value of $\eta_{\max}$ increases when ZT_c increases. However, for given $ZT_c = \sim 10$, the change of ZT_h does not lead to the change of $\eta_{\max}$. Moreover, for $ZT_c > \sim 10$ and $ZT_h > \sim 15$, an *absolute ZT inversion* can occur such that a higher ZT gives a lower $\eta_{\max}$. This inversion is even observed in an average ZT scheme. We use the engineering ZT ($[ZT]_{eng}$) an average scheme for ZT,[13] which is given as follows:

$$[ZT]_{eng} = Z_{eng}\Delta T = \frac{\left(\int_c^h \alpha(T)dT\right)^2}{\int_c^h \rho(T)dT \cdot \int_c^h \kappa(T)dT}(T_h - T_c). \quad (4)$$

	mat1		*mat2*	
	Current	Efficiency	Current	Efficiency
$\gamma = R_L/R$	I (A)	η (%)	I (A)	η (%)
4.10 204	4.52 480	48.518%	4.74 071	46.055%
4.22 449	4.43 005	48.549%	4.65 217	46.210%
4.34 694	4.33 899	48.570%	4.56 684	46.352%
4.46 939	4.25 140	48.581%	4.48 456	46.481%
4.59 184 (*)	**4.16 711**	**48.585**% (*)	4.40 517	46.599%
4.71 429	4.08 595	48.580%	4.32 850	46.707%
4.83 673	4.00 774	48.569%	4.25 442	46.804%
4.95 918	3.93 235	48.551%	4.18 281	46.893%
5.08 163	3.85 962	48.527%	4.11 353	46.972%
…	…	…	…	…
6.30 612	3.25 349	48.035%	3.52 774	47.394%
6.42 857	3.20 289	47.967%	3.47 809	47.407%
6.55 102	3.15 379	47.897%	3.42 979	47.416%
6.67 347	3.10 614	47.824%	3.38 279	47.421%
6.79 592 (**)	3.05 987	47.749%	**3.33 704**	**47.422**% (**)
6.91 837	3.01 492	47.672%	3.29 250	47.420%
7.04 082	2.97 125	47.593%	3.24 912	47.414%
7.16 327	2.92 879	47.512%	3.20 684	47.406%
7.28 571	2.88 749	47.429%	3.16 564	47.394%

The $[ZT]_{eng}$ value of *mat1* (20) is smaller than that of *mat2* ($\sim$29.1): see Table I. This kind of *strong* counterintuitive phenomenon seems not to occur for the *low ZT regime* [see Fig. 3(b)].

Also we find that weak counterintuitive situations can occur for the *low ZT regime*. Figure 4(a) shows the relation between $\eta_{\max}$ and engineering $[ZT]_{eng}$. For the TEP parameter space, we consider the same space as that given in the previous paragraph. In the TEP space, we consider three cases for the Seebeck coefficient curves: the first one is the linear decreasing Seebeck coefficient with 0 at T_h, the second one
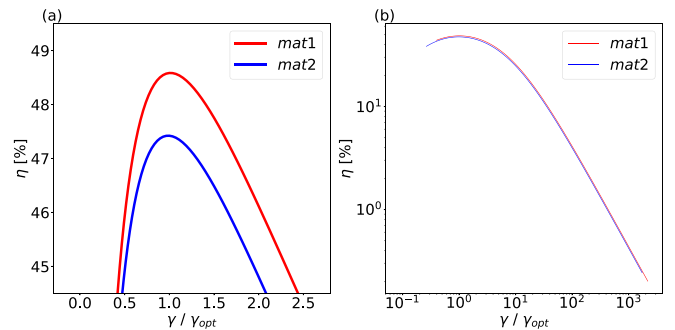

FIG. 2. Calculated conversion efficiency curves as a function of normalized load resistance ratio (γ/γ_{opt}) for thermoelectric heat engines using two imaginary materi-als, *mat1* (red line) and *mat2* (blue line), where γ is R_L/R and γ_{opt} is the optimal load resistance to maximize the efficiency.
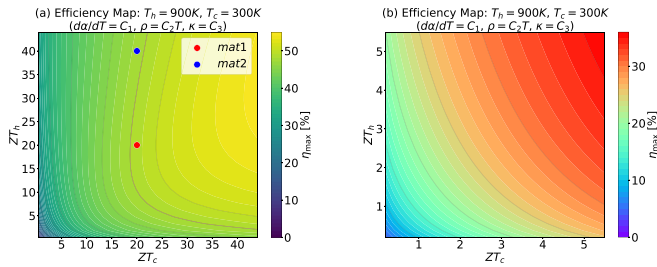
FIG. 3. Contour and color map of the calculated maximum conversion efficiency η_{max} at $T_h = 900$ K and $T_c = 300$ K are drawn (a) for a wide range of hot side ZT (ZT_h) and cold side ZT (ZT_c) and (b) for the realistic low ZT regime. The η_{max}'s are computed for the parameter space of the linear Seebeck coefficient on T ($d\alpha/dT$ = const.), linear electrical resistivity (ρ/T = const.), and constant thermal conductivity. The engine performances of *mat1* and *mat2* are denoted by red and blue filled circles, respectively. In (a), the contour of $\eta_{max} = 48\%$ is represented by the brown solid line.

is constant, and the third one is the linear increasing Seebeck coefficient with 0 at T_c. We find that a large $[ZT]_{eng}$ can provide a small η_{max} for a certain case. For efficiency comparison, three *realistic* materials (*mat3*, mat4, and mat5) are considered, as shown in Table I. They have $[ZT]_{eng}$ values of 0.8, 0.9, and 1.0, respectively. Although *mat3* has the least value of $[ZT]_{eng} = 0.8$, the value of η_{max} of *mat3* is higher than those of *mat4* and *mat5*, and *mat5* has the least value of η_{max}; thus, we find the second type of the ZT paradox, the *average ZT inversion*. Note that this can *occur even in the realistic material* cases of $[ZT]_{eng} \leq 1$.

Figure 4(b) shows the ZT curves of *mat3*, mat4, and mat5. Here, we find the third type of ZT paradox, the *peak ZT inversion*. *mat5* has the highest peak ZT of 4.0 at 900 K and the ZT values of *mat5* are greater than those of *mat4* if $T \geq 585$ K. However, η_{max} of *mat5* is less than that of *mat4*, having a constant ZT of 0.9.

Our finding indicates that efficiency evaluation is important when evaluating a material's thermoelectric performance. As materials of high figure of merit ZT continue to be developed, highly accurate efficiency calculation methods, or exact efficiency evaluation, will be required to properly assess their thermoelectric application, especially
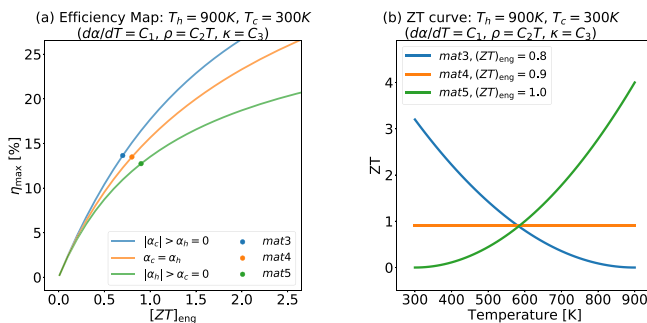
over wide temperature ranges. Even in the low ZT regime, the efficiency can be changed when the shape of the TEP curves varies while the average ZT is kept constant.

The failure of traditional ZT formula in efficiency prediction can be understood by the asymmetric distribution of Joule heat and *non-zero* Thomson effect inside the leg. Since the thermoelectric properties are temperature-dependent, the heat source in Eq. (3) is not uniformly distributed and the temperature solution of the one-dimensional leg can be largely deviated from the quadratic polynomial of the CPM, limiting the applicability of the CPM-based traditional ZT model for efficiency prediction. As shown in Fig. 4, the different slopes in the Seebeck coefficients can significantly affect the efficiency. It implies that, together with ZT, hidden parameters describing the asymmetric Joule heat distribution and Thomson heat generation could be important factors for the determination of efficiency.

In conclusion, we have found a counterintuitive example in the relation between ZT and thermoelectric efficiency in the higher ZT regime. Whereas ZT is widely accepted as a good estimator for thermoelectric material efficiency in the low ZT regime, a higher maximum efficiency can appear with smaller ZT values, if ZT is large enough. Thus, as material ZT values rise, greater care should be taken in the evaluation of materials; efficiency itself, rather than ZT, should be determined and compared.

AUTHORS' CONTRIBUTIONS

B.R. and J.C. found the counterintuitive example. J.C. and B.R. developed a computational code, called *pykeri2019*, for efficiency calculation of one-dimensional thermoelectric heat engines. B.R., J.C., E.A.C., P.Z., and S.D.P. all discussed the results. B.R. wrote the manuscript. S.D.P. advised the project. All authors revised the manuscript.

REFERENCES

[1] G. J. Snyder and E. S. Toberer, Nat. Mater. **7**, 105 (2008).
[2] A. F. Ioffe, *Semiconductor Thermoelements and Thermoelectric Cooling* (Infosearch, London, 1957).
[3] H. J. Goldsmid, *Introduction to Thermoelectricity* (Springer, Berlin, Heidelberg, 2010).
[4] C. Goupil, *Continuum Theory and Modeling of Thermoelectric Elements* (John Wiley & Sons, 2015).
[5] J. Chung and B. Ryu, Math. Probl. Eng. **2014**, 1.
[6] N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Brooks/Cole, 1976).
[7] B. Ryu and M. W. Oh, J. Korean Ceram. Soc. **53**, 273 (2016).
[8] A. Togo, L. Chaput, and I. Tanaka, Phys. Rev. B **91**, 094306 (2015).
[9] B. Ryu, J. Chung, and S. D. Park, arXiv:1810.11148 (2018).

FIG. 4. (a) The calculated maximum conversion efficiency η_{max} under $T_h = 900$ K and $T_c = 300$ K is plotted as a function of $[ZT]_{eng}$ with special conditions of linear Seebeck coefficients. The η_{max}'s of *mat3*, mat4, and mat5 are denoted using blue, orange, and green dots, respectively. (b) The temperature-dependent ZT curves are plotted for *mat3*, mat4, and mat5.

[10]B. Ryu, J. Chung, and S. D. Park, arXiv:1910.11132 (2018).

[11]J. E. Sunderland and N. T. Burak, Solid State Electron. **7**, 465 (1964).

[12]G. J. Snyder and A. H. Snyder, Environ. Energy Sci. **10**, 2280 (2017).

[13]H. S. Kim, W. Liu, G. Chen, C. W. Chu, and Z. Ren, Proc. Natl. Acad. Sci. U. S. A. **112**, 8205 (2015).

[14]H. Armstrong, M. Boese, C. Carmichael, H. Dimich, D. Seay, N. Sheppard, and M. Beekman, J. Electron. Mater. **46**, 6 (2017).

[15]B. Ryu, J. Chung, and S. D. Park, Bull. Am. Phys. Soc. **64**, R47.00007 (2019).

[16]L. D. Zhao, S. H. Lo, Y. Zhang, H. Sun, G. Tan, C. Uher, C. Wolverton, V. P. Dravid, and G. Kanatzidis, Nature **508**, 373 (2014).