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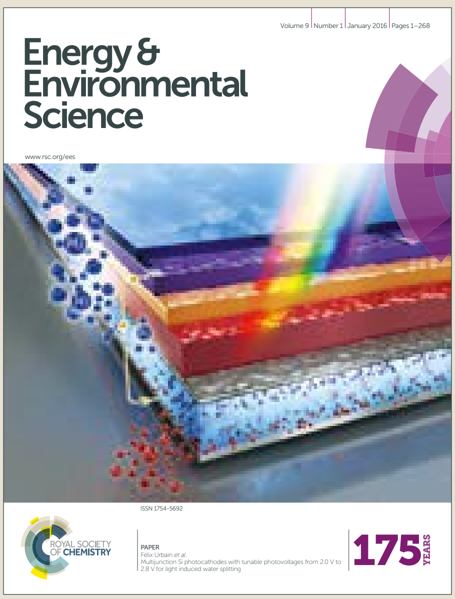

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Figure of Merit *ZT* of a Thermoelectric Device Defined from Materials Properties

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Abstract

While the thermoelectric *materials figure of merit* $zT = \frac{S^2}{\rho\kappa}T$ is a well defined metric to evaluate thermoelectric materials, it can be a poor metric for maximum thermoelectric device efficency because of the temperature dependence of the Seebeck coefficient S, the electrical resistivity ρ, and the thermal conductivity κ where T is the absolute temperature. Historically the field has used a thermoelectric *device figure of merit ZT* to characterize a device operating between a hot side temperature T_h and cold side temperature T_c. While there are many approximate methods to calculate ZT from temperature dependent materials properties, an exact method is given here that uses a simple algorithm that can be performed on a spreadsheet calculator. The figure of merit $ZT = \left(\frac{T_h - T_c(1-\eta)}{T_h(1-\eta)-T_c}\right)^2 - 1$ is defined for a thermoelectric generator using the maximum efficiency of the thermoelectric device η calculated from the exact method.

Broader Impact

Thermoelectrics are the basis of many solid-state thermal to electrical conversion devices or Peltier cooling devices actively considered for waste heat recovery, energy harvesting and cooling applications free of environmentally harmful coolant gasses. With intensifying effort to improve the efficiency of existing thermoelectric materials and find new ones it is important to have a well defined metric to compare performance of different materials. Often peak values of materials figure of merit zT are reported that may not be very relevant to utilizing the material across a large temperature difference. With the device ZT as defined here, the total thermal-to-electric conversion efficiency of different materials can be easily compared. The ZT is calculated from the exact maximum efficiency of the material across a temperature difference using an algorithm that is performed on a simple spreadsheet calculator.

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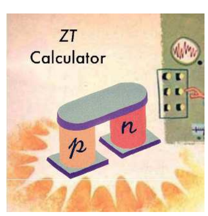

The thermoelectric device ZT is calculated using a simple spreadsheet calculator.

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Thermoelectric Figures of Merit

Thermoelectric devices can convert heat into electricity or transport heat producing cooling using the Seebeck and Peltier effects. The efficiency of this process typically determines the utility and cost of such devices[1] and even the power density.[3] Thus, there is much effort to improve the efficiency of thermoelectric materials or discover entirely new materials.[4]

The maximum efficiency of a thermoelectric material is determined by its thermoelectric figure of merit. The maximum efficiency of the energy conversion process (whether generating power or cooling) at a given point in the material is determined by the *thermoelectric materials figure of merit zT*, given by

$$zT = \frac{S^2}{\rho\kappa}T \tag{1}$$

where S is the Seebeck coefficient, ρ is the electrical resistivity, κ is the thermal conductivity and T is the absolute temperature of the material at the point in question.[5] The figure of merit $zT(T)$ is, in general, a temperature dependent material property derived from temperature dependent material properties $S(T)$, $\rho(T)$, and $\kappa(T)$. An efficient thermoelectric generator, however, must operate across a finite temperature difference $\Delta T = T_h - T_c$ so that these material properties will change from the hot to the cold end.

The maximum efficiency η of a thermoelectric generation device is also traditionally characterized by the *thermoelectric device figure of merit, ZT* where

$$\eta = \frac{\Delta T}{T_h}\frac{\sqrt{1+ZT}-1}{\sqrt{1+ZT}+T_c/T_h} \tag{2}$$

The overall maximum efficiency of the generator is limited by the Carnot factor, $\Delta T / T_h$, and the *reduced efficiency* that depends on ZT, T_h and T_c. Equation 2 is typically derived assuming the thermoelectric materials properties S, ρ, and κ are constant with respect to temperature, exactly matched n-type and p-type legs and 1-dimensional heat flow with no other losses.[2] It is only in this case of constant S, ρ, and κ that the material figure of merit zT (at $T = (T_h + T_c) / 2$) and the device figure of merit ZT (evaluated between T_h and T_c) the same. This derivation and connection between ZT and zT makes device ZT a good descriptor for the maximum reduced efficiency comparable to the zT at the average device temperature and so we shall use equation 2 to motivate the definition of ZT. Note the use of an upper case Z in the *device* figure of merit (Equation 2) and lower case z for *materials* figure of merit (Equation 1)[4] as they are easily and frequently confused.

The device figure of merit ZT can be very different from the material figure of merit zT for several reasons including large temperature variation of zT and poor thermoelectric self compatibility[5] across the temperature range of interest and between the legs. There have been many attempts to describe ZT as an average of the temperature dependent materials properties of the n-leg and p-leg[10] where for small variations in thermoelectric properties between T_h and T_c the averages will be similar but will be quite different for incompatible thermoelectric segments.[9] All proposed averaging methods are inexact approximations as they assume some specific temperature dependence of the thermoelectric properties and ignore the effects of thermoelectric compatibility.[10]

Fortunately, there is a well-defined, simple way to calculate device ZT from thermoelectric material properties. Keeping in mind that the purpose of a figure of merit is to be a useful metric, universally recognized, and easy to use we shall use equation 2 with some qualifications to make it well-defined. First, we think of ZT as a single quantity as opposed to a product of two terms (Z and T). Because the ZT is clearly desired for a single material (as opposed to a combined n-type and p-type couple) we shall use equation 2 to describe the maximum efficiency η of a *single thermoelectric leg* (single n-type or p-type leg). Finally, we shall ignore non-ideal heat & electrical losses and assume 1-dimensional transport, as is done in the derivation of equation 2.

The thermoelectric device ZT of any material, given a finite temperature difference $\Delta T = T_h - T_c$ is then defined from the maximum efficiency η of a single thermoelectric leg and equation 2:

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(3) $$ZT = \left(\frac{T_h - T_c(1-\eta)}{T_h(1-\eta) - T_c} \right)^2 - 1$$

where the maximum efficiency η is calculated from the temperature dependent properties $S(T)$, $\rho(T)$, and $\kappa(T)$ between hot side temperature T_h and cold side temperature T_c.

Exact calculation of maximum efficiency

While there is no analytic expression for η, it can be calculated to any desired accuracy numerically with a simple procedure that can be done on a spreadsheet.[5] The example given here in Table I is available for download in supplemental information or at the website.[8] To calculate the maximum efficiency η and ZT follow these steps:

Table I. Example calculation of ZT from device efficiency. Input data are first 4 columns (blue). The first value for relative current u (orange) is the parameter to be adjusted for optimum efficiency at hot side temperature (light purple). The maximum efficiency for 300K-800K temperature range is 14.0% corresponding to ZT = 0.96 (dark purple) for this material.

T (K)	Seebeck (μV/K)	resistivity (10-3 Ω cm)	thermal cond. (W/m K)	zT	max Red eff	s (1/V)	u (1/V)	Red eff	Φ (V)	efficiency	ZT
300	106	0.71	2.52	0.19	4.3%	2.83	2.7815	4.3%	0.391		
325	119	0.75	2.29	0.27	5.9%	3.26	2.8222	5.8%	0.393	0.4%	0.22
350	131	0.81	2.09	0.36	7.6%	3.58	2.8658	7.3%	0.395	0.9%	0.26
375	142	0.90	1.94	0.43	8.9%	3.70	2.9084	8.6%	0.397	1.4%	0.30
400	154	1.01	1.79	0.52	10.4%	3.79	2.9596	10.0%	0.399	2.0%	0.33
425	166	1.14	1.68	0.61	11.8%	3.81	3.0174	11.4%	0.402	2.7%	0.37
450	178	1.28	1.57	0.71	13.3%	3.84	3.0804	12.9%	0.405	3.3%	0.40
475	191	1.43	1.49	0.81	14.8%	3.83	3.1537	14.4%	0.408	4.0%	0.44
500	205	1.59	1.40	0.95	16.5%	3.86	3.2418	16.2%	0.411	4.8%	0.48
525	219	1.74	1.33	1.08	18.2%	3.87	3.3365	17.9%	0.414	5.6%	0.53
550	229	1.90	1.26	1.21	19.6%	3.85	3.4259	19.4%	0.418	6.4%	0.57
575	239	2.06	1.21	1.31	20.6%	3.79	3.5132	20.6%	0.422	7.2%	0.62
600	247	2.22	1.16	1.42	21.7%	3.74	3.6039	21.7%	0.426	8.1%	0.66
625	254	2.37	1.13	1.50	22.5%	3.66	3.6893	22.5%	0.430	8.9%	0.71
650	258	2.52	1.09	1.58	23.2%	3.60	3.7663	23.2%	0.433	9.7%	0.75
675	262	2.66	1.07	1.63	23.7%	3.51	3.8429	23.6%	0.437	10.5%	0.79
700	266	2.80	1.04	1.70	24.3%	3.45	3.9254	24.1%	0.441	11.3%	0.83
725	269	2.94	1.03	1.74	24.7%	3.35	4.0046	24.1%	0.445	12.0%	0.87
750	269	3.08	1.02	1.73	24.6%	3.23	4.0514	23.7%	0.448	12.8%	0.90
775	268	3.24	1.01	1.70	24.3%	3.10	4.0926	23.0%	0.452	13.4%	0.93
800	268	3.42	1.01	1.67	24.1%	2.95	4.1582	21.9%	0.455	14.0%	0.96

1. Copy your temperature dependent $S(T)$, $\rho(T)$, and $\kappa(T)$ into the T, S, ρ, and κ columns – the first 4 columns in Table I shaded blue. The cold side temperature for the calculation is the first temperature, 300K in Table I. We shall use 800K for hot side temperature for the example in Table I. The example shows 25K temperature intervals between data points, but that can vary. You can use smaller temperature steps for more accurate calculations.

2. Optimize the *first entry* of the relative current value u (shaded orange in Table I) for device efficiency at the hot side (shaded light purple in Table I). The values for u at higher temperature will adjust accordingly – don't change these. This is like setting the electrical current (or load resistance) through the device. The power and therefore efficiency will be low at low values of u because little electrical current will be flowing through the device and low at high values of u because the output voltage will drop at high currents (and even becomes negative). [Figure 1]. For good efficiency the u values should be close to the compatibility factor s in the column next to u. Avoid calculating for u = 0 exactly as some calculations become undefined, but u arbitrarily small is fine (*e.g.* u = 0.001).

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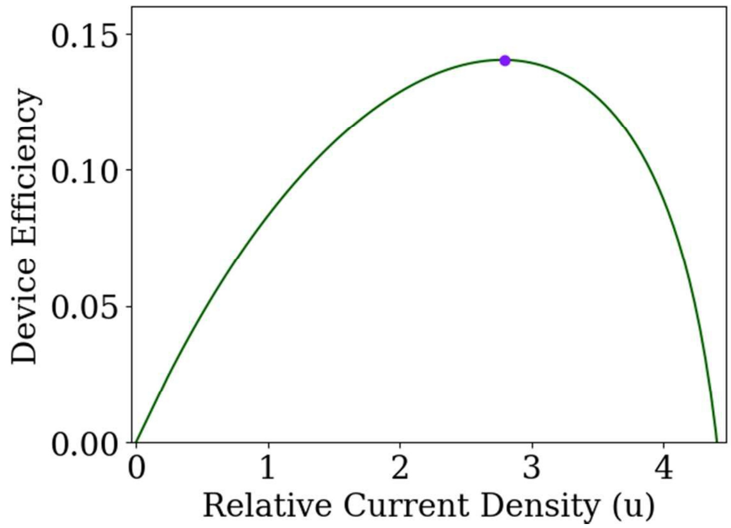

Figure 1. Device Efficiency vs. *u* at T_c from the spreadsheet example. The maximum efficiency (purple dot) is used to determine the figure of merit *ZT*.

The efficiency of this thermoelectric leg is given in the *efficiency* column. The calculation assumes the first row (300K in Table I) is the cold side. For 800K hot side we should optimize the efficiency of the last row (shaded light purple in Table I). For example the data in Table I should optimize to 14.0% when $u = 2.7815$. MS Excel has a *solver* add-in that makes this easy, but other methods or adjusting by hand also works.

3. The device *ZT* is calculated from the *maximum* efficiency value you found by optimizing cold side *u* value and equation 3. In the Table I example we optimize for maximum 800K efficiency so the $ZT = 0.96$ is only for the 300K-800K temperature range. For *ZT* at other T_h or T_c, the *u* value at T_c will need to be re-optimized. For example this same file can be used to calculate $ZT = 0.72$ for the 300K–600K temperature range (not $ZT = 0.66$ in Table I as that *u* was optimized for 300K–800K).

Discussion of calculation method

The calculation also evaluates performance of the thermoelectric from the hot side to the cold side. While the materials figure of merit *zT* determines the maximum possible reduced efficiency η_r (fraction of Carnot efficiency $\eta = \frac{\Delta T}{T_h}\eta_r$),

$$\max \eta_r = \frac{\sqrt{1+zT}-1}{\sqrt{1+zT}+1} \quad (4)$$

the actual reduced efficiency η_r at any given point in a device is lower because the relative current density *u* is not necessarily at the optimum value given by the compatibility factor *s*.

$$\eta_r = \frac{u\left(S - u\rho\kappa\right)}{uS + \frac{1}{T}} \quad (5)$$

The reduced efficiency η_r is maximum when $u = s$ where

$$s = \frac{\sqrt{1+zT}-1}{ST} \quad (6)$$

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The relative current u must change with temperature according to a differential equation[5] that is solved numerically in the spreadsheet using

$$(7) \qquad \frac{1}{u_n} = \frac{1}{u_{n-1}}\sqrt{1-u_{n-1}^2\left(\rho_n\kappa_n+\rho_{n-1}\kappa_{n-1}\right)\left(T_n-T_{n-1}\right)} - \left(\frac{T_n+T_{n-1}}{2}\right)\left(S_n-S_{n-1}\right)$$

The calculation is facilitated by the use of the relative current u and thermoelectric potential Φ.[5, 6]

$$(8) \qquad \Phi = ST + \frac{1}{u}$$

The heat flux ($Q = J\Phi$), voltage ($V = \Delta\Phi$) and power density distribution along the thermoelectric leg can be easily calculated from Φ.[5]

For calculating the efficiency η needed for ZT, $\Phi(T)$ provides a simple expression.[5]

$$(9) \qquad \eta = 1 - \frac{\Phi(T_c)}{\Phi(T_h)}$$

Device *ZT* for Thermoelectric cooling

A somewhat different ZT_{TEC} can be similarly defined for thermoelectric cooling devices. Using a similar exact method to calculate the maximum possible coefficient of performance ϕ, from temperature dependent properties $S(T)$, $\rho(T)$, and $\kappa(T)$ the *thermoelectric cooling device figure of merit* ZT_{TEC} is defined from[7]

$$(10) \qquad \phi = \frac{T_c}{\Delta T}\frac{\sqrt{1+ZT_{TEC}} - T_h/T_c}{\sqrt{1+ZT_{TEC}}+1}$$

Similar to equation 2, this form is derived for thermoelectric materials with constant S, ρ, and κ.[2]

Acknowledgements

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