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Performance optimization of thermoelectric devices and its dependence on materials properties

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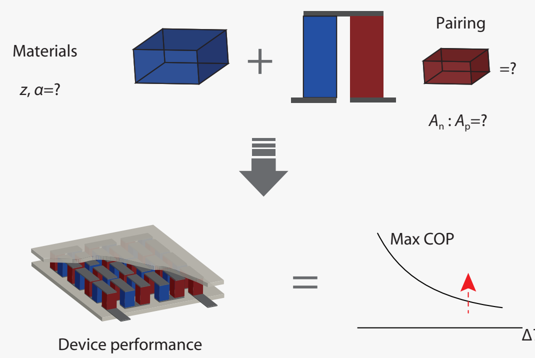
In this perspective, we discuss the optimized performance of thermoelectric cooling devices and how it is affected by materials properties. The discussion is based on simulations using a numerical method with one dimensional transport equations and the concept of relative current density. The coefficient of performance (COP), representing the efficiency of a device, is of key importance such that when designing a new type of device, it is the parameter to be maximized, whereas others such as the cooling power, can be set by adjusting the dimensions of the design. The COP of a single stage device under a given temperature difference, is only determined by the materials' figure of merit zT (or z) and the Seebeck coefficient α. While it is the higher the better for the former, the influence of α is complicated. While higher zTs are always preferred, materials with comparably high zT and very different α could be valuable in constructing graded legs that outperform uniform ones. Lastly, proper pairing of legs is important to ensure the materials properties are used to their full potential.



Thermoelectric devices are small but nimble components used for direct conversion between heat and electrical energy[1]. Devices work under temperature gradients to generate electricity are called thermoelectric generators. Their application on a series of NASA's space missions has showcased the immense value of thermoelectric technology[2]. It has also been actively pursued to use this technology to reduce fossil fuel consumption and pollution. Meanwhile, devices designed for use around room temperature make up a decisive majority of commercial thermoelectric devices, which has a market close to a billion US dollars[3]. They are used for cooling or temperature regulation[4]. Application examples include various consumer products (mini-fridge, car-seat ventilators, dehumidifiers, etc.) and medical equipment (vaccine or insulin storage, PCR thermal cyclers). Thermoelectric devices also provide cooling for microelectronic and telecommunication devices such as laser diodes, photodetectors, and CCD cameras. Thermoelectric devices can also be used in wearable devices to provide personal comfort and temperature regulation[5], such as on biohazard suits. Compared with conventional techniques, thermoelectric coolers are more compact, lighter-weight, more cost effective for many applications.

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A very heavy weight of research effort has been placed on materials development[6]. New researchers learn early on that materials figure of merit $zT = \alpha^2T/\rho\kappa$ (α the Seebeck coefficient, ρ the resistivity, κ the thermal conductivity, T the temperature) dictates device performance. One would wonder to what extent this statement is correct. Also, is zT the only merit index? Under what scenario it's more favorable to have materials better in another property (for instance, the power factor, defined as α^2/ρ), despite of lower zTs? This perspective is devoted to discuss these. The discussion is limited to thermoelectric devices used for cooling. This is because: a) Devices operating at elevated temperatures for power generation faces additional challenges such as diffusion, high temperature stability, or thermal chock, which clearly makes zT not the only measure of a materials worthiness. b) Such devices so far are highly specialized for niche applications. c) Last but not the least, it has been well discussed in literature[7]. While the problem setup is for cooling devices, many conclusions will apply to devices used for generation with small temperature differences around room temperature.

Discussion

The key parameter to measure device performance

Fig. 1 is the performance chart of a typical cooling device. The performance can be discussed in several metrics. The first is the coefficient of performance (COP). This is the rate of heat removed by a heat pump Q on the cold side, divided by the

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power it consumed P, COP = Q/P. The cooling power primarily arise from the Peltier effect. This process consumes power together with Joule heating. Removal of the latter will compromise the device's cooling ability. As the temperature difference across device ΔT increases, the amount of Fourier heat flux (the natural heat flow) will increase. When we factor all these in, it is not surprising to find a device's COP a function of, and decreases with increasing ΔT. This eventually lead to the second metric of TEC performance: ΔT_{max}, at this temperature the heat removal rate from cold side approaches zero, and this is the maximum temperature difference this device could maintain. Lastly, a device has a maximum cooling power Q_{max}, which is the maximum heat-removal rate achieved when there is no temperature difference.

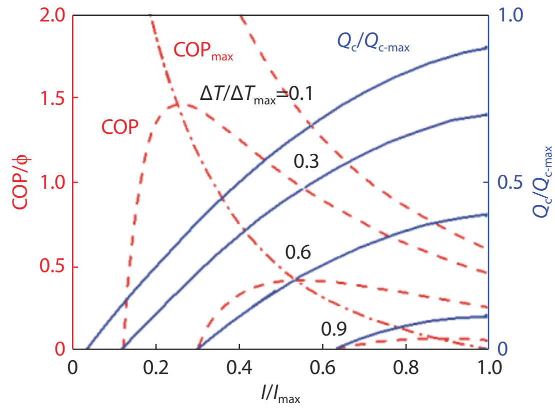

Fig. 1 Performance of a single stage commercial device as functions of relative operating current up to I_{max}.[22] Copyright 2022, Elsevier. The current corresponding to the maximum cooling power when ΔT = 0, $Q_{c\text{-}max}$. Data are shown for four temperature differences across the device, relative to the maximum temperature difference it could maintain ΔT_{max}, 0.1, 0.3, 0.6, and 0.9. Red dashed curves are COPs. The solid, blue curves are cooling power Q_c relative to $Q_{c\text{-}max}$. The red dash-dot line connects the maximum COPs at different temperatures.

Optimizing the three metrics of performance involves different aspects of device design: 1) The cooling power Q (more fundamentally Q_{max}) can be adjusted by changing the size of the device. 2) The efficiency COP and ΔT_{max}, on the other hand, don't scale with dimensions. An optimized device should always have its COP maximized under its designed working condition (temperatures). The required cooling power Q can always be matched by changing its dimension.

Of course, in practice a device might need to remove more (or less) heat than designed from time to time (transient working conditions). This can be done by increasing (or decreasing) the operation current at a cost of lower efficiencies (especially when $\Delta T << \Delta T_{max}$, see Fig. 1). This I (hence Q) dependence of COP (see Fig. 1) is determined by material properties (and shape of the legs). Some applications could have dynamic loads (different from transients), for instance, 50% of time with a cooling power Q_1, while the other 50% with $Q_2 > Q_1$. Designing materials with higher zT, and thus larger peak COP for a single Q, is more practical than looking for materials that lead to a lower peak but a larger average COP among multiple Q values. Our discussion is focused on devices used for a fixed normal working condition. Devices that operate under multiple conditions can be discussed case by case, sometimes with better solutions from system-level design.

Materials properties that affect COP

The basic unit for device performance analysis is a couple made of a n-leg and a p-leg. Electrical and heat flows through the legs have been analyzed using different methods that don't require finite element simulation. Among them is the method based on the concept of relative current density u, which was used by researchers including Müller[8], Seifert[9,10], and Snyder[7,11] in analyzing both thermoelectric generations as well as cooling devices.

Assuming the temperature change monotonously from one side to the other side of legs, we can write the power consumed per length, P, and heat flow, Q, over an infinitesimal segment in the legs as following with vector directions set up as in Fig. 2:

$$P = \alpha \nabla T I + \rho I^2 / A \quad (1)$$

$$Q = \alpha T I - \kappa \nabla T A \quad (2)$$

I is the current through the leg, A is its cross-sectional area. Conservation of energy requires that at steady state $P = \nabla Q$, this lead to the heat flow equation:

$$\nabla(\kappa \nabla T A) = \nabla T \frac{d\alpha}{dT} T I - \rho I^2 / A \quad (3)$$

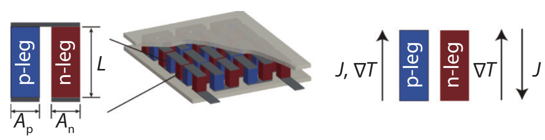

Fig. 2 Problem setup for analysis. The lengths of legs, as well as cross-sectional area are dimensional parameters. Arrows to the right define the vector directions.

The relative current density u for the p-leg is defined as:

$$u = \frac{J}{\kappa \nabla T} \quad (4)$$

J is the current density. For n-leg the expression of u has a minus sign to account for the opposite current direction.

Define the thermoelectric potential for cooling as:

$$\Phi = \alpha T - 1/u \quad (5)$$

We have $Q = \Phi I$, and $P = \nabla Q = \nabla \Phi I$.

The COP of a segment i in a leg is: $COP_i = Q/P\mathrm{d}x = \Phi/d\Phi$. Fig. 3a shows how COP of such a segment changes with u for

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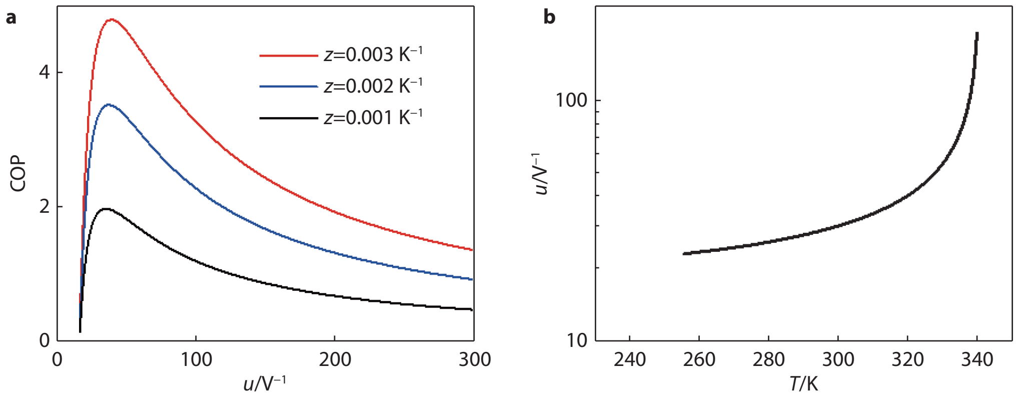

Fig. 3 **a**, COP as a function of u for materials with different z (assuming hot side temperature 300 K, ΔT =10 K, α = 200 μV/K). **b**, u across a p-leg made of commercial material working under maximum ΔT. Instead of position, u is plotted against temperature.

materials with different z values (assuming constants for each segment). Note the optimum u changes only a little for different cases.

Now consider the entire leg as many infinitesimal heat pumps connected in series, each having COP_i, the COP of the leg can be written as:

$$1+\frac{1}{COP}=\frac{Q_{out}}{Q_{in}}=\prod\left(1+\frac{1}{COP_i}\right)= \exp\left[\int \ln\left(1+\frac{1}{COP_i}\right)\right]\approx\exp\left[\int\frac{1}{COP_i}\right] \tag{6}$$

The last step in eq. 6 is a fairly good approximation since COP_i >>1 as ΔT diminishes.

$$1+\frac{1}{COP}=\exp\left[ln\frac{\Phi_H}{\Phi_C}\right]=\frac{\Phi_H}{\Phi_C} \tag{7}$$

Φ_H and Φ_C denotes Φ at the hot side and cold side. Thus:

$$COP=\frac{\Phi_c}{\Phi_H-\Phi_c} \tag{8}$$

u changes across the leg following a master heat equation which is required because $P = \nabla Q$: (A is constant, $\nabla J = 0$)

$$\frac{du}{dT}=\frac{du}{dx}\frac{dx}{dT}=\left[\frac{\nabla J}{k\nabla T}-\frac{J}{(\kappa\nabla T)^2}\nabla(\kappa\nabla T)\right]\frac{dx}{dT}= \left[\frac{\nabla J}{k\nabla T}-\frac{J}{(\kappa\nabla T)^2}\left(T\frac{da}{dT}\nabla TJ-\rho J^2\right)\right]\frac{dx}{dT} \tag{9}$$

Eq. 9 leads to the master heat equation:

$$\frac{du}{dT}=-u^2T\frac{d\alpha}{dT}+\frac{\alpha^2}{z}u^3 \tag{10}$$

u can be solved by dividing a leg into many local segments each spanning over a small ΔT (such as 5 K). Taking T_n as the average temperature in the n^{th} segment while all transport properties with each segment are constants due to the small ΔT, u can be approximated by:

$$\frac{1}{u_n}=\frac{1}{u_{n-1}}\sqrt{1-2u_{n-1}^2\frac{\alpha^2}{z}\Delta T+T_n[\alpha(T_n)-\alpha(T_{n-1})]} \tag{11}$$

Thus, all u_n throughout the leg are fixed once u_0 on the hot end of the leg is set as an initial input, which can take any value regardless of materials properties. Fig. 3b shows an example of how u changes across a p-leg with a commercial material around the room temperature. Once u_{n-1} is known, u_n only depends on zT and α. Combine this with the definition of Φ. We can conclude that: 1) The COP of a device under fixed T_H and T_C is determined by z, α and J (input current density). Other parameters, including ρ, κ, or the often-used power-factor (α^2/ρ), are not indexes of materials performance. 2) Dimensions of legs have no influence on the maximum achievable COP.

What about Q? How to ensure a device working under optimized COP pumps sufficient amount of heat Q_c from the cold end? We can write:

$$Q_c/A=\kappa\nabla T(au_cT-1) \tag{12}$$

We see that the cooling power per area Q_c /A can be readily adjusted by changing ∇T. With temperatures on both sides of a device fixed, ∇T is changed by changing the length: the shorter the legs, the larger the cooling power density. Again, a higher cooling power alone is not equal to a better device design, another design that allows maximum COP can readily have its legs scaled to provide the same cooling power. Even if a higher cooling power density is required, the length of legs can be shortened to deliver it.

This statement reaches its limit as the lengths of legs are reduced to produce larger and larger cooling power densities: the lengths will eventually be short enough that contact resistance is no longer negligible. For Bi_2Te_3 based devices, good electrical contact resistance is[12] around 1μΩ.cm², whereas the materials' resistivities are[13] around 10μΩ.m. This means the contact resistance will be less than 5% of total resistance as long as the length of legs are greater than 0.2 mm. Legs on commercial devices (such as Marlow Industry RC12-2.5, 2 W/cm² cooling power density at 20 °C ΔT) are a few millimeters long, thus by reducing their lengths we could produce 5 to 10 times larger cooling power densities without losing COP due to the contact resistance.

Not only the dimensions of a leg have no impact on its maximum COP, varying the cross-sections across the leg can't make it better, either. We can show that as long as ∇I=0, the master heat equation is still given by eq. 10:

$$\frac{du}{dT}=\frac{d}{dx}\left(\frac{I}{k\nabla TA}\right)\frac{dx}{dT}=\left[\frac{\nabla I}{k\nabla TA}-\frac{I}{(\kappa\nabla TA)^2}\nabla(\kappa\nabla TA)\right]\frac{dx}{dT}= \left[-\frac{I}{(\kappa\nabla TA)^2}\left(T\frac{da}{dT}\nabla TI-\rho I^2/A\right)\right]\frac{dx}{dT}=-u^2T\frac{d\alpha}{dT}+\frac{\alpha^2}{z}u^3 \tag{13}$$

With the same input u_0 thus Φ_H, legs with non-uniform cross-sections produce the same u_n (across its length in term of temperature) thus Φ_C as a leg with uniform shape. Of

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course, the simple model is based on 1D conduction, which is only for the case where each segment is approximately uniform, and between two neighboring segments the flow of charge and heat quickly redistribute and resume 1D conduction over a negligibly small distance compared with the segment length. Thus, eq.13 would be mostly accurate with a) slower changes in the cross-section, and b) smaller ∇T thus each segment being longer. In addition, for cases where 3D conduction can't be neglected, we could argue that such legs will at best be as good as uniform ones. Since any lateral component of the electric current will generates Joule heat without useful heat removal.

Goldsmid pointed out[14] that using trapezoidal legs can't make devices better (without elaborating why). There have also been a few works[15,16] that compared devices with legs of different shapes and came to the same conclusion in term of performance. In some reports[17–19] a more favorable shape was identified but only due to a set limitation in the dimensions, such as the height. Moreover, it's necessary to point out here that Wu et al. has suggested[20] that by engineering the shape of segmented legs better thermoelectric generators can be made. Their study was based on the same mathematical model used here, however, the finding is incorrect due to a mistake in the setup of the problem (*P* and *Q* was defined as the power density and heat flux, which is not suitable for the geometries discussed). In fact, the same conclusion should hold for generators, that varying the cross-section of a leg will not produce better efficiencies.

There are two materials properties that matter: z and α. The overwhelmingly dominant factor is z, which is a pleasant relief for materials researchers that take higher zTs the only target when developing new materials (given the small relevant T span, we consider zT and z interchangeably in this discussion). In theory, α could drastically change COP with zT remaining the same, as shown in Fig. 4. In reality, however, keeping in mind that greater z is always preferred, and transport physics determines what values α could be. For inorganic semiconductors, $|\alpha|$ is often around 250 μV/K when zT is at its peak for a compound as the carrier density is optimized, this can be shown from transport theory as well as survey of known examples[21].

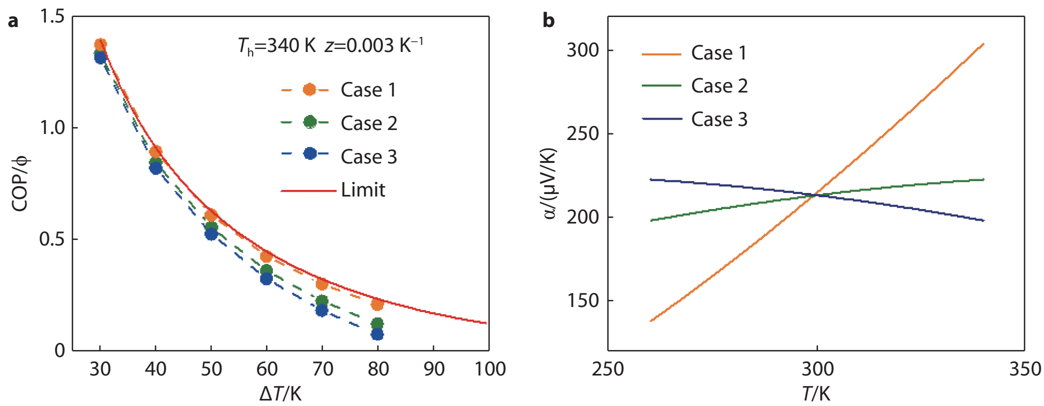

Fig. 4 **a**, Maximum COP of a single leg for three hypothetical cases, all have the same constant $z = 0.003$ K^{-1}. The limit COP is obtained when all segments along a leg could operate at the most efficient conditions. See more discussion in section 2.4. **b**, The temperature dependence of α for each case. Case 2 is the dependence of α in commercial p-type Bi_2Te_3 alloy.

In a previous work[22], we evaluated the possible difference in COP caused by differences in α from hypothetical, homogeneous materials, where it changes within a realistic range (note this doesn't mean a real material is available). For a single leg made of materials all with $zT = 1$, one can expect a 33% difference at $\Delta T = 80$ K (hot side at 340 K). The best scenario is a small $|\alpha|$ with a large temperature dependence dα/dT. Nonetheless, the difference is most significant under large ΔTs close to its maximum. It diminishes (to < 1%) at small $\Delta T = 10$ K. If significantly better materials can be found in the future, the importance of α can become more significant.

Pairing of legs

Discussion of device performance must include a pair of legs, and a better leg does not always lead to a better device. The pair of n- and p-legs should be optimized such that: a) If the two materials have similar zTs (i.e., the two legs have similar COPs), the legs' cross-sections should be designed to allow each leg to have the optimum initial relative current density $|u_0|$ such that each leg reaches maximum COP at the same time. b) If the two legs have notably different COPs, the design should allow the better leg to operate under its maximum COP, whereas the other leg may operate under a less-than-optimum COP in favor of less power consumption (i.e., less relative contribution to the pair's total COP). c) In extreme cases, the less efficient legs should be replaced by a conducting wire to minimize its power consumption, forming a 'uni-leg' structure. Fig. 5 provides a hypothetical example, where two n-type materials (with constant zT = 0.1 and 0.2) and a Cu wire were compared. The p-leg case is a material with zT = 0.5, which is comparable to the performance of some composites. A material with zT = 0.1 is irrelevant for application in this case -- a uni-leg would readily deliver a better performance. On the other hand, a material with zT > 0.2 can be justified for use in devices, with the optimized couple efficiency better than a uni-leg (despite not significant). Note even though the zT = 0.2 leg can't achieve ΔT = 30 K on its own, using it to pair with a zT = 0.5 leg is still a reasonable choice.

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When a pair is made of dissimilar materials, the material's zT for the less efficient leg becomes not as important to the pair's performance as to the leg's. If we construct a pair using the commercial Bi_2Te_3 alloy ($Bi_2Te_{2.7}Se_{0.3}$) as the n-leg, our simulation found (Fig. 6) that whether choosing a PEDOT:PSS with[23] zT = 0.42, or a PEDOT:PSS + Bi_2Te_3 composite with[24] zT = 0.58, makes essentially no difference in device performance: a 35% greater zT yet not better device performance in this particular case.

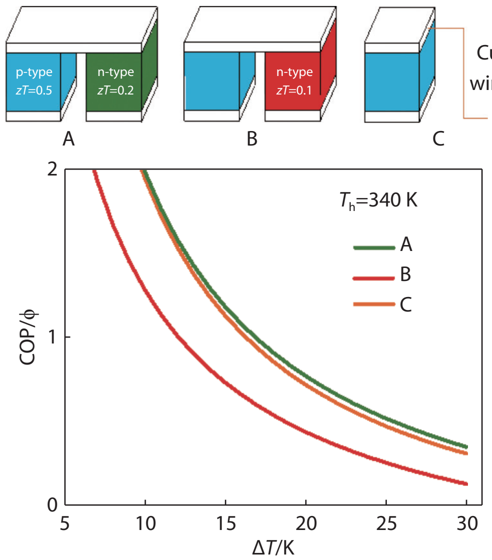

Fig. 5 Optimized couple COP for three hypothetical cases. p-leg is a material using $Bi_{0.5}Sb_{1.5}Te_3$ properties except for thermal conductivity which is scaled to have zT = 0.5. n-legs are different materials based on $Bi_2Se_{0.3}Te_{2.7}$ but scaled to have **A**: zT = 0.2, and **B**: zT = 0.1. **C** is an uni-leg design with Cu wire. Dimensions of legs are not to scale.

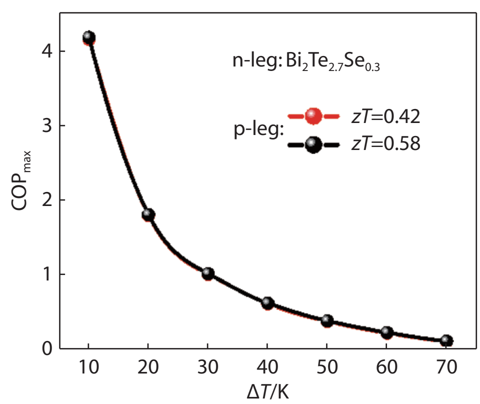

Fig. 6 Maximum COP under different ΔT for two devices with p-legs made with **a** zT=0.42 and α=70 μV/ K, **b** zT=0.58 and α=170 μV/K.22 Copyright 2022, Elsevier.

Some discussions based on COP of a single leg need to be revisited for pairs of legs. For instance, for a single leg, the magnitude of α (same zT) causes negligible difference in COP when the temperature dependence $d\alpha/dT$ is weak. In a pair, however, this depends on the other leg. For the cases considered in Fig. 7, $|\alpha|$ makes little difference same as for a single leg if materials for both legs have similar zTs. But if their zTs are different, then α could make a significant difference at all temperatures. The reason is because in such pairs, optimum running conditions don't always require the less efficient leg to reach its best COP. Note the optimum size ratios between the two legs are different in these cases.

More detailed discussions related to Fig. 5 - 7, as well as on material selection and size ratio optimization in general, can be found in our previous article[22]. It is necessary to point out here, that the size ratio is simply one in commercial devices using Bi_2Te_3 alloys. This is because the materials for the two legs have very similar zT and $|\alpha|$, thus legs with the same dimension is readily close enough to the optimized design. This does not mean, nonetheless, that when new devices are designed, one can simply duplicate the layout of commercial Bi_2Te_3 devices.

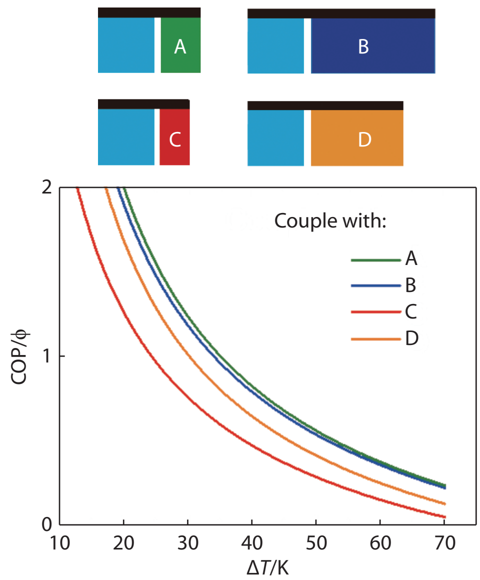

Fig. 7 Optimized couple COP for four couples. p-legs (light blue) are commercial Bi_2Te_3 (see Fig. 4b); n-legs are: **A**, a hypothetical material with zT same as n-Bi_2Te_3, while α = −300 μV/K; **B**, same as A with α = −100 μV/K; **C**, a hypothetical material with zT half of commercial n-Bi_2Te_3, and α = −300 μV/K; **D**, same as C but α = −100 μV/K. The illustrations represent optimized cross-sectional area ratios assuming square or circular cross-sections.

Beating the limit from *zT* with graded legs

Graded legs are not new to thermoelectric devices. Although, the idea of grading (or, segmentation) stems from the temperature dependence of z or zT, such that stacking different materials with highest zT at different temperatures can potentially increase the device performance[25–28]. This is more beneficial for thermoelectric generators working under large temperature differences. For thermoelectric coolers, the same idea is hardly an option, because the temperature differences are smaller, and there are no better alternatives to the Bi_2Te_3 alloys within such temperature ranges.

Even if materials with higher zTs are not available, there is still room for improvement. Fig. 8 shows the distribution of u along a leg made of commercial p-type Bi_2Te_3 alloy operating under maximum temperature difference of 85 K (hot side at

340 K), together with the u required (called the compatibility factor, s) for each segment to operate at its maximum efficiency. This relation has been pointed out by Snyder et al.[11], suggesting that most part of the leg is actually operating far from optimum while the leg as a whole is. If somehow the mismatch can be reduced, one can expect better leg performance (remember, this is not always equal to device performance), even without a higher zT. One obvious way to do so is to allow the current density J to be adjusted amid the leg, such that one can redefine a second input u_0 amid the leg. This can be realized with cascaded or multi-stage cooling devices and accounts for part of the reason why they can reach larger ΔTs. With only one input u_0, a strategy is to adjust the temperature dependence of u and s, since z should be maintained as high as possible, the most likely solution is graded legs using dissimilar materials. Earlier articles by Bian et al.[29], Muller et al.[8], and Snyder et al.[11] have pointed out this. An inhomogeneous leg design was described by Bian et al.[29], which utilized a fast-increasing α profile at the hot end albeit zT was actually lower along most part of the leg. This design can be realized using different Bi_2Te_3 alloys, and is expected to result in a 27% increase in maximum ΔT (from 67 K for commercial devices to 84 K, 300 K hot side). Another design by Muller et al.[8] was expected to achieve an 15% increase in maximum ΔT.

Similarly, as shown in Fig. 9, we considered a segmented p-leg made with commercial Bi_2Te_3 for the lower temperature section and graded materials for the rest (60% in length, 30 K in temperature drop). The graded section has α fast increasing from 210 μV/K to 400 μV/K and a lower zT (assumed constant $zT = 0.7$ for simplicity). The α and zT profiles are achievable, based on available reports. Our simulation has indicated, that despite of a lower overall zT, this leg performs better at large ΔT (> 72 K) compared with a homogeneous, commercial leg. The maximum temperature difference (set by COP ≥ 0.1) is increased by 6% from 85 K to 90 K (hot side 340 K). COP at $\Delta T = 80$ K can increase by 14%. This improvement is not as great as that suggested by Bian et al. or Muller et al., however, we used COP ≥ 0.1 to define maximum ΔT and it is not clear what criteria was used in the literature. As COP approaches zero one can expect the difference to increase rapidly.

Since few material could offer comparable zT (or z) as Bi_2Te_3 based alloys, developing devices with better performance than state-of-the-art today using this strategy is not very rewarding. Instead, if we consider new devices such as printed coolers, the best available zTs are mostly between 0.5 and 1. Graded design would be more beneficial in this case while easier to implement at the same time. If we assume all materials to have similar zTs of 0.5. The p-leg is made of four segments with different α = 100, 200, 300 and 400 μV/K (numbered 1 through 4, due to small ΔTs their temperature dependences are neglected). Fig. 10a shows the simulated device performance (from a pair of legs, uniform n-leg zT = 0.5). Compared with a uniform p-leg, the segmented design reduced the mismatch between s and u (Fig. 10b). The maximum temperature difference can be extended by 10 K, with maximum COP at $\Delta T = 50$ K increased by 48%.

Table 1 below listed materials having zT around 0.5 at 300K with different α. Even though not all of them are printable, candidates can be found to prove the concept shown in Fig. 10.

Constructing such a graded leg is arguably no less difficult than developing materials with higher zTs. And it is true that progresses, although slow, are still being made in term of zTs around room temperature. The highest zT achieved in labs today[30] is now over 1.6 at 300 K, in contrast, zTs of materials used in commercial devices are a little less than one. Nonetheless, graded designs aim at reducing the mismatch between u and s, representing a paralleled approach independent of progresses in materials' zTs.

Summary

We have pointed out that for a thermoelectric cooling device, the key index of merit is its COP (cooling efficiency), whereas the cooling power, or cooling power densities, are just parameters to be adjusted to specific applications. The better device design, in term of performance, is always the

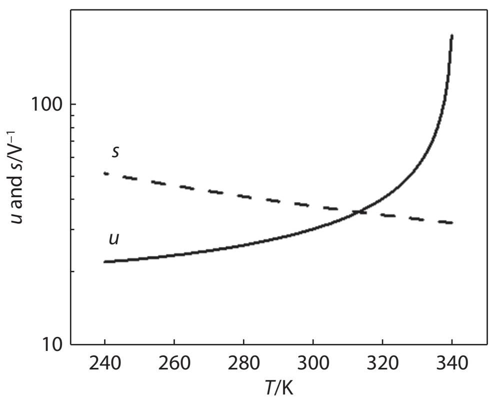

Fig. 8 u and s across a p-leg of commercial Bi_2Te_3 alloy operating under maximum ΔT with hot side temperature 340 K.

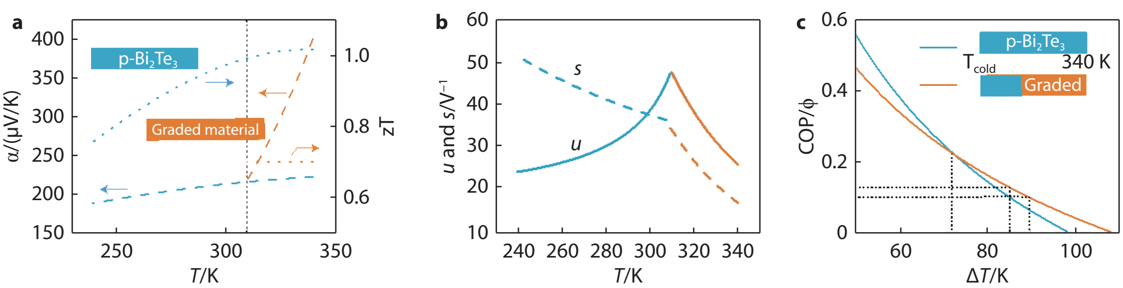

Fig. 9 Comparison of two leg designs: one is commercial (blue) and the other a hybrid with commercial material and a graded section. **a**, Seebeck coefficient α and zT as functions of temperature. **b**, The u and s profile in the hybrid design. **c**, Maximum COP as a function of ΔT.

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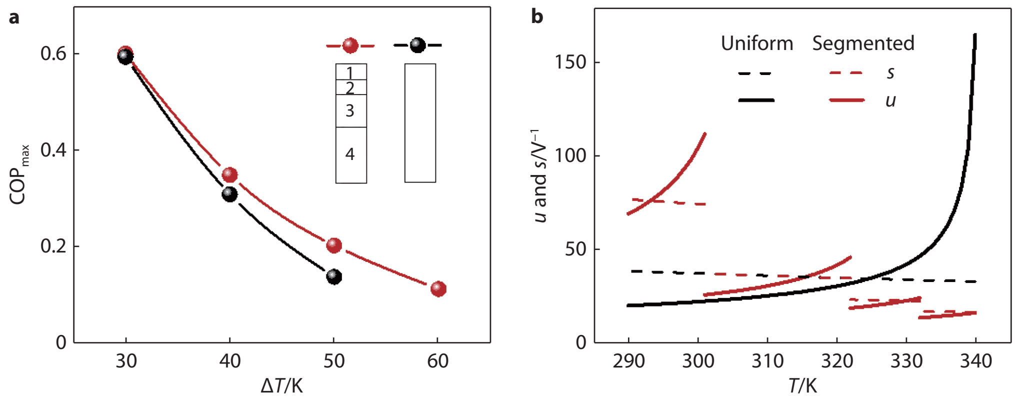

Fig. 10 **a**, Simulated performance of two devices with hot side at 340 K. One with a four-segmented p-leg (numbered 1 through 4 from the cold side to the hot side), and the other with a uniform p-leg. Relative length for each segment is illustrated. **b**, *s* and *u* in each device.

Table 1. p-type materials with reported zT around 0.5 at 300 K. The Seebeck coefficient α vary across a wide range, which can be utilized to construct the discussed, graded legs.

Material (ref.)	α (μV/K)	zT
PEDOT:PSS[23]	70	~0.4
Cu_2Se[31]	150	0.5
PEDOT:PSS+Te-NW[32]	110	~0.4
PEDOT:PSS+Bi_2Te_3[24]	170	~0.6
$AgSbTe_2$[33,34]	300	0.8
Tellurene[35]	410	0.6

one with a higher COP under a designed operation condition, and is not the one with a larger cooling power. This is subject to only rare exceptions, such as when there are multiple operation conditions with small and large ΔTs each with different need of cooling power. For materials, their index of merit in term of performance is predominantly zT or z. Parameters like the power factor, electrical resistivity and thermal conductivity, can't be used to suggest better materials. The Seebeck coefficient α, especially its temperature dependence, has some impact on COP on the single-leg level. As most new designs deal with small ΔT ($zT < 1$), such impact is often insignificant. The magnitude of α becomes important when the n- and p-leg have different zTs, it is better for the less efficient leg to have lower $|\alpha|$. While developing new materials with higher zT should be the primary goal for materials research, it is meaningful to identify materials having relatively high zTs with small and large α. In most inorganic semiconductors with single-parabolic-band behavior, α should be around 250 μV/K when zT is optimized. However, higher α can result in systems with multiple bands separated by a small energy offset. On the other hand, α in organic and composite systems tend to be significantly lower than 250 μV/K when zT peaks, which is favorable when they are used for the less efficient legs. Moreover, a series of materials with similar zTs but very different α can be used to construct graded legs, which will perform better at large ΔTs than these materials alone.

Aside of a leg's performance, pairing is also critical for device design. Considerations include choosing the most suitable material candidate, as well as setting the right size ratio of the two legs. For the former, material with a higher zT don't necessarily lead to better device performance, especially when used as the less efficient leg. On the other hand, a material could be useful for certain applications even if its zT seems too low to achieve the sufficient ΔT. This is because it can help make a pair that out-performs a uni-leg. Setting the right size ratio is essential in this case and in general. The optimum is not always achieved when both legs are operating at their own best COP, nonetheless, the best ratio can be determined by relatively simple numerical methods. We hope the discussion here could help the development of new thermoelectric devices.

For devices used for generation with small temperature differences around room temperature, many conclusions here can also be applied (note the details can be different). This include the dominant importance of z and α for efficiency, the ineffectiveness of using complex shapes for legs to improve performance, and the importance of proper leg pairing.

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■ CONFLICT OF INTEREST

The authors declare no conflict of interest.

■ AUTHORS' CONTRIBUTIONS

H. Wang and Z. Pan designed the research. Z. Pan conducted the modeling and analysis. H. Wang wrote the paper. H. Wang and Z. Pan edited the paper and approved the final version.

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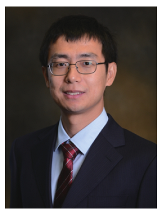
Biography



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