Is Thermoelectric Conversion Efficiency of a Composite Bounded by its Constituents?

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Abstract

We analyze the conversion efficiency of thermoelectric composites, and conclude that thermoelectric figure of merit ZT as we know it is ill-defined for composites, and is irrelevant for their conversion efficiency. In addition, we prove that thermoelectric conversion efficiency of a composite is not bounded by its constituents, and can be higher than all its constituents in the absence of size and interface effects, in contrast to previous claim. Conditions on constituent phases for enhanced conversion efficiency in layered composites are also identified, and the upper bound on their conversion efficiency is established. This points to a new route for high efficiency thermoelectric materials.

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Thermoelectric materials have attracted significant interests in recent years due to their capability to convert heat directly into electricity and vice versa[1], which promises a wide range of energy and environmental applications in waste heat recovery[2,3], solid state cooling and thermal management[4], solar energy harvesting[5], and carbon reduction[6], among others. In this letter, we examine whether the conversion efficiency of a thermoelectric composite is bounded by its constituents in the absence of size and interfacial effects, motivated by the reality that the wide spread applications of thermoelectric materials are largely hindered by their relatively low efficiency[7]. It is well known that thermoelectric conversion is governed by the figure of merit ZT of materials[8],

$$ZT = \frac{\varepsilon^2 \sigma T}{\kappa}, \tag{1}$$

wherein high conversion efficiency requires not only high Seebeck coefficient ε, but also high electric conductivity σ and low thermal conductivity κ. These competing requirements turn out to be rather difficult to satisfy simultaneously in a single-phase thermoelectric since all these properties are intimately connected to each other[9,10], and much of the recent advances in thermoelectrics originates from nanostructured materials with prominent quantum confinement effects or phonon scattering at interfaces.[11–24].

While many properties of composite materials can be enhanced with respect to their constituent phases as demonstrated by both theories and experiments[25–27], it was suggested from micromechanical analysis that the thermoelectric figure of merit of a composite is bounded by its constituents in the absence of size and interfacial effects[28,29]. As a result, majority of the efforts in thermoelectric composites focus on quantum confinement at nanoscale and phonon scattering at interfaces[30–33]. The analysis, however, was based on a rather strong assumption that both $T\varepsilon\sigma$ and $T\varepsilon^2\sigma$ are constants independent of temperature T, which is not realistic. In this work, we revisit the problem, and conclude that (1) thermoelectric figure of merit ZT as we know it is ill-defined for composites, and is irrelevant for their conversion efficiency; (2) thermoelectric conversion efficiency of a composite is not bounded by its constituents, and can be higher than all its constituents; and (3) conditions on constituent phases for enhanced conversion efficiency in layered composites are identified, and the upper bound on their conversion efficiency is established. This thus points to a new route for high efficiency thermoelectric materials that does not rely on either size or interfacial
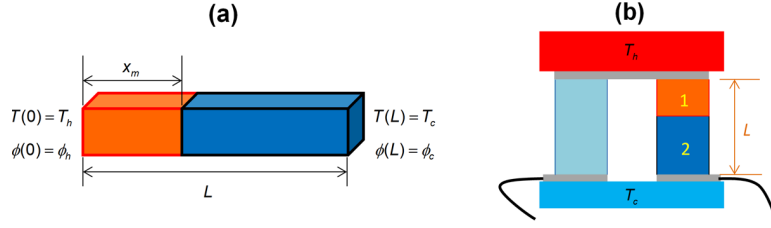
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effects.

FIG. 1: Schematics of (a) a bilayered composite and (b) a fictitious thermoelectric module.

To this end, we analyze a bilayered composite consisting of two constituent phases, as schematically shown in Fig. 1a. For each individual phase, the nonlinearly coupled transport of electric current density $\mathbf{J}$ and heat flux $\mathbf{J}_Q$ are governed by[34]

$$-\mathbf{J} = \sigma\nabla\phi + \sigma\varepsilon\nabla T, \tag{2}$$

$$\mathbf{J}_Q = -T\varepsilon\sigma\nabla\phi - (T\varepsilon^2\sigma + \kappa)\nabla T, \tag{3}$$

wherein all the material coefficients are assumed to be independent of temperature as well as boundary conditions for the time being, which can be relaxed later. Under such conditions, the distributions of temperature and potential in the bilayered composite are both piece-wise quadratic[35],

$$T_i = -\frac{J^2}{2\sigma_i\kappa_i}x^2 + a_ix + b_i, \tag{4}$$

$$\phi_i = \frac{\varepsilon_i J^2}{2\sigma_i\kappa_i}x^2 - (\frac{J}{\sigma_i} + \varepsilon_i a_i)x + c_i, \tag{5}$$

and the uniform current density can be derived as

$$J = \frac{1}{2\Omega}\{-[\Phi + \Gamma(\Delta\phi + \varepsilon_2 T_c - \varepsilon_1 T_h)]$$
$$+ \sqrt{[\Phi + \Gamma(\Delta\phi + \varepsilon_2 T_c - \varepsilon_1 T_h)]^2 - 4\Omega(\Psi\Delta T + \Theta\Delta\phi)}\}, \tag{6}$$

where subscript i is used to indicate quantities for phase i, and relevant constants are listed in the supplementary information. From the distributions of temperature and potential in the bilayered composite, it is possible to define the effective thermoelectric coefficients using a set of equivalency principle[35]. However, unlike a homogeneous material, these effective

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properties are not really material constants anymore as they depend on boundary conditions, which is a well known issue for nonlinear composites[25–27,36]. Furthermore, in order to define the three effective thermoelectric constants, two sets of thermoelectric boundary conditions are necessary, which is impossible to match the working boundary conditions of thermoelectric modules simultaneously. For example, by expanding current density J into Taylor series of $(\varepsilon_2 - \varepsilon_1)$, we can derive the effective electric conductivity of the bilayered thermoelectric to the first order of $(\varepsilon_2 - \varepsilon_1)$ as[35],

$$\sigma^*(\Delta\phi) = \frac{\sigma_1\sigma_2}{\sigma_1(1-f) + \sigma_2 f} - \frac{f(1-f)\sigma_1^2\sigma_2^2\Delta\phi(\varepsilon_2 - \varepsilon_1)}{2[\sigma_1(1-f) + \sigma_2 f]^2[\kappa_1(1-f) + \kappa_2 f]}, \tag{7}$$

where f is the volume fraction, which clearly depends on the imposed potential difference at boundaries. As such, the thermoelectric figure of merit ZT as we know it becomes ill-defined for the composite, depending on the imposed potential difference or load resistance. Thus we have to examine the thermoelectric conversion efficiency directly for a composite material, rather than relying on the concept of thermoelectric figure of merit. This is the first point we hope to make, which will be elaborated further later.

Another difficulty is that thermoelectric conversion efficiency is a performance measure for devices instead of materials, depending on both legs of thermoelectric module. In order to evaluate the thermoelectric conversion performance of a material, we propose a thermoelectric module as schematically shown in Fig. 1b, with one leg made of material of interest, and the other leg made of fictitious material with zero Seebeck coefficient and thermal conductivity, yet infinite electric conductivity. As such, this fictitious leg only serves as a path for electric current, and is not involved in energy conversion. The conversion efficiency of this idealized thermoelectric module, as a result, measures only the performance of material of interest. With this idealized model, the thermoelectric conversion efficiency H of the material can be derived using standard procedure[8],

$$H = \frac{AJ^2R}{J_U|_{x=0}}, \quad J_U = -\kappa\nabla T + \varepsilon TJ + \phi J, \tag{8}$$

with A being the cross-section area and the current density derived from $\oint \nabla\phi \cdot d\mathbf{l} = 0$ across the circuit. For a homogeneous material with optimal load resistance, this leads to classical

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formula relating conversion efficiency to ZT[8],

$$H_{\text{opt}} = \frac{T_h - T_c}{T_h} \frac{\sqrt{1 + Z\frac{T_h + T_c}{2}} - 1}{\sqrt{1 + Z\frac{T_h + T_c}{2}} + \frac{T_c}{T_h}}, \tag{9}$$

but for composite materials, such simple relationship is no longer available, and we have to evaluate Eq. (8) numerically in general.
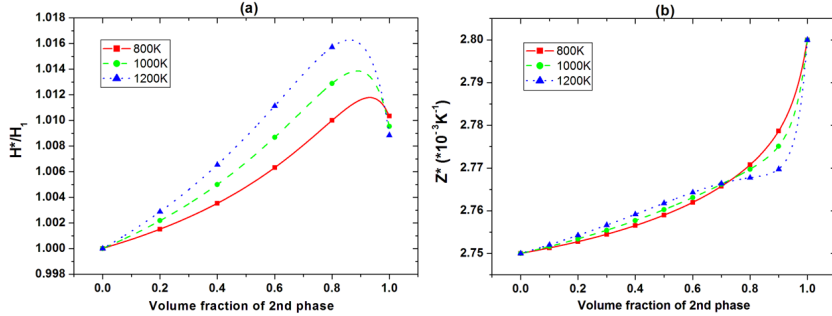

FIG. 2: Conversion efficiency of the bilayered composite consisting of Bi_2Te_3 and an optimally second phase for different temperatures; (a) enhanced conversion efficiency of the composite versus the volume fraction of the second phase, normalized by the efficiency of the first phase; (b) the effective figure of merit versus the volume fraction calculated from the effective thermoelectric properties.

To examine if the composite can have higher conversion efficiency than both of its constituent, we calculate efficiency of a bilayered composite consisting of Bi_2Te_3 and a second phase optimally matched (in a sense to be elaborated later) with Bi_2Te_3 under different temperatures, with $T_c = 300K$ and T_h chosen to be $800, 1000, 1200K$, respectively. The material constants used in the calculation are listed in the supplement information. The results are illustrated as a function of volume fraction of the second phase in Fig. 2a, and it is observed that higher efficiency than both constituents is indeed possible, in contrast to previous claim. Furthermore, we evaluate the corresponding effective Z^* with the effective Seebeck coefficient and thermal conductivity calculated under open circuit condition and the effective electric conductivity derived under optimal thermoelectric loading condition. As evident in Fig. 2b, it shows no enhancement at all and there appears no correlation between the effective Z^* and the conversion efficiency of the composite, which further supports our point that thermoelectric figure of merit ZT as we know it is irrelevant to their conversion efficiency. Alternatively, we can define the effective thermoelectric properties using equiv-

alency principle under optimal working condition in combination with the requirements of Eqs. (1) and (9) instead, and these three conditions allow us to solve for three effective thermoelectric constants simultaneously. Interestingly, this leads to two sets of effective properties, as shown in Fig. 3 along with the effective Z^* evaluated from Eq. (9). This further demonstrates that the effective thermoelectric properties of composite is ill-defined, and we have to examine the conversion efficiency directly.
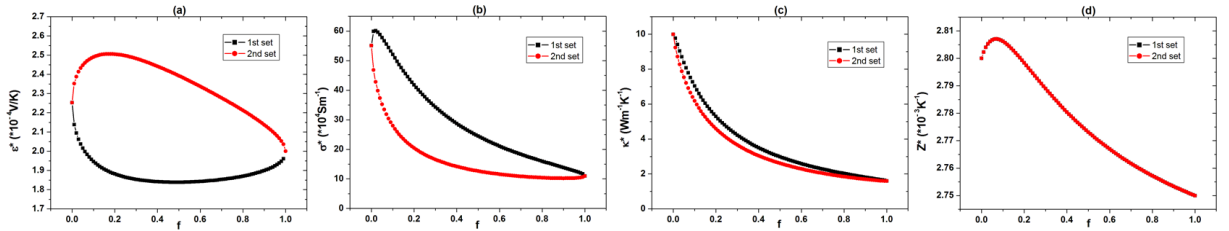

FIG. 3: Two sets of effective thermoelectric properties corresponding to a given conversion efficiency evaluated at $T_h = 800$K, with the second phase optimally matched with Bi$_2$Te$_3$; (a) electric conductivity; (b) Seebeck coefficient; (c) thermal conductivity; and (d) figure of merit.

In order to understand the enhanced conversion efficiency in bilayered composite, we rewrite the conversion efficiency as

$$H = \frac{\phi_c J}{J_U|_{x=0}} = \frac{\phi_c J}{T_h \alpha J - \frac{J^2 L}{2\sigma} + \frac{\kappa(T_h - T_c)}{L}} \qquad (10)$$

for a homogeneous material, which can be optimized with respect to current density for given temperatures,

$$J_{\text{opt}} = \frac{\sqrt{2\kappa} \sigma \varepsilon (T_h - T_c)}{[\sqrt{2\kappa} + \sqrt{2\kappa + \sigma \varepsilon^2 (T_h + T_c)}] L}. \qquad (11)$$

Since current density is a constant in the layered composite, this points to a need for carefully matching the optimal current density in constituent phases for the optimal overall conversion efficiency. Indeed, we can compare the bilayered composite with its homogenous constituents in Fig. 4a, all operating at optimal conditions for respective overall conversion efficiency. The temperature at the interface of the bilayer is labeled as T_m, which is also identified in its homogeneous constituents. It is evident that the bilayered composite can have its constituent phases matched for identical optimal current density by tailoring the material properties, which is impossible for homogeneous materials to do. This is clearly illustrated

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in Fig. 4b, where it is observed that the optimal current density for the bilayered composite between T_h and T_c is identical to that for its constituent phases between T_h and T_m as well as between T_m and T_c. For homogeneous material, on the other hand, the optimal current density for the overall structure between T_h and T_c is different from that for individual segments between T_h and T_m or between T_m and T_c. In other words, both segments of bilayered composite operate at optimal condition, while those of homogeneous materials operate under less optimal ones. This explains higher conversion efficiency in optimally matched bilayered composite, which can be rigorously proven, as shown in the supplement information.
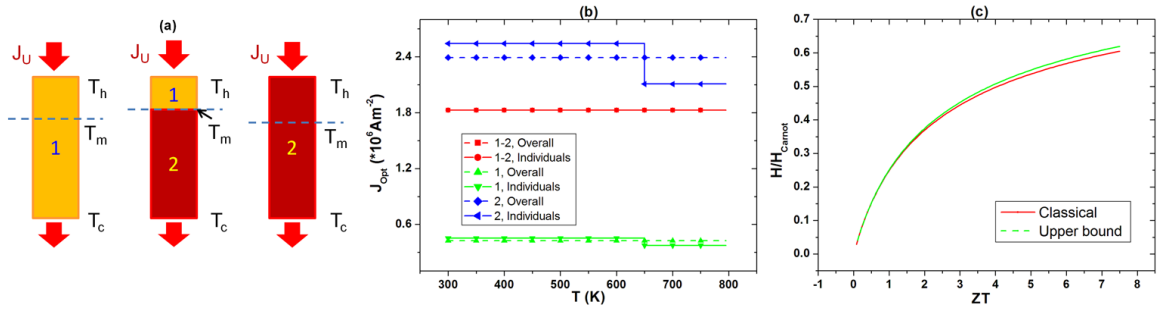

FIG. 4: Understanding enhanced efficiency in layered composites; (a) schematics for bilayered composite and its homogeneous contituent phases; (b) optimal current density for each segment under respective temperature difference; and (c) upper bound on the conversion efficiency in term of figure of merit ZT, compared with classical formula, evaluated at $T_c = 300$K and $T_h = 1200$K.

The analysis on bilayered composite points to a direction for optimal conversion efficiency of thermoelectric module, wherein the optimal current density is matched everywhere, resulting in highest conversion efficiency possible. To this end, we reorganize Eq. (11) by replace L with dx, leading to a point-wise optimal current density of

$$J_{\text{opt}} = -\kappa \nabla T \frac{\sqrt{1 + ZT} - 1}{\varepsilon T}, \tag{12}$$

which corresponds to maximum local conversion efficiency of

$$dH_{\text{max}} = \frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + 1} \frac{dT}{T}. \tag{13}$$

This is equivalent to the concept of compatibility factor[37]. When the optimality is realized

everywhere, maximum overall efficiency is realized as

$$
\begin{aligned}
H_{\max} &= 1 - \exp(-\int_{T_c}^{T_h} \frac{\sqrt{1+ZT}-1}{\sqrt{1+ZT}+1}\frac{dT}{T}) \\
&= 1 - \exp(\frac{2}{\sqrt{1+ZT_c}+1} - \frac{2}{\sqrt{1+ZT_h}+1} + 2\ln\frac{\sqrt{1+ZT_c}+1}{\sqrt{1+ZT_h}+1}), \qquad (14)
\end{aligned}
$$

where we have taken Z to be a constant for simpler derivation. This is in fact the upper bound on the conversion efficiency for the layered composite consisting of materials with constant Z, and its comparison with classical conversion efficiency of a homogeneous material with identical Z and boundary condition is shown in Fig. 4c, where a small yet definite enhancement is evident.

Finally, we point out that our analysis is related to functionally graded thermoelectrics, where it was suggested that the device thermoelectric figure merit can be higher than that of materials[38,39], for which the maximum thermoelectric performance for constant Z or ZT was also discussed[40–42]. Our point, however, is that thermoelectric figure of merit ZT is ill-defined for composites, and is irrelevant for their conversion efficiency, which was not noted before. Furthermore, it is shown that thermoelectric conversion efficiency of a composite is not bounded by its constituents, with the conditions on constituent phases for enhanced conversion efficiency in layered composites identified, and the upper bound on their conversion efficiency established. In this spirit, we note that Bergman and Levy's analysis[28] was based on local constant ZT in a heterogeneous material that linearizes the transport equation, from which it was concluded that the composite ZT is bounded by that of its constituents. Such local ZT, however, is not relevant for the overall conversion efficiency of thermoelectric composite, since the conversion efficiency of the composite is not bounded by that of its constituents as we demonstrated. This thus points to a new route for high efficiency thermoelectric materials that does not rely on either size or interfacial effects.

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[1] F. J. DiSalvo, Science **285**, 703 (1999).

[2] J. H. Yang, and T. Caillat, MRS Bulletin **31**, 224 (2006).

[3] D. Narducci, Appl. Phys. Lett. **99**, 102104 (2011).

[4] T. M. Tritt, and M. A. Subramanian, MRS Bulletin **31**, 188 (2006).

[5] D. Kraemer, B. Poudel, H. P. Feng, J. C. Caylor, B. Yu, X. Yan, Y. Ma, X. W. Wang, D. Z. Wang, A. Muto, K. McEnaney, M. Chiesa, Z. F. Ren, and G. Chen, Nature Materials **10**, 532 (2011).

[6] L. E. Bell, Science **321**, 1457 (2008).

[7] T. Caillat, J. P. Fleurial, G. J. Snyder, A. Zoltan, D. Zoltan, and A. Borshchevsky, Thermoelectrics, 1999. Eighteenth International Conference on , 473 (1999).

[8] T. C. Harman and J. M. Honig, 1967. Thermoelectric and thermomagnetic effects and applications, McGraw-Hill, New York.

[9] G. S. Nolas, D. T. Morelli, and T. M. Tritt, Annual Review of Materials Science **29**, 89 (1999).

[10] G. J. Snyder, and E. S. Toberer, Nature Materials **7**, 105 (2008).

[11] B. Poudel, Q. Hao, Y. Ma, Y. C. Lan, A. Minnich, B. Yu, X. A. Yan, D. Z. Wang, A. Muto, D. Vashaee, X. Y. Chen, J. M. Liu, M. S. Dresselhaus, G. Chen, and Z. F. Ren, Science **320**, 634 (2008).

[12] Y. Z. Pei, J. Lensch-Falk, E. S. Toberer, D. L. Medlin, and G. J. Snyder, Advanced Functional Materials **21**, 241 (2011).

[13] W. J. Xie, X. F. Tang, Y. G. Yan, Q. J. Zhang, and T. M. Tritt, Applied Physics Letters **94**, 102111 (2009).

[14] M. Zhou, J. F. Li, and T. Kita, Journal of the American Chemical Society **130**, 4527 (2008).

[15] H. Lin, E. S. Bozin, S. J. L. Billinge, E. Quarez, and M. G. Kanatzidis, Physical Review B **72**, 174113 (2005).

[16] N. Gothard, X. Ji, J. He, and T. M. Tritta, Journal of Applied Physics **103**, 054314 (2008).

[17] R. G. Yang, and G. Chen, Physical Review B **69**, 195316 (2004).

[18] A. Minnich, and G. Chen, Applied Physics Letters **91**, 073105 (2007).

[19] J. Zhou, X. B. Li, G. Chen, and R. G. Yang, Physical Review B **82**, 115308 (2010).

[20] F. Yang, T. Ikeda, G. J. Snyder, and C. Dames, Journal of Applied Physics **108**, 034310 (2010).

[21] P. N. Alboni, X. Ji, J. He, N. Gothard, and T. M. Tritt, Journal of Applied Physics **103**, 113707 (2008).

[22] Y. Q. Cao, X. B. Zhao, T. J. Zhu, X. B. Zhang, and J. P. Tu, Applied Physics Letters **92**, 143106 (2008).

[23] I. U. Arachchige, J. Wu, V. P. Dravid, and M. G. Kanatzidis, Advanced Materials **20**, 3638 (2008).

[24] X. Z. Ke, C. F. Chen, J. H. Yang, L. J. Wu, J. Zhou, Q. Li, Y. M. Zhu, and P. R. C. Kent, Physical Review Letters **103**, 145502 (2009).

[25] G. W. Milton, 2002. The theory of composites, Cambridge University Press, Cambridge; New York.

[26] S. Nemat-Nasser, and M. Hori, 1999. Micromechanics: overall properties of heterogeneous materials, Elsevier, Amsterdam; New York.

[27] P. Ponte Castaneda, and P. Suquet, Advances in Applied Mechanics **34**, 171 (1998).

[28] D. J. Bergman, and O. Levy, Journal of Applied Physics **70**, 6821 (1991).

[29] D. J. Bergman, and L. G. Fel, Journal of Applied Physics **85**, 8205 (1999).

[30] J. P. Heremans, C. M. Thrush, D. T. Morelli, and M. C. Wu, Physical Review Letters **88**, 216801 (2002).

[31] G. H. Zhu, H. Lee, Y. C. Lan, X. W. Wang, G. Joshi, D. Z. Wang, J. Yang, D. Vashaee, H. Guilbert, A. Pillitteri, M. S. Dresselhaus, G. Chen, and Z. F. Ren, Physical Review Letters **102**, 196803 (2009).

[32] H. J. Kim, E. S. Bozin, S. M. Haile, G. J. Snyder, and S. J. L. Billinge, Physical Review B **75**, 134103 (2007).

[33] D. Vashaee, and A. Shakouri, Physical Review Letters **92**, 106103 (2004).

[34] H. B. Callen, 1960. Thermodynamics; an introduction to the physical theories of equilibrium thermostatics and irreversible thermodynamics, Wiley, New York.

[35] Y. Yang, S. H. Xie, F. Y. Ma, and J. Y. Li, J. Appl. Phys. **111**, 013510 (2012).

[36] L. P. Liu, International Journal of Engineering Science **55**, 35 (2012).

[37] G. J. Snyder, and T. S. Ursell, Physical Review Letters **91**, 148301 (2003).

[38] B. Sherman, R. R. Heikes, and R. W. Ure, J. Appl. Phys. **31**, 1 (1960).

[39] E. Muller, C. Drasar, J. Schilz, and W. A. Kaysser, Materials Science and Engineering **A362**, 17 (2003).

[40] L. J. Ybarrondo, Solid State Electron **10**, 620 (1967).

[41] G. J. Snyder, Thermoelectric Power Generation: Efficiency and Compatibility, in: Thermo- electrics Handbook, edited by D.M. Rowe (Taylor and Francis, Boca Raton, London, New York, 2006), chap. 9.

[42] W. Seifert, K. Zabrocki, G. J. Snyder, and E. Muller, Phys. Status Solidi A **207**, 760 (2010).

[43] E. E. Antonova, and D. C. Looman, Thermoelectrics, 2005. ICT 2005. 24th International Con- ference on , 215 (2005).