Thermoelectric power factor: Enhancement mechanisms and strategies for higher performance thermoelectric materials

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ABSTRACT

Thermoelectric research has witnessed groundbreaking progress over the past 15–20 years. The thermoelectric figure of merit, ZT, a measure of the competition between electronic transport (i.e. power factor) and thermal transport (i.e. total thermal conductivity), has long surpassed once a longtime barrier of ~ 1 and thermoelectric scientists are targeting $ZT > 2$ as the new goal. A majority of this recent improvement in ZT has been achieved through the reduction of lattice part of thermal conductivity (κ_l) using nanostructuring techniques. The rapid progress in this direction focused the efforts on the development of experimental methods and understanding phonon transport to decrease lattice thermal conductivity. This fact left the development of ideas to improve electronic transport and thermoelectric power factor rather overlooked. With thermal conductivity of the potential thermoelectrics approaching the minimum theoretical limit, on the journey to higher ZT values, a paradigm shift is necessary toward the enhancement of the thermoelectric power factor. This article discusses the ideas and strategies proposed and developed in order to improve the thermoelectric power factor and thus hopefully move us closer to the target of a $ZT > 2$!

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1. Introduction

The direct energy conversion between heat and electricity based on thermoelectric effects is a topic of long-standing interest in condensed matter materials science. Experimental and theoretical investigations in order to understand the mechanisms involved and to improve the materials properties and conversion efficiency have been ongoing for more than half a century. The potential of a material for thermoelectric (TE) applications, both power generation and refrigeration, is determined in general by a measure of material's dimensionless figure of merit, ZT, defined as

$$ZT = \frac{\alpha^2 \sigma T}{\kappa} = \frac{PF}{\kappa} \qquad (1)$$

where α is the Seebeck coefficient, σ the electrical conductivity, κ the total thermal conductivity, and T the absolute temperature in Kelvin. Figure of merit, in essence, is a measure of the competition between electronic transport (i.e. power factor, herein defined as $PF = \alpha^2 \sigma T$)[1] and thermal transport (i.e. total thermal conductivity) in a material.

For a long time, the progress had a slow pace and the best known thermoelectric materials were bismuth telluride-based alloys with a ZT around 1. However, since the renaissance of the thermoelectric materials research, which was started in early 1990s with the seminal paper of Hicks and Dresselhaus [1] that introduced the nanostructure concept as an improvement tool, groundbreaking progress has been achieved. The majority of the efforts to improve the ZT of thermoelectric materials have been focused in two main directions: (i) the reduction of lattice part of thermal conductivity by introducing rattler atoms in cage-like structures, embedding nanoparticles in the host matrix, or nanostructuring in more conventional materials, and (ii) the enhancement of the power factor. While groundbreaking success has been achieved through the former direction, progress has not developed as rapidly for the latter. With thermal conductivity of the potential thermoelectrics approaching the minimum theoretical limit, on the journey to higher ZT values, a paradigm shift is necessary toward the enhancement of thermoelectric power factor. There have been a number of excellent reviews on TE materials focusing on the progress in different classes of TE materials [2,3], nanostructured thermoelectrics [4], and interfaces in bulk thermoelectrics [5]. There have also been excellent focused reviews on specific enhancement mechanisms to improve electronic transport [6–8]. Nevertheless, we believe that a place for a review on the power factor is missing. In this article, we aim to comprehensively review the mechanisms and approaches proposed in order to improve the thermoelectric power factor.

Fig. 1(a) and (b) shows the temperature dependence of thermoelectric power factor reported for different classes of high performance n- and p-type TE materials. It is observed that the majority of high performance thermoelectric materials possess power factor values between 0.8 and 2.5 W m^{-1}K^{-1}. The largest power factor values reported in n-type materials belong to intermediate-valence YbAl$_3$. Multiple filled skutterudites, half-Heusler alloys and SiGe are close seconds while they exhibit the largest reported values in p-type materials. Power factor values $PF \leq 0.8$ W m^{-1}K^{-1}

are reported for glass-like thermal conductivity materials (with $\kappa_l < 1$ W m^{-1}K^{-1}) such as Zintl phases, disordered Zn$_4$Sb$_3$, La$_{3-x}$Te$_4$ and SnSe compounds. In order to be able to modify charge transport to our advantage to improve the thermoelectric power factor, we first need to understand the inherent materials properties. We start by briefly reviewing the main characteristics of good thermoelectrics, particularly favorable features of electronic band structure, which benefit the thermoelectric charge carrier transport and have been used traditionally as guidelines for materials selection. It should be noted that these are just general guiding principles that assist researchers in identifying new potential materials for TE applications. As we will see not all high-ZT materials follow these criteria. Due to the inherent trade-off between electrical conductivity and Seebeck coefficient, many of these selection rules are partially contradictory. In the second part of the article, we review the proposed enhancement mechanisms for power factor improvement.

2. Best electronic band structure

Ioffe's observation in doped semiconductors served as the first empirical attempt which highlighted the carrier concentration "sweet spot" of good thermoelectrics to be $n \sim 10^{18}$–10^{20} cm^{-3}, corresponding to degenerate semiconductors or semimetals. This follows the behavior of electronic transport in real-life materials as a function of carrier concentration. As the doping concentration increases, the electrical conductivity increases and the Seebeck coefficient decreases. Therefore there exists an optimum power factor versus doping concentration at relatively high concentrations and chemical potentials, E_F,[2] close to, or inside the conduction or valence band. The position of the optimum chemical potential depends on the type of the material and on the operating temperature. At room temperature, the optimum chemical potential for a low effective mass material such as GaAs is around 50 meV [39] and for a heavy effective mass material such as silicon is around 200 meV [40] above the bottom of the conduction band.

The intriguing question of "What is the best electronic band structure a thermoelectric material can have?" has been the subject of theoretical studies and experimental exploration for more than 30 years. The connection between band structure calculations and electronic transport coefficients is made via kinetic (or Boltzmann) transport theory [41]. This approach is valid for diffusive transport (i.e. dimensions larger than carrier mean free path) when the semiclassical picture is valid (i.e. mean free path larger than atomic distances). The Bloch–Boltzmann expressions for electrical conductivity (along x direction) and Seebeck coefficient are given by [42]

$$\sigma_x = e^2 \int_0^\infty g(E) v_x^2(E) \tau(E,T) \left(-\frac{\partial f(E)}{\partial E} \right) dE, \qquad (2)$$

$$\alpha = \frac{k_B}{e} \left[\frac{\int_0^\infty g(E) v_x^2(E) \frac{E - E_F}{k_B T} \tau(E,T) \left(-\frac{\partial f(E)}{\partial E} \right) dE}{\int_0^\infty g(E) v_x^2(E) \tau(E,T) \left(-\frac{\partial f(E)}{\partial E} \right) dE} \right], \qquad (3)$$

where e is the electron charge, m^* the density-of-states effective mass, $\tau(E)$ the momentum relaxation time for charge carriers, $g(E)$ the total electronic density-of-states (DOS) and $f(E)$ the energy distribution function. The Fermi window factor $(-\partial f(E)/\partial E)$ is a bell-shaped function centered at $E = E_F$ and has a width of $\sim k_B T$, where k_B is the Boltzmann constant and T the temperature. This factor is responsible for the fact that at a finite temperature only electrons near the Fermi surface contribute to the conduction

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[1] Traditionally, thermoelectric "power factor" is defined in the context of Z (not ZT) as $\alpha^2 \sigma$ and has been used with the units of μW cm^{-1}K^{-2}. However, defining the power factor as $\alpha^2 \sigma T$ brings about several advantages including (i) following SI units with the unit of W m^{-1}K^{-1}, (ii) similar unit for the powder factor as that of thermal conductivity allows the researcher to easily compare different materials and readily estimate the figure of merit, ZT, knowing the thermal conductivity values, and (iii) it exhibits the true maximum potential of electronic transport in a material entailing the temperature dependent nature of properties. This refers to the fact that the maximum of $\alpha^2 \sigma$ vs. T might happen at a different temperature than the maximum of $\alpha^2 \sigma T$ vs. T plot that comes into ZT calculation.

[2] To avoid confusion between the symbols for chemical potential and mobility, we use μ for carrier mobility and E_F for chemical potential. E_F is typically used for the Fermi energy, which is the chemical potential at $T = 0$ K.