Carriers: the Less, the Faster

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Abstract

Thermoelectric (TE) community has long believed that high TE performance requires an optimal carrier concentration traditionally locating in the range of ~10^{19} to ~10^{21} cm^{-3}. Herein, we propose that potential high TE performance might also be achieved at lower carrier concentrations of ~10^{18} to ~10^{19} cm^{-3}. At this range, extremely large Seebeck coefficient with low thermal conductivity can be effortlessly obtained. The next step to achieve high *ZT* values is boosting the carrier mobility. We then propose two aspects for carrier mobility optimization, including the strategies of preparing single crystals, improving crystal symmetry, texturing, controlling microscopic defects, sharpening bands, aligning bands, and modulation doping. We also suggest it rather essential to utilize multiple of the strategies to achieve the significant optimization of carrier mobility. Our proposal will be the important guidance for realizing promising performance in new TE materials as well as revisiting the TE performance for traditional systems.

Key words: Thermoelectric; Carrier concentration; Carrier mobility; Defects engineering

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Main text

Thermoelectric (TE) technology has gradually become an irreplaceable key technology in the energy field since it enables the direct and reversible conversion between heat and electric energy[1]. TE materials and their devices have practical and potential applications for both power generation and electronic cooling in the fields of aerospace, weaponry, industrial waste heat recovery, 5G chip refrigeration, and civil facilities, etc. The further and large-scale application for TE technology is dramatically limited by its conversion efficiency, determined by the dimensionless figure of merit, $ZT = S^2\sigma T/\kappa$, in which S, σ, T, and κ represent the Seebeck coefficient, electrical conductivity, absolute temperature, and total thermal conductivity (a sum of electronic thermal conductivity κ_{ele} and lattice thermal conductivity κ_{lat}), respectively. Apparently, the ideal high-efficiency TE material requires excellent electrical transports ($PF = S^2\sigma$), i.e., large Seebeck coefficient and high electrical conductivity, with low thermal conductivity, and that is, the concept of "phonon-glass electron-crystal" (PGEC)[2]. However, these TE parameters intensely couple with each other, making it challenging for improving the overall *ZT* value. During the past decades, researchers have developed enormous strategies for thermoelectric optimization, mainly including carrier concentration adjustment[3], band structure modification[4,5], atomic and nanostructure engineering[6,7], electron and phonon transports decoupling[8], and searching for new TE materials[9].

Tuning carrier concentration is the most basic but essential step for achieving high *ZT* values. Initially, TE researchers mainly focused on metals, while the switch to semiconductors became a real breakthrough in this field. Generally, the holes in *p*-type semiconductors and the electrons in *n*-type semiconductors are called major carriers, while the electrons in *p*-type semiconductors and the holes in *n*-type semiconductors are called minor carriers. The TE parameters are more or less determined by the carrier concentration *n* as:

$$S = \frac{8\pi^2 k_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n}\right)^{2/3} \quad (1)$$

$$\sigma = ne\mu \quad (2)$$

$$\kappa = \kappa_{lat} + \kappa_{ele} = \kappa_{lat} + L\sigma T \quad (3)$$

in which e, h, k_B, m^*, μ and L denote the electron charge, Planck constant, Boltzmann constant, carrier effective mass, carrier mobility, Lorenz number, respectively. The above equations indicate these parameters require to be synergized to realize the optimized final *ZT* by manipulating an appropriate carrier concentration *n*. To predict the proper *n* range for high TE performance, the classical band models are frequently utilized with the assumptions that the electronic band structure does not change from light doping and has negligible fluctuations with temperature. Resultantly, based on the single band model, the carrier concentration dependent TE parameters are illustrated as solid lines in Figure 1. Traditionally, the optimal carrier concentration for most high-performance TE materials is approximately in the range of ~10^{19} to ~10^{21} cm^{-3}, with the corresponding Fermi level close to the valence/conduction band edge (i.e., within 0.1 eV)[10].

At low carrier concentrations (< 10^{19} cm^{-3}), poorer electrical transports would result in inferior thermoelectric proper-

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ties. However, we here propose that potential high *ZT* values might also be obtained at lower carrier concentrations of ~10^{18} to ~10^{19} cm^{-3}, as shown in Figure 1. At this potential optimal *n* range, an extremely large Seebeck coefficient with a low thermal conductivity can be effortlessly obtained. The only factor that limits the thermoelectric performance is the low electrical conductivity σ. From Equation (2), carrier mobility μ is another key parameter to determine σ in spite of *n*. Therefore, to achieve high *ZT* values at this potential optimal *n* range, boosting carrier mobility is crucial.

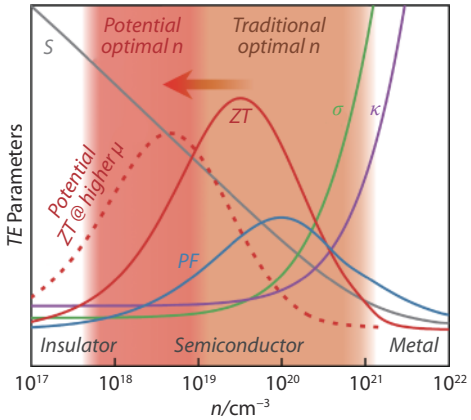

Fig. 1 Thermoelectric parameters as a function of carrier concentration predicted by the single band model. The dotted *ZT* curve indicates that potential high thermoelectric performance can be expected in the range with lower carrier concentrations through optimizing the carrier mobility.

Basically, the carrier mobility can be substantially optimized by regulating the crystal defects since all kinds of crystal imperfections and lattice distortions will hinder the carrier transport and deteriorate the carrier mobility. In polycrystalline TE materials, high density grain boundaries strongly scatter carriers, damage the carrier mobility and inhibit the improvement of TE performance. By preparing high-quality single crystals, the grain boundaries can be effectively eliminated, leading to much higher carrier mobility[11]. In terms of crystal structure, higher carrier mobility can also be achieved by improving the crystal symmetry. In materials with anisotropic structures, highly oriented and textured polycrystalline samples with most grains arranged in a specific direction can be obtained by deformation treatment, and their anisotropy can be fully utilized to achieve high carrier mobility close to the single crystal along certain directions[12]. Similarly, by grain boundary modification in isotropic materials like Pb*Q* (*Q* = Te, Se, S), the larger grained samples with reduced densities of grain boundaries and higher carrier mobility can be obtained[13]. In addition, through the fine control of micro-defects and the construction of sub-nanostructures, lower lattice thermal conductivity with highly maintained carrier mobility can be obtained, leading to the substantial improvement on *ZT* values. In PbTe and PbSe thermoelectrics, the mean free path of phonons (0.1–10 nm, sub-nanoscale) is much smaller than that of carriers (10^2–10^3 nm, nanoscale). Therefore, the introduced sub-nanostructures (atomic interstitials and interstitial clusters, etc.) can scatter phonons without affecting the carrier transport[14].

In addition to the above strategies at the crystal level, the carrier mobility can also be effectively optimized through decoupling the TE parameters by band structure engineering since μ is strongly affected by the effective mass m^* with $\mu = e\tau/m^*$, in which τ is the carrier relaxation time. At this level, the first method to optimize μ is to depress m^* by band sharpening since shaper bands correspond to smaller effective mass. Secondly, in TE materials with second phases, the electronic bands alignment strategy minimizes the energy difference between the matrix and the second phases, thereby weakening the carrier scattering at the interface with energy barriers, and thus maintaining high carrier mobility and electrical transports[15]. Modulation doping is another strategy that has been successfully utilized to optimize the carrier mobility in thermoelectrics through tuning the position of Fermi level[16], which is especially effective for the TE systems with extremely low μ, such as TE oxides.

It is worth mentioning that the potential optimal *n* proposed here is not entirely different from the traditional optimal *n* strategies, but only provides a potential strategy of another direction. Especially for TE systems with intrinsic low carrier concentrations, the focus on the carrier mobility might lead to exceptional results. For example, in *n*-type SnS, traditional doping fails to realize a proper carrier concentration much higher than 10^{19} cm^{-3}, but higher TE performance can be obtained in single-crystal samples along the in-plane direction with a much higher carrier mobility[17]. Similar effects may also be achieved in *p*-type Mg_3Sb_2 and *n*-type BiCuSeO materials. The defects engineering is rather effective to increase μ in Pb*Q* (*Q* = Te, Se, S) systems by compensating the intrinsic Pb vacancy or S vacancy with extra small atoms such as Cu, Zn, Ni. We here propose that by self-compensation with excessive Pb atoms in PbTe/PbSe and S atoms in PbS, lower *n* with much higher *S* and μ can be simultaneously achieved, might leading to exceptional *PF* outperforming the extrinsic-compensation samples. The self-compensation concept may also play a key role in TE systems in which it is rather challenging to achieve opposite transport behaviors, such as *p*-type $BiSbSe_3$ and *n*-type (Ge/Sn)Te.

In addition, it is rather essential to utilize multiple of the above strategies to achieve the significant optimization of carrier mobility. For example, by combining the band sharpening with crystal modulation, ultra-high carrier mobility was obtained in Te-alloyed SnSe crystals[18]. Moreover, based on the decreased m^* through band sharpening, the predicted optimal *n* will also be pushed lower, and better *ZT* values are expected especially at low temperature since the optimal carrier concentration from single band model approximately obeys the $T^{3/2}$ law[19]. In this term, the combination of the proposed carrier mobility optimization strategies based the potential optimal *n*, will be crucial to achieve higher TE performance at low temperatures. Based on present perspective, some traditional mid-temperature systems can be revisited, such as Pb*Q* (*Q* = Te, Se, S) and (Ge/Sn)Te, might open a new rethinking for the application of these materials for thermoelectric cooling beyond power generation.

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Conflict of interest

The authors declare no conflict of interest.

Author contributions

The manuscript was drafted by Dr. Bingchao Qin and revised by Prof. Li-Dong Zhao. All authors had approved the final version of the manuscript.

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