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Band engineering and rational design of high-performance thermoelectric materials by first-principles

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Abstract

Understanding and manipulation of the band structure are important in designing high-performance thermoelectric (TE) materials. Our recent work has involved the utilization of band structure in various topics of TE research, i.e., the band convergence, the conductive network, dimensionality reduction by quantum effects, and high throughput material screening. In non-cubic chalcopyrite compounds, we revealed the relations between structural factors and band degeneracy, and a simple unity-η rule was proposed for selecting high performance diamond-like TE materials. Based on the deep understanding of the electrical and thermal transport, we identified the conductive network in filled skutterudites with the "phonon glass-electron crystal" (PGEC) paradigm, and extended this concept to caged-free Cu-based diamond-like compounds. By combining the band structure calculations and the Boltzmann transport theory, we conducted a high-throughput material screening in half-Heusler (HH) systems, and several promising compositions with high power factors were proposed out of a large composition collection. At last, we introduced the Rashba spin-splitting effect into thermoelectrics, and its influence on the electrical transport properties was discussed. This review demonstrated the importance of the microscopic perspectives for the optimization and design of novel TE materials.

Keywords: Thermoelectric materials; First-principles; Band engineering; Transport properties

Contents

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1. Introduction

In recent years, thermoelectrics has made a remarkable progress for its potentially broad applications in refrigeration, waste heat recovery, solar energy conversion, etc [1–7]. These solid state devices have no moving parts, are environmentally friendly, and are extremely reliable. The shortcoming of the existing thermoelectric (TE) materials is their relatively low energy conversion efficiency. The efficiency of TE materials depends on the dimensionless figure of merit $zT = S^2\sigma T/(\kappa_e + \kappa_L)$, where S is the Seebeck coefficient, σ is the electrical conductivity, T is the absolute temperature, and the thermal conductivity in denominator which can be divided to the electronic part κ_e and lattice part κ_L. Among those quantities, S, σ, and κ_e are related to the electronic structure of the material and κ_L is related to its phonon vibration. One possible way to optimize zT is to reduce the lattice thermal conductivity without significantly altering the electronic transport properties of the material. This strategy has been explored extensively by alloying, doping, and nano-composition [1,4,5] for the enhancement of phonon scattering. Another strategy is to maximize the power factor ($S^2\sigma$). This can be achieved by the band engineering and scattering engineering [8].

The band structures of materials describe the available energy levels for electrons, which are usually presented in the reciprocal space due to the periodicity of the lattice. The band structure is one of the basic characteristics of materials, as well as the vital tool in understanding, optimizing, and even designing novel functional materials. Since the electrical transport properties are directly determined by the band structures near the Fermi levels, the study of TE materials from the band structure perspective demonstrates as a model case which bridges the macroscopic electrical transport and the microscopic extremes of the materials. Explicitly, the power factor of the TE materials can be enhanced if one can manipulate the electronic density of states (DOS). This can be achieved by either band convergence as commonly accepted, or introducing new physical phenomena which alter the electronic structure [9–12]. In TE materials with complex structures, the electrical transport properties can be safely tuned if one can identify the conductive network as well as the out-of-network atoms of the materials, by electronic structure calculations. Combining with the Boltzmann transport theory, we can also use the band structures as the screening tools for predicting new TE materials with high power factors.

The three quantities like the Seebeck coefficient, electrical conductivity and electronic thermal conductivity are paradoxical, and the optimal power factor depends on the carrier concentrations. In degenerate semiconductors, the Seebeck coefficient under parabolic band approximation can be written as [13]:

$$S = \frac{8\pi^2 k_b^2 T}{3qh^2} m_d^* \left(\frac{\pi}{3n}\right)^{2/3}, \quad (1)$$

where m_d^* is the DOS effective mass, q the carrier charge, n the carrier concentration. Based on equation (1), a high S needs a high DOS (or m_d^*) at given Fermi level (carrier concentration). Since $m_d^* = N_v^{2/3} m_b^*$, where N_v is the band degeneracy and m_b^* is the band effective mass. There are two methods to increase the m_d^*, including increasing the effective mass of the single pocket m_b^* or the band degeneracy [14,15]. However, a high m_b^* always leads to a low carrier mobility due to their inversion relation. Band engineering, increasing the factor N_v without changing much of m_b^*, can effectively solve the paradox between the DOS effective mass and carrier mobility, and has been treated as an efficient strategy to improve TE performance [8,13,15,16]. Some excellent TE performance has been obtained by the band structure engineering. Through a distortion of the electronic DOS by doping Tl in PbTe, a doubling of zT in PbTe above 1.5 was obtained in 2008 [13]. By introducing multiple valley degeneracy, Pei et al. realized a high zT of 1.8 in doped $PbTe_{1-x}Se_x$ [15]. By solid solutions, band convergence was realized in $Mg_2Si_{0.35}Sn_{0.65}$, and a 65% improvement of power factor was obtained [17]. Tan et al. investigated the transport properties of Mn doped SnTe, and the results showed a high thermoelectric figure of merit of 1.3 at 900 K by the band modification [18]. Similar results were obtained by Pei et al. [19]. The band structure engineering mentioned above were caused by doping impurities in the framework. Besides these experiment results, some theoretical work also showed improved electrical transport properties by band convergence [9–12]. Recently, by tuning the structural parameters, Zhang et al. demonstrated a new strategy to achieve large band degeneracy that can predict and design high-performance non-cubic diamond-like TE materials, and the method can be used in layered compounds, such as Zintl compounds [20,21]. Besides, the Rashba spin splitting effect that can lead to lower-dimensional DOS and increase the S has been reported, which offers a new direction for electrical transport optimization [22–29].

It is critical for the improvement of TE materials to develop the corresponding novel concept and mechanism. Since the introduction of "Phonon glass-electron crystal" (PGEC) by Slack in 1995 [30], many TE materials with complex structures have been discovered, such as clathrates [31], skutterudites [32–36], zintl phases [37], diamond-like compounds [20], and liquid-like Cu_2Se or similar compounds etc [38]. Due to the various types of chemical bonds in complex compounds, and the fact that the electrical transport is determined by the band structures in a very small energy range, it is possible that only the fractions of the compounds dominate the electrical transport. This directly leads to the concept of the conductive network, with the in-network atoms constructing the "framework" and contributing to σ, and the out-of-network atoms acting as the carrier reservoirs. In some of the complex compounds, the out-of-network atoms, due to their loose bonding to the framework, their localized atomic motions can cause rattling modes in phonon spectra and reduce the κ_L. Our recent work on skutterudites and diamond-like compounds show that the TE performance can be improved by utilizing the conductive network, and this concept can be extended to other complex compounds [33,39–42].