热点追踪

【编者按】光电材料和能源材料是 2014 年度美国 MRS 秋季会议 4 大主题中的两个。科学界开展的新型热电材料研究，对全球环境污染、能源危机等问题来说有着很强的现实意义。核燃料能量密度大、成本低、运输存储方便，且在发电过程中不产生任何大气污染，但如何高效、安全处置核废料一直是国际社会关注的热点话题。2014 年 12 月 1 日 ~5 日，在美国波士顿 MRS 秋季大会上，本刊记者有幸邀请到在麻省理工学院材料科学与工程系作博士后工作的 Dr. Zhu Hong 和韩国浦项工科大学材料科学与工程学院及先进核能中心的徐凯博士，分别就目前热电材料的研究进展、核废料的科学管理与处置研究等相关工作撰文，与读者分享。

Ideas to Advance Thermoelectric Materials Development

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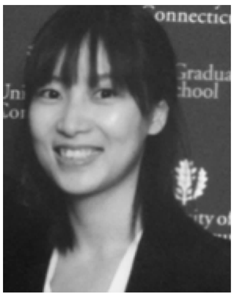

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Abstract: In light of the conflict between energy shortage and increasing energy demand, a secure energy future needs solutions that come from a diverse energy portfolio. Thermoelectrics, which could convert waste heat to electrical power, is an important clean and renewable energy technology, especially considering the fact that more than half of the energy input is lost as waste heat. The development of thermoelectric materials with high figure of merit(ZT) is needed to increase the efficiency of heat-electricity conversion, which involves multivariate optimizations to achieve low thermal conductivity, high Seebeck coefficient and high electrical conductivity simultaneously. In this short report, I will discuss the new ideas that have advanced the development of thermoelectric materials during the last two decades.

Key words: thermoelectrics materials; design principle; phonon scattering; band structure engineering; figure of merit (ZT); MRS

推进热电材料发展的新思路

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摘　要：由于能源短缺与不断增加的能源需求间的矛盾，为保证未来能源的安全性，需要一个多元化的能源组合结构。由于世界上有将近 50% 的能源输入以废热的方式被浪费掉，应用热电效应将这部分废热有效地转换为电能是一种重要的清洁、可再生能源技术。为了提高热 - 电转换效率，需要开发出具有高材料优值(ZT)的热电材料。然而，改善热电材料是一个复杂的多变量优化问题——即降低热导率、增加塞贝克系数和升高电导率。就近年来一些成功提高热电材料 ZT 值的思路和想法作简要的报道。

关键词：热电；优化设计新思路；声子散射；能带工程；ZT 值；MRS

1 Introduction

Thermoelectrics, which converts heat to electricity and vice-versa, is discovered by Thomas Seebeck and Charles Peltier in the 18th century and has been actively studied for the use in the waste heat recovery and solid-state cooling/heating since the 19th century[1]. A thermoelectric device has two basic components, namely p-type and n-type thermoelectric materials as shown in Fig. 1. In the presence of the temperature gradient, a voltage is generated due to the Seebeck effect, which causes the flow of carriers or electrical current. The efficiency of thermoelectric device is mainly limited by the figure of merit of the thermoelectric materials, namely the ZT value ($ZT = S^2\sigma T/\kappa$ where S is the Seebeck coefficient, σ is the electrical conductivity, κ is the thermal conductivity, and T is temperature). By the end of the 1960's, the attainable ZT value is ~ 1. The basic science of thermoelectric materials was established around that time. For example, heavily doped semiconductor, reduced lattice thermal conductivity through point defects, the combination of high mobility and effective mass have been identified to be important for good thermoelectrics. However, the pace of progress has slowed down from 1960 ~ 1990 and the ZT value of ~ 1.0 was thought to be the maximum attainable value for a couple of decades[2]. In the 1990's, a series of concepts have emerged, which lead to the renaissance of thermoelectrics and brought the state-of-the-art ZT value as high as 2.6[3]. The two broad strategies for improving ZT are to enhance the power factor ($S^2\sigma$) and to reduce the thermal conductivity, κ, of the materials, as will be discussed below.

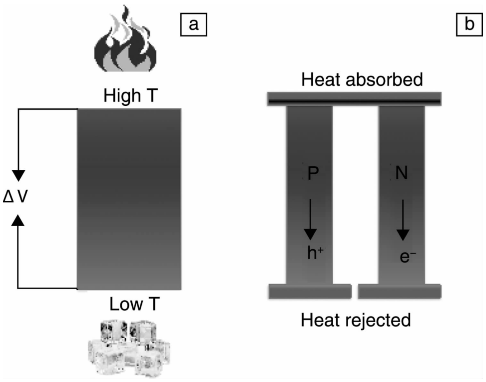

Fig. 1 Voltage generated in a thermoelectric material due to temperature gradient (Seebeek effect) (a) and Thermoelectric module containing one P-type and one N-type thermoelectric material, which have a temperature gradient and hence a seebeck-effect caused voltage/current flow (b)

2 Thermal conductivity reduction

Within the last two decades, the enhancement of the ZT value is mainly due to the successful minimization of lattice thermal conductivity. In the early 1990's, Glen Slack suggested that the best bulk thermoelectric materials shall be phonon-glass/electron-crystal (PGEC)[1]. In other words, it has the electrical properties of crystalline materials and thermal properties of an amorphous or glass-like material [4]. The most prominent of these bulk materials are cage-like materials (such as skutterudites and clathrates). These materials have voids, in which "rattler" atoms are inserted and can effectively scatter phonon and lower the thermal conductivity[5]. Fig. 2a shows the structure of $CoSb_3$ skutterudite, which contains corner-sharing $CoSb_6$ octahedra (black) and a rattling atom (gray).

Besides using large/complex unit cell, the successful minimization of lattice thermal conductivity can be also achieved with the grain-boundary/interface scattering in nanostructures (Fig. 2a), which was firstly proposed by Hicks and Dresselhaus and have been widely used sincethen[6]. Due to the difference in the mean free path of phonons and electrons, internal interfaces found in nanostructures could be applied to reduce the thermal conductivity rather than the electrical conductivity and hence enhance the ZT value. As phonons with a wide range of mean free path could contribute to the lattice thermal conductivity or heat transport[7], all-scale-hierarchical architecture to scatter most phonons has been proposed and demonstrated in $Pb_{1-x}Sr_xTe$ by Kanatzidis in 2012. Using alloy doping, nanostructuring and grain-boundary control, the phonons with atomic scale, nanoscale, mesoscale mean free path have been effectively scattered, leading to a high ZT of ~ 2.2 at 915 K[8].

Some substructure materials also have thermal conductivity as low as its amorphous limit when the phonon mean free path approaches the interatomic distance[9]. In 2014, a single crystal material, SnSe, has shown the lattice thermal conductivity as low as 0.23 W/mK and a moderate $S^2\sigma$, leading to the ZT value ~ 2.6[3]. Such a substructure (Fig. 2a) has SnSe blocks weekly bonded to each other, which scatters phonons similar to the effect of interface/grain boundary found in nanostructures. Similar substructure materials could be Na_xCoO_2, where Co-O layers are separated by a disordered Na layer[10].

3 Power factor enhancement

Compared to the success to increase ZT through reduced thermal conductivity, the alternative approach-the power factor enhancement has been only realized recently through engineering the band structure of the thermoelectric materials (Fig. 2b). Resonant doping which increases the density of states (DOS) around the Fermi level (E_F) within a small energy range has been found able to increase the Seebeck coefficient, e. g., Tl doped PbTe[11]. As a combined result of increased Seebeek coefficient and reduced thermal conductivity, the ZT value of p-type PbTe doubles upon 2% Tl dopants. Other successful example of resonant state to increase ZT includes n-type Al-doped PbSe[12], p-type In-doped SnTe[13], etc.

Similar to resonant doping, the density of states and hence the Seebeek coefficient could be also enhanced without sacrificing electrical conductivity by increasing the number of bands that participate the electron transport, or higher band degeneracy. For p-type PbTe, it is found that the L and Σ valence band maxima can be converged with temperature increase, which leads to a high ZT of 1.8 for larger DOS[14]. Similar enhancement of ZT by converging multiple bands can be also achieved through alloying, which has been demonstrated in n-type $Mg_2Si_{1-x}Sn_x$, p-type $Sn_{1-x}Cd_xTe$, p-type Cu_2MGeSe_4, and etc[15-17].

At the meanwhile, modulation doping has been recently found as an efficient way to further enhance the ZT value of nanostructure materials. A modulation-doped sample usually consists of two types of nano grains as shown in Fig. 2b. Compared to the matrix or host grain, the other type of grain is doped with specific elements, such that the relative band structures across the interface favors the separation of charges and results in enhanced mobility of carriers. The electrical conductivity of the modulation-doped sample is higher compared to uniformly doped samples. For example, it has been found that modulation doped sample $(Si_{80}Ge_{20})_{80}$-$(Si_{100}P_3)_{20}$ shows higher power factor compared to uniformly doped $Si_{84}Ge_{16}P_{0.6}$[18].

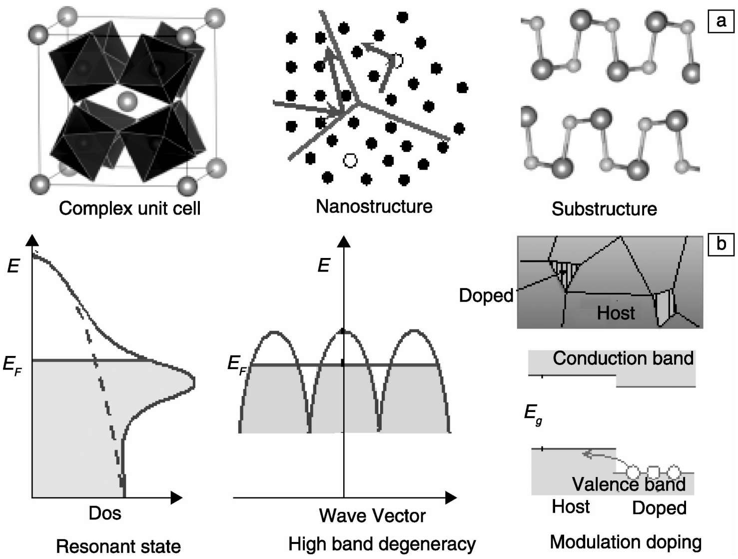

Fig. 2 Several approaches to reduce the lattice thermal conductivity (a) and enhance the power factor (b) for a higher *ZT* value of thermoelectric materials .

4 Summary

In the last two decades, great progress has been made to advance thermoelectrics, especially thanks to the emerging new ideas, some of which are briefly discussed above. How to better apply these ideas to better design thermoelectrics may benefit from a combined experimental and theoretical effort. Not only studies on fundamental understanding/mechanism but also new material/property prediction through high throughput computations are important to expedite the development of thermoelectric materials. Currently, there are more and more efforts devoted to this area. At the meanwhile, as Dr. Dresselhaus pointed out during the 2014 Materials Research Society Fall meeting, except these known design principles or concepts, new ideas, understandings and design principles are very welcomed for the future design or optimization of thermoelectric materials. (DOI: 10.7502/j. issn. 1674 -3962. 2015. 02. 10)

References

[1] Slack G, Rowe D M, *CRC Handbook of Thermoelectrics* [M]. Boca Raton, FL: CRC Press, 1995.

[2] Heremans J P, DresselhausM S, BellL E, *et al*. When Thermoelectrics Reached the Nanoscale [J]. *Nature Nanotechnolgy*, 2013, 8: 471-473.

[3] Zhao L D, LoS H, Zhang Y, *et al*. Ultralow Thermal Conductivity and High Thermoelectric Figure of Merit in SnSe Crystals[J]. *Nature*, 2014, 508: 373-377.

[4] DresselhausM S, Chen G, Tang M Y, *et al*. New Directions for Low-Dimensional Thermoelectric Materials [J]. *Advanced Mateials*, 2007, 19: 1 043-1 053.

[5] Snyder GJ, Toberer ES. Complex Thermoelectric Materials [J]. *Nature Materials*, 2008, 7: 105-114.

[6] Hicks L, Dresselhaus M. Effect of Quantum-Well Structures on the Thermoelectric Figure of Merit [J]. *Physical Review B*, 1993, 47: 12 727-12 731.

[7] Lee S, Esfarjani K, Luo T, *et al*. Resonant Bonding Leads to Low Lattice Thermal Conductivity [J]. *Nature Communications*, 2014, 5: 3 525.

[8] Biswas K, He J, Blum I D, *et al*. High-Performance Bulk Thermoelectrics with All-Scale hierarchical Architectures [J]. *Nature*, 2012, 489: 414-418.

[9] Cahill D, Watson S, Pohl R. Lower Limit to the Thermal Conductivity of Disordered Crystals[J]. Physical Review B, 1992, 46: 6 131-6 140.

[10] Fujita K, Mochida T, Nakamura K. High-Temperature Thermoelectric Properties of $Na_xCoO_{2-\delta}$ Single Crystals [J]. *Japanese Journal Applied Physics*, 2001, 40: 4 644-4 647.

[11] Heremans J P, Jovovic V, Toberer E S, *et al*. Enhancement of Thermoelectric of the Electronic Density of States [J]. *Science*, 2008, 321: 554-558.

[12] Zhang Q, Wang H, Liu W, *et al*. Enhancement of Thermoelectric Figure-of-Merit by Resonant States of Aluminium Doping in Lead Selenide[J]. *Energy and Environmental Science*, 2012, 5: 5 246-5 251.

[13] Zhang Q, Liao B, Lan Y, *et al*. High Thermoelectric Performance by Resonant Dopant Indium in Nanostructured SnTe [J]. *Proceedings of the National Academy of Sciences of the United States of America*, 2013, 110: 13 261-13 266.

[14] Pei Y, Shi X, LaLonde A, *et al*. Convergence of Electronic Bands for High Performnce Bulk Thermoelectrics [J]. *Nature*, 2011, 473: 66-69.

[15] Tan G, Zhao L D, Shi F, *et al*. High Thermoelectric Performance of p-type SnTe via a Synergistic Band Engineering and Nanostructuring Approach[J]. *Journal of the American Chemical Society*, 2014, 136: 7 006-7 017.

[16] Liu W, Tan X, Yin K, *et al*. Convergence of Conduction Bands as a Means of Enhancing Thermoelectric Performance of n-Type $Mg_2Si_{1-x}Sn_x$ Solid Solutions[J]. *Physical Review Letters*, 2012, 108: 166 601.

[17] Zeier W G, Zhu H, Gibbs Z M, *et al*. Band Convergence in the Non-cubic Chalcopyrite Compounds Cu_2MGeSe_4 [J]. *Journal of Materials Chemistry C*, 2014, 2: 10 189-10 194.

[18] Zebarjadi M, Joshi G, Zhu G, *et al*. Power Factor Enhancement by Modulation Doping in Bulk Nanocomposites[J]. *Nano Letters*, 2011, 11: 2 225-2 230.

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