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热电材料与器件研究进展

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随着人类社会对气候变化的关注程度不断增强和对化石能源的过分依赖, 更加刺激了世界范围内开发新能源技术的行动。热电技术是最简单的可以实现热能和电能直接相互转化的技术, 能把太阳能、地热、机动车和工业废热转化成电, 反之也能作为热泵实现制冷。热电器件具有全固态、重量轻、结构紧凑、响应快、无运动部件和有害工质等优点。模块化的特点使其易与其他能量转换技术联用, 这是 21 世纪能源应用非常重要的特征, 因为没有单一的技术能够满足世界能源的需求。

热电转换技术的核心问题主要是寻求高热电优值(*ZT*)的材料。高优值热电材料应该具有“声子玻璃–电子晶体”的特点, 即具有低的热导率、高的电导率和温差电动势(Seebeck 系数)[1], 但是这些特点在一个简单的晶体材料中难以同时满足, 因为三个热电参数之间相互耦合, 优化一个参数就会导致其他参数的恶化[2]。在复杂的晶体材料中, 不同的结构模块可以分别对热电输运起主导作用, 有利于热电性能的解耦和优化, 填充型方钴矿、Cu_2Se 基离子导体、BiCuSeO 和新型 Zintl 化合物等都是实现这类调控的典型例子[3-5]。

在过去的十几年间, 追求高优值热电材料的努力一度使纳米结构热电材料成为焦点[2-3]。这方面的研究最初来源于一个猜想：低维材料比块体材料具有更强的热电性能。事实上, 纳米结构对电性能的改善非常有限, 仅仅提供了更多散射不同波长声子(降低热导率)的可能性, 包括质量波动、晶界、应变等在不同温度区间起作用的多重散射机制, 使人们可以在多尺度层面上增强声子散射, 比电子散射更有效。

尽管增大热电优值一直是热电学研究的中心任务, 但近年来热电材料的环境相容性和原料成本也引起了越来越多的关注。好的热电材料不仅应该具有高的热电优值, 还需要由无毒、来源丰富的元素组成, 具有优良的化学稳定性和热稳定性, 满足实用的要求。目前用于热电发电和制冷的性能优异的热电材料大多是半导体碲化物, 如 Bi_2Te_3, PbTe 和 GeTe-$AgSbTe_2$ 等[3,6]。碲有毒, 在地壳中的丰度仅在十亿分之一的数量级。因此开发不含 Pb 和 Te 的高性能热电材料具有重要意义。在这样的原则下, 半赫斯勒热电半导体和 Mg 基化合物成为非常有前景的实用型热电材料[7]。

目前热电材料已经形成了一个庞大的家族, 包括半导体、氧化物和聚合物, 结晶形式从单晶到多晶再到纳米复合物。进一步改善材料性能需要深入理解热电输运机制及其影响因素[8], 而后者依赖于热电参数的可靠测量[9]。近年来材料基因组计划的启动加速了新材料的发现和优化设计, 基于机器学习的大数据挖掘和高通量计算与表征, 有望加快新型高效热电材料的筛选。然而, 面向应用的热电模块和系统的设计、组装与评价技术等则相对滞后, 尽管已经取得了显著进展, 但仍然不能满足工业应用的要求[10]。为了实现热电技术的规模化应用, 仍需要热电研究者的不断努力。

Recent Advances in Thermoelectric Materials and Devices

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The increasing concern on climate change and over-reliance on fossil fuels have spurred an urgent action worldwide in developing alternative energy technologies. Thermoelectricity is the simplest technology applicable for direct heat-electricity energy conversion. Heat from different sources such as solar heat, geothermal heat, and waste heat from automobiles or other industrial processes can be directly converted into clean electricity by a thermoelectric device. A thermoelectric device can also work in reverse as a heat pump. Thermoelectric devices are of all solid-state assembly, lightweight and compact, rapid responsiveness. They possess the absence of moving parts or hazardous working fluids, and have the feasibility for miniaturization. The modular aspects of thermoelectricity make it easy to work in tandem with other energy conversion or alternative energy technologies. This is a very important feature because no single technology can meet the world's energy needs in 21st century, We need a combination of many technologies.

The fundamental issue of thermal-electrical energy conversion is primarily the pursuit of thermoelectric materials with high figure of merit *ZT*. The high *ZT* materials should be a "Phonon-Glass Electron- Crystal" (PGEC) that simultaneously possesses a high Seebeck coefficient α, a high electrical conductivity σ and a low thermal conductivity κ[1]. It is difficult to satisfy these criteria in a simple crystalline bulk material since all the three quantities that govern *ZT* are inter-related, and a modification to any of these quantities often adversely affects the others[2]. In complex crystal systems composed of building modules with different compositions, structural symmetries and TE functions, sometimes called "hybrid crystal", the electrical and thermal transport can be decoupled and optimized. The filled skutterudites, Cu_2Se based ion conductors, BiCuSeO and novel Zintl-phase compounds provide examples of such control[3-5].

Over the past decade, the efforts of pursuing high *ZT* materials in thermoelectric study have culminated into a new paradigm, *i.e.* nanostructured thermoelectric materials[2-3]. This direction started ten years ago with the speculation that low dimensional materials would have enhanced properties over those of similar materials in bulk form. The nanomaterials can provide several opportunities for phonon scattering, *e.g.*, the mass fluctuation alloying, grain boundary, strain fields, which cover wide ranges of phonon wavelength and temperature. The multiscale complexity can be tuned so as to scatter phonons more than electrons.

While improving the *ZT* values has always been the central task of thermoelectric study, in recent years increasing attention is being paid to the environmental friendliness and the availability of the specific thermoelectric materials. This requires not only a good thermoelectric material with a high *ZT* value but also it is comprised of non-toxic and abundantly available elements with high chemical and thermal stability. It is noted that most state-of-the-art thermoelectric materials are semiconducting tellurides, such as Bi_2Te_3, PbTe and GeTe-$AgSbTe_2$ compounds that are widely used for thermoelectric power generation and refrigeration[3,6]. Tellurium is toxic and its abundance is only on the order of one billionth on earth. Hence it is highly desirable and urgent to identify and develop Te- and Pb-free high performance thermoelectric materials. In this spirit, the half-Heusler semiconductors and Mg-based compounds are outstanding among the most promising candidates[7].

Thermoelectric materials have been developed into a big family, including semiconductors, oxides and polymers, possessing various crystalline forms from monocrystals and polycrystals to nanocomposites. Further performance improvement needs the better understanding of thermoelectric transport mechanisms and related impacting factors[8], which has to be based on the reliable measurements of thermoelectric parameters[9]. Recently, The Materials Genome Initiative is speeding up the discovery and design of materials based on big data and high-throughput methods including calculations and characterization, which is promising for the screening of novel thermoelectric materials. However, the design principle, assembly methods and testing technique of thermoelectric module and system, although developing quickly, still lag relatively behind and fail to meet the needs of industrial applications[10]. Many challenges still lie ahead and continuous efforts have to be done in the future.

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