



“二维声子-三维电荷”热电传输特性研究进展

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2024-07-20 收稿, 2024-08-17 修回, 2024-08-19 接受, 2024-08-20 网络版发表

国家杰出青年科学基金(51925101)、太原科技大学引进人才科研启动基金(20232094)和山西省优秀来晋博士科研资助项目(20242010)资助

摘要 高性能热电材料追求实现“声子玻璃-电子晶体”的传输特性, 即同时拥有低的热输运特性和高的电输运特性。然而, 材料声子与电子之间的强耦合关系为实现这一目标带来极大挑战。近年来, 在n型各向异性层状硒化锡晶体中发现的“二维声子-三维电荷”热电传输特性在解耦“声-电”矛盾上表现出了十分优异的潜力, 引起了热电领域的广泛关注。本文主要介绍了“二维声子-三维电荷”热电传输特性的机理, 围绕晶格热导率、载流子迁移率及塞贝克系数分析了“二维声子-三维电荷”热电传输特性的优势, 总结了具有“二维声子-三维电荷”热电传输特性材料的研究进展, 并对如何利用与增强“二维声子-三维电荷”热电传输特性实现优异热电性能进行了展望。

关键词 热电材料, “声-电”解耦, 各向异性, 层状结构, 电荷密度

热电能源转换技术是一种能够依托热电器件实现热能与电能之间直接相互转换的技术, 在温差发电及精准控温等领域具有非常广阔的应用前景^[1~3]。热电器件的能量转换效率主要由构成热电器件的热电材料的无量纲热电优值(ZT)决定: $ZT = (\sigma S^2 / \kappa_{\text{tot}}) T$, 其中 σ 为电导率, S 为塞贝克系数, σS^2 为功率因子(power factor, PF), κ_{tot} 为总热导率(由晶格热导率 κ_{lat} 和电子热导率 κ_{ele} 组成), T 为热力学温度^[4,5]。 ZT 越大, 能量转换效率越高。高性能热电材料需要同时具备低的热导率、高的电导率 and 大的塞贝克系数, 即实现“声子玻璃-电子晶体”热电传输特性。为尽可能实现这一热电输运特性, 科研人员利用能带简并^[6]、引入共振态^[7]等提升态密度有效质量 m^* 的方式优化 S , 通过能带锐化^[8]、能带对齐^[9]、晶体结构对称性调控^[10,11]等优化载流子迁移率 μ 的方式提升 σ , 以及引入多尺寸缺陷设计^[12~15]增强声子散射的方式降低 κ_{lat} , 成功开发出一系列最大 $ZT > 2$ 的高性能热

电材料^[10,15~21], 推动了热电领域的迅速发展。然而, 热电材料较低的性能仍然是限制热电能源转换技术广泛应用的重要因素之一。

材料声子与电子的强耦合关系限制了通过改变某一热电参数来提高热电性能的优化效果, 是制约材料热电性能进一步提升的关键因素^[22,23]。为进一步降低“声子-电子”之间的耦合程度, 研究人员提出了开发本征低热导率材料热电性能的策略, 这一策略有效避免了为降低 κ_{lat} 而引入额外声子散射中心产生的对材料电输运性能及高温稳定性带来的负面影响^[24]。硒化锡(SnSe)是一种具有各向异性层状结构的本征低热导率材料^[25~27]。得益于本征较低的晶格热导率与面内方向(晶体学 bc 平面方向)的高载流子迁移率特点, 本征SnSe晶体(p型)可在923 K实现高达2.6的最大 $ZT(ZT_{\text{max}})$, 掺杂优化后的p型SnSe晶体甚至可在300~773 K的宽温域内实现~2的平均 $ZT(ZT_{\text{ave}})$, 证明了开发本征低热导率材

引用格式: 高天, 宿力中, 赵立东. “二维声子-三维电荷”热电传输特性研究进展. 科学通报, 2025, 70: 636–644

Gao T, Su L Z, Zhao L-D. Recent progress in “2D phonon-3D charge” thermoelectric transport (in Chinese). Chin Sci Bull, 2025, 70: 636–644, doi: [10.1360/TB-2024-0793](https://doi.org/10.1360/TB-2024-0793)

料这一策略的有效性^[19,28]。值得注意的是, p型SnSe晶体是在SnSe的面内方向实现高热电性能的, 其面外方向(晶体学 a 轴方向)的热电性能显著低于面内方向。虽然SnSe沿其面内方向已经具有了较低的 κ_{lat} , 但其面外方向实际上具有更低的 κ_{lat} 。SnSe的本征低热导率优势在p型SnSe热电材料中并没有被充分利用。造成这一现象的原因是p型SnSe晶体沿面外方向的载流子迁移率(μ)很低, 仅为面内方向 μ 的~20%^[29]。因此, 若能在SnSe晶体的层间构建出一条允许载流子高速通过的通道, 提升载流子面外方向的 μ , 则可充分利用SnSe面外方向的超低热导率优势实现“声子玻璃-电子晶体”的传输特性, 从而有望获得更高的 ZT 。

卤素掺杂的n型SnSe晶体在面外方向表现出明显高于p型SnSe的 μ , 展现“二维声子-三维电荷”热电传输特性^[30-32]。2018年, Chang等人^[30]通过溴(Br)掺杂成功实现了本征p型的SnSe晶体向n型半导体的转变, 并发现其面外方向的 μ 在300 K时高达 $\sim 120 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, 远高于同载流子浓度(n)下Na掺杂p型SnSe晶体的 $\sim 60 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, 面外方向电子输运相比于空穴有着明显优势^[28]。n型与p型SnSe晶体沿面外方向 μ 的巨大差别由层间电荷密度分布的差异导致, 如图1(a)所示。n型SnSe由于电子离域交叠杂化形成了在层间交叠的电荷密度分布, 成功地在面外方向构建出一条可供电子快速通过的特殊通道; p型SnSe层间的电荷密度并没有发生交叠, 使得空穴难以在面外方向高速运动。此外, SnSe沿其面外方向有着远低于面内的 κ_{lat} , 300 K时Br掺杂的n型SnSe晶体在面外方向的 κ_{lat} 为 $\sim 0.77 \text{ W m}^{-1} \text{ K}^{-1}$, 面内方向则为 $\sim 1.28 \text{ W m}^{-1} \text{ K}^{-1}$; 773 K时面外方向的 κ_{lat} 进一步降低至 $\sim 0.18 \text{ W m}^{-1} \text{ K}^{-1}$, 面内方向则为

$\sim 0.57 \text{ W m}^{-1} \text{ K}^{-1}$ 。面外方向的高 μ 与超低 κ_{lat} 使n型SnSe表现出独特的“二维声子-三维电荷”热电传输特性, 获得了十分优异的高温热电性能($ZT_{\text{max}} \sim 2.8 @ 773 \text{ K}$)。氯(Cl)、碘(I)元素掺杂的n型SnSe晶体同样具有相似的“二维声子-三维电荷”热电传输特性^[31,32]。以Cl掺杂和铅(Pb)固溶的n型SnSe晶体为例, 其面外方向的 ZT_{max} 为 ~ 3.1 , 300~773 K的 ZT_{ave} 为 ~ 1.7 , 远高于面内方向($ZT_{\text{max}} \sim 1 @ 673 \text{ K}$; $ZT_{\text{ave}} \sim 0.7 @ 300 \sim 773 \text{ K}$)。“二维声子-三维电荷”热电传输特性显著增强了n型SnSe晶体的综合热电性能, 促进了“声子-电子”的进一步解耦, 如图1(b)所示^[31]。随后, n型二硫化铅锡(PbSnS_2)晶体被发现同样具有“二维声子-三维电荷”热电传输特性, 在面外方向获得了1.2的 ZT_{max} , 在硫族化合物中处于领先地位^[33-36]; 此外, 一些理论计算表明硫化锡(SnS)^[37]、二硒化铅锡(PbSnSe_2)^[38]、硒化锗(GeSe)^[39]等材料同样具有“二维声子-三维电荷”热电传输特性, 是潜在的高热电性能材料。这些结果表明“二维声子-三维电荷”热电传输特性为热电材料实现“声子玻璃-电子晶体”的传输效果、获得更高热电性能的突破带来了全新思路, 在本征低热导材料中筛选具有“二维声子-三维电荷”热电传输特性的材料正逐步成为开发新型高性能热电材料的标准之一。因此, 本文围绕“二维声子-三维电荷”这一热电传输特性, 介绍了其产生的机理, 讨论了其对材料 μ 与 S 的影响, 总结了具有该热电传输特性的热电材料的研究进展, 并对如何利用与增强该热电传输特性实现优异热电性能进行了展望。

1 “二维声子-三维电荷”热电传输特性机理

“二维声子-三维电荷”热电传输特性首先在Br掺杂

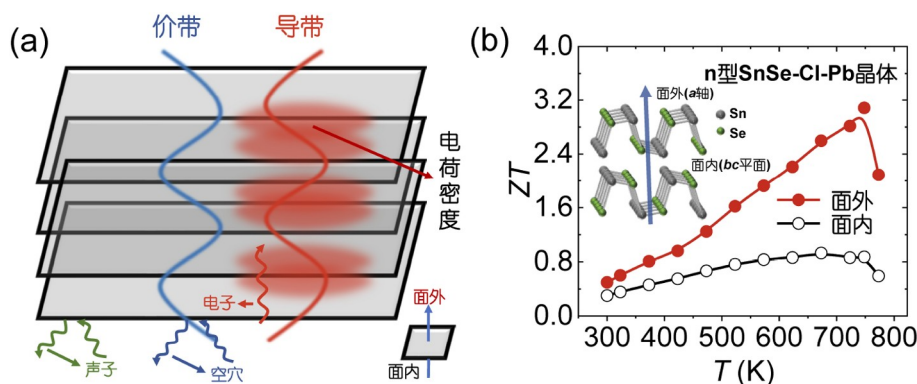


图1 (网络版彩色)(a) “二维声子-三维电荷”热电传输特性示意图; (b) n型SnSe-Cl-Pb晶体面外与面内 ZT ^[31]

Figure 1 (Color online) (a) Schematic of “2D phonon-3D charge” thermoelectric transport; (b) ZT values for n-type SnSe-Cl-Pb crystals along the out-of-plane and in-plane directions^[31]

的n型层状SnSe晶体中被发现,这一传输特性使n型SnSe晶体面外方向拥有极低热导率的同时保持了较为良好的电输运性能,获得 ~ 2.8 的 $ZT_{\max}^{[30]}$. 本征SnSe在室温下属于 $Pnma$ 空间群,双原子层沿晶体学 a 轴(面外方向)堆叠形成层状正交结构,可视为扭曲的岩盐结构. 同时,SnSe也展现出极强的各向异性价键连接,1个Sn原子与7个Se原子相连接形成高度扭曲的 SnSe_7 多面体,4个强Sn-Se键处于层内,在层间则存在另外3个弱Sn-Se键^[28,40]. SnSe各向异性的晶体结构与化学键导致了非常强的非谐振效应. 格林内森常数($\gamma = -\frac{V}{\omega} \frac{\partial \omega}{\partial V}$, 其中 V 与 ω 分别表示晶格体积与声子频率)可以展现非谐振效应的强弱, γ 越大,非谐振性越强, κ_{lat} 越小. SnSe沿 a 、 b 、 c 轴的平均 γ 与其晶体结构一样具有各向异性,分别为4.1、2.1和2.3^[41,42]. 与其他低热导材料如PbTe(1.65)、PbSe(1.69)、PbS(1.67)、AgSbTe₂(2.05)相比^[43],SnSe晶体具有更大的 γ ,尤其在面外方向具有更大的优势. SnSe较大的 γ 使其 κ_{lat} 远低于PbTe($\sim 2.3 \text{ W m}^{-1} \text{ K}^{-1}$)、PbSe($\sim 2.64 \text{ W m}^{-1} \text{ K}^{-1}$)、PbS($\sim 2.8 \text{ W m}^{-1} \text{ K}^{-1}$)等材料^[43]. 钠(Na)掺杂p型SnSe晶体的 κ_{lat} 在面内方向为 $\sim 0.73 \text{ W m}^{-1} \text{ K}^{-1}$;得益于面外方向更强的非谐振性,其面外方向的 κ_{lat} 仅为 $\sim 0.46 \text{ W m}^{-1} \text{ K}^{-1}$,是面内方向的 $\sim 63\%$,由此可见SnSe晶体在面外方向具有更低的 κ_{lat} ,表现出“二维声子”的传输特性^[29].

SnSe各向异性的层状晶体结构使其在电输运特性中也存在着较强的各向异性^[30,44]. 总体而言,层状热电材料沿面内方向的 μ 一般高于面外方向,但n型SnSe晶体在相同 n 的情况下沿面外的 μ 远大于p型SnSe晶体. Yang等人^[45]在2015年通过第一性原理计算发现,p型SnSe晶体在价带顶(valence band maximum, VBM)所形成的反键态阻碍空穴沿 a 轴传输,导致了很低的电输运性能,而n型SnSe晶体在导带底(conduction band minimum, CBM)由于强电子离域交叠杂化而形成了一条利于电子沿着 a 轴方向传输的通道,从而可在面外获得较为优异的电输运特性及更高的热电性能. 2016年,Duong等人^[46]通过铋(Bi)在SnSe晶体中掺杂实现了n型转变,在773 K时沿平面内实现了2.2的 $ZT_{\max}$,但面外的 $ZT_{\max}$ 仅为0.8,没有实现理论计算预测的高面外热电性能. 然而,2018年报道的Br掺杂n型SnSe晶体在面外方向获得了 ~ 2.8 的 $ZT_{\max}$ ，“二维声子-三维电荷”热电传输特性在获得优异热电性能方面的潜力首次展现. Bi与Br掺杂n型SnSe晶体表现出的性能差异可能取决于“三维电荷”输运特性的形成机理. SnSe导带与价带的态密

度(density of states, DOS)来自不同原子的电子轨道的贡献,Se的pz轨道对价带DOS贡献最大,而Sn的px轨道对导带DOS贡献最大,如图2(a)所示^[30]. 这表明在SnSe的价带中DOS倾向于沿面内方向分布,而导带中DOS则更倾向于沿面外方向分布,导致了p型与n型SnSe表现出明显不同的电荷密度分布,如图2(b)所示^[30]. p型SnSe晶体的电荷密度在层间分布极少,主要分布于面内方向;n型SnSe晶体中的电荷密度则更倾向于沿层间分布,这使其电荷密度在层间发生交叠,为电子在面外方向的传输提供了一条特殊通道,使得n型SnSe晶体在面外方向具有更高的载流子迁移率,实现了“三维电荷”的电输运特性. 在Sn位掺杂Bi元素虽能使SnSe转变为n型半导体,但Bi的引入可能破坏了原本由Sn的电子轨道主导的SnSe的导带结构,使其难以表现出“二维声子-三维电荷”热电传输特性;Br、Cl、I等卤素元素在Se位的高效掺杂不仅能使SnSe转变为n型半导体,还能保持SnSe原有的导带特性,从而通过“二维声子-三维电荷”热电传输特性表现出优异热电性能.

2 “二维声子-三维电荷”热电传输特性优势

沿面外方向的超低晶格热导率是具有“二维声子-三维电荷”热电传输特性的层状热电材料实现高热电性能的基础. 图3(a)给出了不同层状材料面外 κ_{lat} 与面内 κ_{lat} 的比值($\kappa_{\text{lat, Out}}/\kappa_{\text{lat, In}}$),图中所有样品的 $\kappa_{\text{lat, Out}}/\kappa_{\text{lat, In}}$ 均小于1,Cl掺杂和Pb固溶的n型SnSe晶体以及Cl掺杂的n型PbSnS₂晶体中 $\kappa_{\text{lat, Out}}/\kappa_{\text{lat, In}}$ 在整个温区中甚至小于0.5,表明了层状材料在面外方向显著的低晶格热导率优势.

面外方向高效的载流子迁移是具有“二维声子-三维电荷”热电传输特性的层状热电材料的主要优势. 图3(b)给出了不同层状热电材料的面外 μ_{Out} 与面内 μ_{In} 的比值($\mu_{\text{Out}}/\mu_{\text{In}}$). 在p型SnSe以及Bi掺杂的n型SnSe晶体中, $\mu_{\text{Out}}/\mu_{\text{In}}$ 在全温区的范围内基本一致,普遍分布在0.2左右;而在n型SnSe、n型PbSnS₂等具有“二维声子-三维电荷”热电传输特性的材料中,300 K时 $\mu_{\text{Out}}/\mu_{\text{In}}$ 均处于 ~ 0.7 左右,远高于p型SnSe晶体、p型SnS晶体及Bi掺杂的n型SnSe晶体;随着温度的升高,具有“二维声子-三维电荷”热电传输特性的材料层间电荷密度的交叠程度进一步得到增强,使得这些材料的 $\mu_{\text{Out}}/\mu_{\text{In}}$ 不断增大,在673 K后趋于或超过1,即面外的 μ 甚至高于面内,表明“二维声子-三维电荷”热电传输特性的面外方向高载流子迁移率优势可随温度的提升不断增强. 为评估“三维电荷”带来的迁移率提升对Cl掺杂SnSe面外热电性

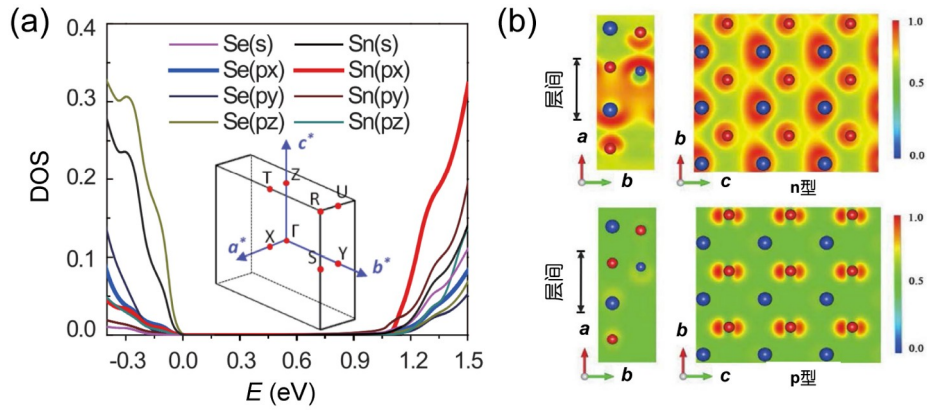


图 2 (a) SnSe在费米能级附近的DOS及各原子轨道的贡献, 插图显示了SnSe的布里渊区. (b) 计算得到的n型(上)和p型(下)SnSe的电荷密度分布^[30]. Copyright © 2018, American Association for the Advancement of Science

Figure 2 (a) Projected DOS of SnSe near the Fermi energy level and contributions from various atomic orbitals. The insert diagram shows the Brillouin zone of SnSe. (b) Calculated charge density distributions of n-type (top) and p-type (bottom) SnSe^[30]. Copyright © 2018, American Association for the Advancement of Science

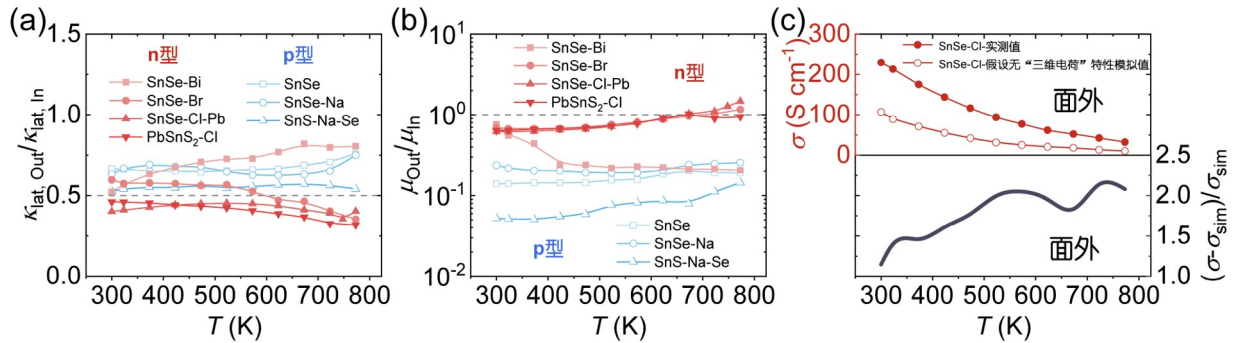


图 3 不同元素掺杂的SnSe、SnS及PbSnS₂晶体的面外晶格热导率与面内晶格热导率的比值 $\kappa_{\text{lat, Out}}/\kappa_{\text{lat, In}}$ (虚线表示 $\kappa_{\text{lat, Out}}/\kappa_{\text{lat, In}}=0.5$)(a)和面外迁移率与面内迁移率的比值 $\mu_{\text{Out}}/\mu_{\text{In}}$ (虚线表示 $\mu_{\text{Out}}/\mu_{\text{In}}=1$)(b)^[28-31,33,46,47]. (c) Cl掺杂SnSe面外电导率的实测值 σ , 假设Cl掺杂SnSe拥有与Na掺杂SnSe相同的 $\mu_{\text{Out}}/\mu_{\text{In}}$ 时, 依据Cl掺杂SnSe面内电导率的实测值计算出来的面外电导率的模拟值 σ_{Sim} , 以及“三维电荷”特性为Cl掺杂SnSe带来的面外电导率提升

Figure 3 The ratio of lattice thermal conductivity (dotted line indicates $\kappa_{\text{lat, Out}}/\kappa_{\text{lat, In}}=0.5$) (a) and carrier mobility (dotted line indicates $\mu_{\text{Out}}/\mu_{\text{In}}=1$) (b) for SnSe, SnS and PbSnS₂ crystals along the out-of-plane direction to the in-plane direction^[28-31,33,46,47]. (c) Measured electrical conductivity for Cl-doped SnSe along the out-of-plane direction σ , the simulated electrical conductivity for Cl-doped SnSe along the out-of-plane direction σ_{Sim} which is calculated based on the measured electrical conductivity of Cl-doped SnSe along the in-plane direction (assuming that Cl-doped SnSe possesses the same $\mu_{\text{Out}}/\mu_{\text{In}}$ as Na-doped SnSe), and the enhancement of electrical conductivity along the out-of-plane direction due to “3D charge”

能的贡献, 图3(c)给出了假设Cl掺杂SnSe拥有与Na掺杂SnSe相同的 $\mu_{\text{Out}}/\mu_{\text{In}}$ 时, 依据Cl掺杂SnSe面内电导率的实测值计算出来的面外电导率的模拟值(σ_{Sim}). 可见室温下“三维电荷”特性为Cl掺杂的SnSe带来了~110%的面外 σ 的提升, 随着温度的升高, 其带来的提升不断增大, 高温下“三维电荷”特性对Cl掺杂SnSe的面外 σ 的提升甚至达到~200%, 这对其面外热电性能的提升产生极大贡献.

面外更大的塞贝克系数为具有“二维声子-三维电荷”热电传输特性的层状热电材料的另一个优势. 具有“二维声子-三维电荷”热电传输特性的层状热电材料沿

其面内与面外方向会表现 S 的各向异性^[31-33]. 以SnSe为例, 图4(a)中Na掺杂的p型SnSe晶体中展现出明显的各向同性 S ; 与此相反, Cl掺杂的n型SnSe中却展现出较强的各向异性 S , 其在面外方向具有更大的 S , 且随着温度的升高, 面外比面内的 S 优势逐渐增大. 此外, Na掺杂的p型SnSe晶体的 σ 在两个方向上随温度升高呈现出一致的变化, 而Cl掺杂的n型SnSe晶体的 σ 在面外与面内方向随温度的变化则为不同的趋势, 如图4(b)所示. 这一现象反映出Cl掺杂的n型SnSe晶体沿其面外与面内方向具有不同的载流子散射机制与不同的载流子散射因子 r . 实际上, 造成Cl掺杂n型SnSe晶体各向异性 S 的原

因正是由其层间交叠电荷密度导致的各向异性的载流子散射因子 r ^[32]. Cl掺杂n型SnSe晶体沿其面内方向的 r 在300~773 K内保持稳定(-0.48), 较为符合声学声子散射; 但其面外方向的 r 在300~523 K时为-0.31, 523~773 K时甚至提升至0.62, 严重偏离声学声子假设. 考虑 r 的各向异性后, 利用单抛物带模型计算得到的Cl掺杂n型SnSe晶体的简约费米能级 η 与态密度有效质量 m^* 在两方向上取得了良好的一致性, 证明了面外更大的 r 是导致Cl掺杂n型SnSe晶体在面外方向具有更大 S 的原因. 图4(c)给出了假设Cl掺杂SnSe沿其面外方向的塞贝克系数与其面内方向的塞贝克系数相同时, 计算出来的面外功率因子的模拟值(PF_{sim}), 该值可以用于估计“三维电荷”带来的面外塞贝克系数提升对Cl掺杂

SnSe面外热电性能的贡献. 可见室温下“三维电荷”带来的 S 提升为Cl掺杂的SnSe带来了30%的PF提升, 随着温度升高, 该提升持续增大并在600 K后达到了60%, 对Cl掺杂的SnSe面外热电性能的提升同样做出较大贡献.

“二维声子-三维电荷”热电传输特性的晶格热导率、载流子迁移率以及塞贝克系数优势使具有此性质的材料沿其面外方向的热电性能在整个温区内都优于面内方向. 图5(a)展示了不同层状热电材料面外 ZT 与面内 ZT 的比值(ZT_{out}/ZT_{in}). p型材料及Bi掺杂的n型SnSe晶体在面内方向具有更高的热电性能; 而在具有“二维声子-三维电荷”热电传输特性的材料中, 面外方向有着更加出色的热电性能, 且随着温度的升高, 得益于其更具优势的晶格热导率与层间交叠的电荷密度增强所带来

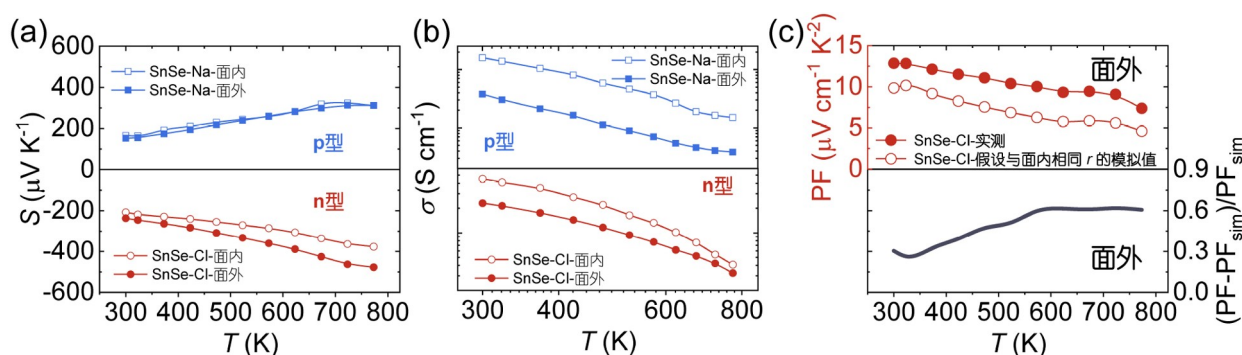


图4 (网络版彩色) Na掺杂的p型SnSe和Cl掺杂的n型SnSe晶体在面内与面外方向的电输运特性^[29,32]. (a) 塞贝克系数 S ; (b) 电导率 σ ; (c) Cl掺杂的SnSe面外功率因子的实测值PF, 假设Cl掺杂SnSe沿其面外方向的塞贝克系数与其面内方向的塞贝克系数相同时计算得到的面外功率因子的模拟值 PF_{sim} , 以及各向异性的散射因子带来的面外功率因子的提升

Figure 4 (Color online) The electrical properties for Na-doped p-type SnSe and Cl-doped n-type SnSe crystals along the out-of-plane and in-plane directions^[29,32]. (a) Seebeck coefficient S ; (b) electrical conductivity σ ; (c) measured power factor PF for Cl-doped SnSe along the out-of-plane direction, simulated values of the calculated power factor along the out-of-plane direction (assuming that the S of Cl-doped SnSe along the out-of-plane direction is equal to the S along the in-plane direction), and the enhancement of power factor along the out-of-plane direction due to the anisotropic scattering factor

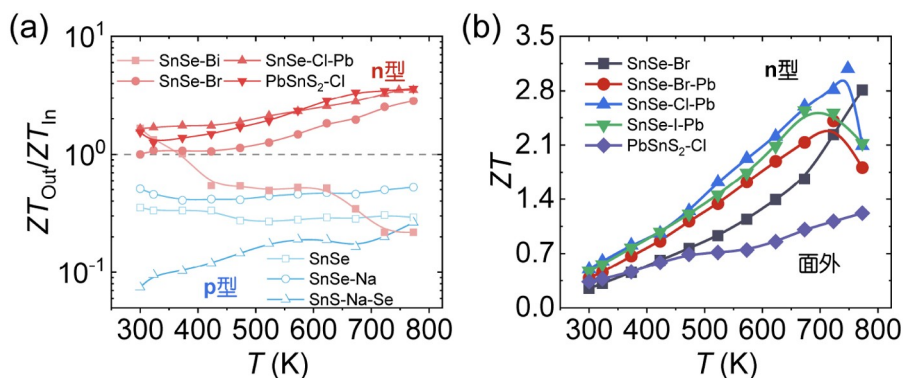


图5 (网络版彩色) (a) 不同元素掺杂的SnSe、SnS及PbSnS₂晶体的 ZT_{out}/ZT_{in} (虚线表示 $ZT_{out}/ZT_{in}=1$)^[28-31,33,46,47]; (b) 具有“二维声子-三维电荷”热电传输特性材料的 ZT ^[10,30-33]

Figure 5 (Color online) (a) The ratio of ZT values for SnSe, SnS and PbSnS₂ crystals along the out-of-plane direction to the in-plane direction (dotted line indicates $ZT_{out}/ZT_{in}=1$)^[28-31,33,46,47]; (b) ZT value of materials with “2D phonon-3D charge” thermoelectric transport^[10,30-33]

的优异电输运性能, $ZT_{\text{out}}/ZT_{\text{in}}$ 不断增大, 其面外热电性能展现出更大的优势. 图5(b)展示了已经报道的具有“二维声子-三维电荷”热电传输特性材料的 ZT . Br掺杂n型SnSe晶体利用“二维声子-三维电荷”热电传输特性在高温下实现了~2.8的超高 ZT_{max} ; 随后, Su等人^[31]利用Cl掺杂和Pb固溶成功增强了n型SnSe晶体的“二维声子-三维电荷”热电传输特性, 进一步促进了“声-电”解耦, 实现了~3.1的超高 ZT_{max} , 同时Pb的固溶提升了整个温区的热电性能, 使其在300~773 K的温区中取得了~1.7的 ZT_{ave} , 这不仅远高于Br掺杂的n型SnSe晶体 (ZT_{ave} ~1.1@300~773 K), 并与p型SnSe晶体的 ZT_{ave} 逐渐接近, 为实现全SnSe基热电器件迈出关键一步. 2023年, Zhan等人^[33]在Cl掺杂的n型PbSnS₂晶体中也发现了“二维声子-三维电荷”热电传输特性, 且在300~773 K得到了0.75的 ZT_{ave} , 这也使其成为了可与p型SnS匹配的极具潜力的n型材料. 此外, 一些理论计算工作表明n型SnS、GeSe、PbSnSe₂等本征低热导层状材料同样具有“二维声子-三维电荷”的热电传输特性, 并具有不俗的热电性能潜力. Jiang等人^[37]通过第一性原理计算预测n型SnS晶体可在750 K时实现~3.1的 ZT_{max} ; Fan等人^[39]预测n型GeSe晶体则可在700 K时实现~2.5的 ZT_{max} ; Wang等人^[38]预测n型PbSnSe₂晶体有望在700 K时实现~3的 ZT_{max} . 这些理论计算工作有力支撑了“二维声子-三维电荷”热电传输特性在实现优异热电性能上的优势, 也表明在本征低热导材料中筛选具有“二维声子-三维电荷”热电传输特性的材料正逐步成为开发新型高性能热电材料的标准之一.

3 总结与展望

“二维声子-三维电荷”热电传输特性使热电材料在拥有极低热导率的同时保持了较为良好的电输运

特性, 在解耦“声-电”矛盾、实现“声子玻璃-电子晶体”传输方面表现出了巨大潜力. 当前, 具有“二维声子-三维电荷”热电传输特性的材料均为本征低热导率的n型层状晶体材料, 其沿面外方向的超低晶格热导率是形成“二维声子-三维电荷”热电传输的基础; 此外, 层间交叠的电荷密度建立起面外方向电荷的快速迁移通道, 使“二维声子-三维电荷”热电传输具有了面外方向高载流子迁移率的主要优势; 最后, 各向异性电荷密度导致了面外更大的载流子散射因子, 使“二维声子-三维电荷”热电传输在面外方向进一步具有了更大的塞贝克系数优势. “二维声子-三维电荷”热电传输特性使得n型SnSe晶体获得了十分优异的高温热电性能, 增强n型SnSe晶体的“二维声子-三维电荷”热电传输特性也能进一步优化其宽温域热电性能.

鉴于具有“二维声子-三维电荷”热电传输特性材料的优异热电性能, 利用理论计算寻找具有“二维声子-三维电荷”热电传输特性的本征低热导率的材料有望成为开发新型高性能热电材料的参考之一; 除开发新材料外, 利用元素掺杂尝试在材料能带结构中构建各向异性的态密度及电荷密度分布, 有望在已有材料中实现“二维声子-三维电荷”热电传输特性; 对于已具备“二维声子-三维电荷”传输特性的各类层状材料, 晶体对称性调控是优化其载流子迁移率及宽温域热电性能的有效手段, 引入插层原子也可能通过增强电荷密度在层间的交叠程度而实现“二维声子-三维电荷”热电传输特性的增强. 正如前文所述, 目前具有“二维声子-三维电荷”热电传输特性的均为层状晶体材料, 晶体材料较为苛刻的生长条件与较差的机械性能为这些材料未来的大规模应用带来挑战, 构成了这类材料走向应用的重点和难点.

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Summary for “‘二维声子-三维电荷’热电传输特性研究进展”

Recent progress in “2D phonon-3D charge” thermoelectric transport

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Thermoelectric materials can directly convert thermal and electrical energy to each other and have a huge potential in power generation and precise temperature control. High-performance thermoelectric materials pursue to achieve “phonon glass-electron crystal” transport, which requires both low thermal and high electrical transport properties. However, the strong coupling between the phonon and the electron in materials poses a significant challenge in realizing the “phonon glass-electron crystal” transport. Developing the thermoelectric performance of intrinsically low thermal conductivity materials, such as layered structure materials, is an effective strategy to promote the “phonon-electron” decoupling. Tin selenide (SnSe) is an intrinsically low thermal conductivity layered material. The low lattice thermal conductivity along the in-plane direction endows the basis of the excellent thermoelectric performance for p-type SnSe crystals. Layered structure materials possess much lower lattice thermal conductivity along the out-of-plane direction than in-plane generally. If the carrier mobility of SnSe and other intrinsically low thermal conductivity layered structure materials along the out-of-plane direction can be increased, the ultra-low thermal conductivity of layered structural materials along this direction can be utilized to form “two-dimensional (2D) phonon and three-dimensional (3D) charge” thermoelectric transport, which can be further realized “phonon glass-electron crystal” transport. Anion-doped n-type SnSe crystals possess overlapping interlayer charge density resulting in a large enhancement of carrier mobility along the out-of-plane direction, and thus show “2D phonon-3D charge” thermoelectric transport and have attracted huge attention in the thermoelectric field due to their excellent performance. Therefore, more materials with “2D phonon-3D charge” thermoelectric transport are being discovered and show exciting potential for thermoelectric performance. Seeking materials with “2D phonon-3D charge” thermoelectric transport among intrinsically low thermal conductivity materials is gradually becoming one of the criteria for the development of new high-performance thermoelectric materials.

In this review, we first introduced the mechanism of “2D phonon-3D charge” thermoelectric transport. The intrinsically low thermal conductivity along the out-of-plane direction of the layered material forms the “2D phonon” transport, which is the basis for obtaining excellent thermoelectric performance. The overlapping interlayer charge density can facilitate electron transport along the out-of-plane direction, and thus forms the “3D charge” transport which is the key to obtaining excellent thermoelectric performance. We also introduced the advantages of “2D phonon-3D charge” thermoelectric transport with lattice thermal conductivity, carrier mobility, and the Seebeck coefficient. The overlapping interlayer charge density leads not only to high carrier mobility along the out-of-plane direction, but also to the higher scattering factor than the in-plane direction and thus to the larger Seebeck coefficients along the out-of-plane direction than in-plane. Finally, we summarized the research progress of materials with “2D phonon-3D charge” thermoelectric transport, and gave an outlook on how to utilize and enhance “2D phonon-3D charge” thermoelectric transport to realize high thermoelectric performance, as well as the challenges for the future development of thermoelectric materials with “2D phonon-3D charge” thermoelectric transport. This review can help researchers comprehensively understand the “2D phonon-3D charge” thermoelectric transport and also contribute to the development of new high-performance thermoelectric materials.

thermoelectric materials, phonon-electron decoupling, anisotropy, layered structure, charge densitydoi: [10.1360/TB-2024-0793](https://doi.org/10.1360/TB-2024-0793)