

载流子迁移率在解耦电-声输运矛盾中的作用

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摘 要: 热电材料研究的核心在于协调和优化多种相互制约的热电参数以解耦电-声输运矛盾。近年来, 提升载流子迁移率已成为提高材料热电性能的重要策略。通过简化的解耦电-声输运参数模型和 Kane 热电参数模型, 系统地探讨了迁移率提升对解耦电-声输运矛盾的作用和规律。结果表明: 电子热导率与晶格热导率之比是限制热电性能增幅的关键因素。如何在提升迁移率的同时有效操控电-声输运解耦, 实现最优的宽温域乃至近室温热电性能, 是未来热电材料在发电和制冷应用领域中的重要挑战。

关键词: 热电材料; 载流子迁移率; 电子热导率; 晶格热导率; 电-声输运
中图分类号: TB34 **文献标志码:** A **文章编号:** 0454-5648(2025)04-0733-09
网络出版时间: 2025-02-18



热电材料在过去几十年中引起广泛关注, 源于其在热能与电能直接转化中的独特能力。这为在可持续发电和半导体制冷领域的应用提供了重要潜力^[1-4]。热电材料研究的基础在于优化多种相互矛盾的特性, 热电优值(ZT)是评估热电材料的重要指标^[5-8]:

$$ZT = \frac{S^2 \sigma T}{\kappa_{\text{ele}} + \kappa_{\text{lat}}} \quad (1)$$

其中: S 、 σ 、 κ_{ele} 和 κ_{lat} 分别为 Seebeck 系数、电导率、电子热导率和晶格热导率; T 为绝对温度。为了最大化 ZT 值, 热电材料需要具备较大的温差电动势(Seebeck 系数)、高电导率和低热导率。然而, 这些传输特性相互依赖于半导体材料的多种性质, 呈现出强烈的电-声输运耦合。因此, 为实现最佳 ZT , 需要对多个参数进行解耦和协同优化^[9-11]。

在半导体材料中, 理想情况下应仅存在单一类型的载流子。因为混合的 n 型和 p 型导电会导致电子和空穴同时朝着冷端移动, 从而抵消所产生的 Seebeck 电压^[12]。通常, 对于金属或简并半导体,

其 Seebeck 系数的定义为^[13-14]:

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

其中: k_B 、 e 、 h 、 m_{DOS}^* 和 n 分别代表 Boltzmann 常数、电子电荷、Planck 常数、载流子的态密度有效质量和载流子浓度。因此, 具有低载流子浓度的宽带隙半导体通常具有较大的 Seebeck 系数。然而, 低载流子浓度也会造成半导体材料具有较差的电导率。电导率与载流子浓度的关系式为:

$$\sigma = ne\mu \quad (3)$$

其中: μ 为载流子迁移率。在复杂的热电参数中, Seebeck 系数与电导率之间的竞争关系通过载流子浓度得以体现。较低的载流子浓度通常有助于提高 Seebeck 系数, 但可能会导致电导率下降, 反之亦然。

此外, Seebeck 系数和电导率相互竞争的矛盾还可以通过有效质量得以体现。大的态密度有效质量通常会产生高的热电势(大的 Seebeck 系数), 但也

收稿日期: 2024-11-14。 修订日期: 2024-11-28。

基金项目: 国家杰出青年科学基金(51925101); 国家自然科学基金(52450001, 22409014); 北京市杰出青年科学基金(JQ18004); 高等学校学科创新引智计划(B17002); 博士后创新人才支持计划(BX20230456); 中国博士后科学基金面上项目(2024M754057)和科学探索奖。

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Received date: 2024-11-14. Revised date: 2024-11-28.

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会损害载流子迁移率而导致低的电导率。载流子迁移率与态密度有效质量的关系为^[15]:

$$\mu = \left(\frac{4}{3\pi^{1/2}} \right) \left\{ \frac{e\tau_0 (k_B T)^{-1/2}}{m_{\text{DOS}}^*} \right\} \quad (4)$$

$$m_{\text{DOS}}^* = (m_x^* m_y^* m_z^*)^{1/3} \quad (5)$$

其中: m_x^* 、 m_y^* 和 m_z^* 分别为电子或空穴在各晶向上的有效质量。态密度有效质量是表征材料中电子或空穴在能带结构中的一重要参数, 主要用于定量描述电子态密度随能量变化的情况^[16]。相比实际的电子有效质量, 态密度有效质量更侧重于能带结构对态密度分布的影响。通常, 能带较平坦的材料, 其态密度有效质量较大, 反映出该类能带中较高的电子或空穴局域性与较低的载流子迁移率。因此, 有效质量和迁移率的关系是复杂的, 它主要依赖于材料的电子结构、散射机制和各向异性^[17]。一般情况, 具有高迁移率和小有效质量的热电材料通常源于其组成元素间电负性差异较小, 如 PbSe 和 Bi₂Te₃ 等^[18–19]。相反, 具有大的有效质量和低迁移率的材料往往为窄带隙的化合物, 如 BiCuSeO 和 Mg₃Bi₂ 等^[20–21]。因此, 实现增强态密度有效质量与保持较高迁移率之间的权衡, 是优化热电性能的关键。实验上可采用多能带对齐^[22–23]、晶格量化^[24–28]和能带锐化^[29–30]等策略实现。

除此之外, 在调控热电材料的电输运性质时, 也不能忽视其热输运。电输运和热输运通过电子热导率耦合, 它们之间的相互作用会影响材料的整体热电性能。总热导率的公式为:

$$\kappa_{\text{tot}} = \kappa_{\text{ele}} + \kappa_{\text{lat}} \quad (6)$$

显然, 总热导率由载流子携带的热量(κ_{ele})和穿越晶格的声子传导所贡献的热量(κ_{lat})共同构成。由 Wiedemann–Franz 定律可知^[14], 电子热导率与电导率直接相关, 公式为:

$$\kappa_{\text{ele}} = L\sigma T = Lne\mu T \quad (7)$$

其中: L 为 Lorentz 系数, 其值不仅依赖于载流子浓度的变化, 还决定了电子热导率的准确评估。在低载流子浓度材料中, Lorentz 系数可能会相较于自由电子值($L = 2.48 \times 10^{-8} \text{ J}^2 \cdot \text{K}^{-2} \cdot \text{C}^{-2}$)降低多达 20%, 这源于载流子散射机制对于电子热导率的影响。因此, 载流子浓度是导致高电子热导率的主要因素。由 Wiedemann–Franz 定律揭示材料中固有的电导率和热导率矛盾, 可以发现 ZT 可以表示为:

$$ZT = \frac{S^2 / L}{1 + \frac{\kappa_{\text{ele}}}{\kappa_{\text{lat}}}} \quad (8)$$

当载流子浓度较高时($\kappa_{\text{ele}}/\kappa_{\text{lat}} \rightarrow \infty$), 这导致 ZT 仅由 Seebeck 系数主导。而 Seebeck 系数与载流子浓度呈反比关系[见式(2)], 在此条件下难以优化 ZT 。因此, 只有通过调整载流子浓度, 使电子热导率与晶格热导率处于相近水平($0.1 < \kappa_{\text{ele}}/\kappa_{\text{lat}} < 10$), 才能实现最优 ZT 。同时, 这也决定了热电性能优化的载流子浓度在 $10^{19} \sim 10^{21} \text{ cm}^{-3}$ 之间^[5]。此外, 在实验研究中, 提高载流子迁移率被认为是优化整个温度范围内热电性能的有效策略^[17]。特别是在低载流子浓度范围 ($10^{18} \sim 10^{19} \text{ cm}^{-3}$), 载流子既少又快的特性可以有效解决载流子迁移率与有效质量之间的矛盾^[13, 31–32]。然而, 载流子迁移率对解耦电–声输运矛盾中的作用仍需进一步深入探讨。

在本工作中, 基于合理的假设对复杂且相互竞争的热电参数模型进行了简化, 以探讨热电材料中载流子迁移率对于解耦电–声输运矛盾的作用。针对先前工作中报道的热电参数潜在优化区域 ($10^{18} \sim 10^{19} \text{ cm}^{-3}$), 该区域表现出载流子浓度和 Seebeck 系数变化较小的特点^[13]。在此研究背景下, 假设 Seebeck 系数和载流子浓度保持恒定, 可以有效简化理论模型。结合实验数据和简化的理论模型, 重点分析迁移率提升过程中电子热导率与晶格热导率比值对 ZT 增幅的影响, 以阐明载流子迁移率优化对于实现电–声解耦的重要性。如图 1 所示, 简化后的

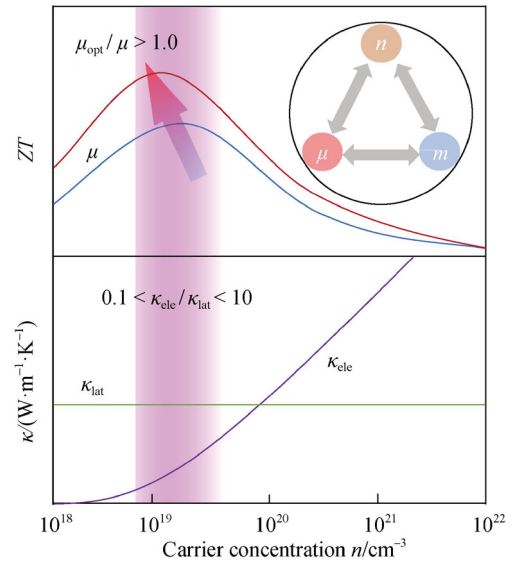


图 1 载流子迁移率提升与电–声解耦优化热电性能
Fig. 1 Enhancement of carrier mobility and electron–phonon decoupling for optimizing thermoelectric performance

模型计算与结果分析显示, 载流子迁移率提升对于实现低载流子浓度以及中低温乃至近室温区域的电-声输运解耦的作用尤为明显, 表明优化载流子迁移率这一策略在提升材料宽温域乃至近室温热电性能、优化热电器件转换效率以促进其大规模关键应用方面的重要价值。

1 计算方法

1.1 电-声解耦参数模型

假设 Seebeck 系数和载流子浓度保持恒定 ($S \equiv S_0, n \equiv n_0$), 有效简化理论模型以评估 ZT 与电子热导率和晶格热导率比值(电-声解耦程度)的关系。假设在迁移率提高时($\mu_{\text{opt}}/\mu > 1.0$), 电-声解耦参数模型为:

$$\begin{aligned} \frac{ZT_{\text{opt}}}{ZT} &= \frac{S_0 n_0 e \mu_{\text{opt}} T}{[(\mu_{\text{opt}}/\mu) \kappa_{\text{ele}}/\kappa_{\text{lat}} + 1] \kappa_{\text{lat}}} \times \frac{(\kappa_{\text{ele}}/\kappa_{\text{lat}} + 1) \kappa_{\text{lat}}}{S_0 n_0 e \mu T} \\ &= \frac{(\mu_{\text{opt}}/\mu)(\kappa_{\text{ele}}/\kappa_{\text{lat}} + 1)}{[(\mu_{\text{opt}}/\mu) \kappa_{\text{ele}}/\kappa_{\text{lat}} + 1]} \end{aligned} \quad (9)$$

其中: 电子热导率与迁移率提高的倍数保持一致[见式(7)]; 晶格热导率则主要受晶体结构、缺陷和各向异性等复杂因素影响, 故不作详细考虑, 可视为常数项。需要指出的是, 实际情况下, 当载流子迁移率的提升源于有效质量的下降或散射作用的减弱时, 其往往伴随着 Seebeck 系数的降低或晶格热导率的增大。因此, 在这类情况下, 本假设模型对于最终 ZT 值提升幅度的计算和预估会偏高。但实际研究中也存在载流子迁移率提升并不伴随着 Seebeck 系数的降低和晶格热导率的提升, 如晶格素化等条件。本假设模型对于评估载流子迁移率在解耦电-声输运矛盾以提升 ZT 值中的作用仍具有重要的参考价值。

1.2 Kane 热电参数模型

根据单能带 Kane 模型, 载流子浓度可由式(10)表示^[33]:

$$n = A^{-1} \frac{N_v (2m_b^* k_B T)^{3/2}}{2\pi^2 \hbar^3} {}^0F_0^{3/2} \quad (10)$$

其中: e 为电子电荷数; N_v 为能带简并数; m_b^* 为单带的有效质量; k_B 为 Boltzmann 常数; T 为绝对温度; $\hbar$ 为约化 Planck 常数; A 为 Hall 因子, 可由式(11)表示:

$$A = \frac{3K(K+2) {}^0F_{-4}^{1/2} \cdot {}^0F_0^{3/2}}{(2K+1)^2 ({}^0F_2^1)^2} \quad (11)$$

其中: K 为横向与纵向载流子有效质量的比值; ${}^nF_k^m$ 是与 Fermi 积分具有相似的形式, 可由式(12)表示:

$${}^nF_k^m = \int_0^\infty \left(-\frac{\partial f}{\partial \varepsilon}\right) \varepsilon^n (\varepsilon + \alpha \varepsilon^2)^m \left[(1 + 2\alpha \varepsilon)^2 + 2\right]^{k/2} d\varepsilon \quad (12)$$

其中: f 为 Fermi 分布; ε 为约化的电子态能量; α 由 $k_B T / E_g$ 决定, 而 E_g 为能带带隙。

载流子迁移率由式(13)表示:

$$\mu = A \frac{2\pi \hbar^4 e C^1}{m_l^* (2m_b^* k_B T)^{3/2} (E^{\text{def}})^2} \frac{{}^3F_2^1}{{}^0F_0^{3/2}} \quad (13)$$

其中: C^1 为杨氏模量; m_l^* 为载流子的惯性有效质量; E^{def} 为形变势常数。

ZT 由式(14)表示:

$$ZT = \frac{\left(\frac{{}^1F_{-2}^1}{{}^0F_{-2}^1} - \xi\right)^2}{\left[\frac{{}^2F_{-2}^1}{{}^0F_{-2}^1} - \left(\frac{{}^1F_{-2}^1}{{}^0F_{-2}^1}\right)^2\right] + \frac{1}{3 {}^0F_{-2}^1 B}}, B = \frac{2Tk_B^2 \hbar C^1 N_v}{3\pi m_l^* (E^{\text{def}})^2 \kappa_L} \quad (14)$$

其中: ξ 为约化的 Fermi 能级。

2 结果与讨论

2.1 迁移率提升对于电-声解耦的影响

电子热导率和晶格热导率是热电材料中 2 个重要的热导率参数, 而它们的区别在于热传导的机制和主要载体。电子热导率是由自由电子传导引起的热导率, 它与载流子迁移率及散射机制密切相关^[34-35]。然而, 晶格热导率主要与材料的晶体结构、晶格缺陷和温度等因素相关, 声子的散射和传播是决定晶格热导率的主要因素^[36-39]。因此, 迁移率提升可以显著影响电子热导率而非晶格热导率。对于不同的体系, 晶格热导率则表现出显著差异, 由此可以得到:

$$\frac{ZT_{\text{opt}}}{ZT} = \frac{(\mu_{\text{opt}}/\mu)(\kappa_{\text{ele}} + \kappa_{\text{lat}})}{[(\mu_{\text{opt}}/\mu) \kappa_{\text{ele}} + \kappa_{\text{lat}}]} \quad (15)$$

通过调整式中晶格热导率的值, 研究不同体系下迁移率提升时电子热导率对优化 ZT 的关系函数, 如图 2 所示。

一方面, 在保持晶格热导率不变的前提下, 迁移率的提升显著增强了体系的 ZT 值, 且其提升效果随着迁移率的增加而愈加显著。例如, 在相同晶格热导率的体系中, 当晶格热导率占主导地位时, 迁移率提升 2 倍或 3 倍将导致 ZT 值相应提高 2 倍或 3 倍。另一方面, 对于具有较低晶格热导率的体

系, 使用优化策略提升迁移率时, 需要将电子热导率保持在较低水平, 以期实现最佳调控优化。而在具有较高晶格热导率的体系中, 达到最优调控状态时, 允许电子热导率的值相对前者较大。上述分析表明, 在不同体系中通过提升迁移率来优化 ZT 时, 必须重视电子热导率与晶格热导率的比值关系(电-声解耦程度), 因为这一比值直接决定了 ZT 提升的幅度。

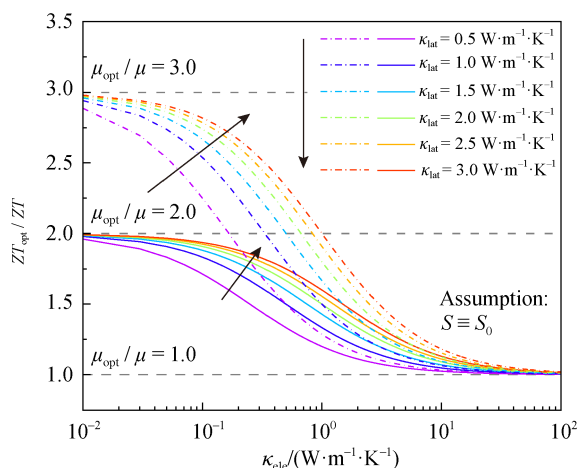


图2 在不同晶格热导率和不同载流子迁移率条件下, ZT 值提升幅度作为电子热导率的函数关系

Fig. 2 Enhancement of ZT as a function of electronic thermal conductivity under different lattice thermal conductivity and carrier mobility

2.2 电-声解耦对于 ZT 值提升的影响

根据式(9), 体系 ZT 值提升幅度与电子热导率和晶格热导率的比值之间存在函数关系, 具体表现如图3所示。通常, 在 $\kappa_{\text{ele}}/\kappa_{\text{lat}} < 0.1$ 时, ZT 提升幅度由晶格热导率主导; 在 $\kappa_{\text{ele}}/\kappa_{\text{lat}} > 10$ 时, ZT 提升幅度由电子热导率主导。因此, 当 ZT 值作为载流子浓度的函数达到峰值时, 电子热导率与晶格热导率的比值通常限制在[0.1, 10]的范围内, 这一范围确保了材料在热电转换过程中的最佳性能。在此基础上, 电-声解耦程度达到较高水平($\kappa_{\text{ele}}/\kappa_{\text{lat}} \approx 0.1$), ZT 因迁移率的提高也会获得大幅提升。同时, 随着迁移率的提高, ZT 增幅也会显著增加。例如, 当电子热导率与晶格热导率的比值为 0.1 时, 曲线的切线斜率的绝对值与迁移率的提升倍数呈正比。此外, 在半导体材料中, 随着温度升高, 电子热导率通常会显著增加, 因为更多的电子被热激发至导带, 增强了电子在热导中的贡献。同时, 晶格热导率可能因声子散射增强而趋于饱和或下降。因此, 在这种

情况下, 电子热导率相对于晶格热导率的比值会随温度升高而增加。这表明, 优化载流子迁移率对于提升近室温热电性能的效果将更加显著。

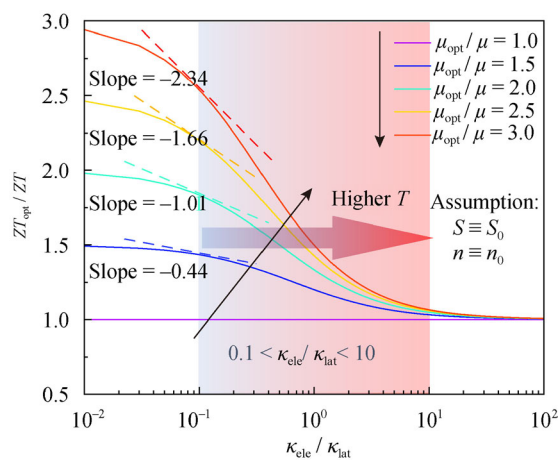


图3 在不同迁移率提升倍数的条件下, ZT 值提升幅度作为电子热导率与晶格热导率比值的函数关系

Fig. 3 Enhancement of ZT as a function of the ratio of electronic to lattice thermal conductivity at different carrier mobility enhancement factors

由于载流子浓度与电子热导率呈正比, 而晶格热导率并不依赖于载流子浓度, 所以载流子浓度和电子热导率与晶格热导率的比值呈正相关。这意味着, 随着载流子浓度的增加, 电子热导率的提升速率相对较快, 从而导致二者的比值增大。为了更直观地揭示迁移率提升时载流子浓度与 ZT 提升幅度的关系, 假设比值与载流子浓度之间存在一一对应的线性关系。例如, 假设电子热导率与晶格热导率的比值 0.1 对应载流子浓度为 10^{18} cm^{-3} , 而比值 10 对应载流子浓度为 10^{20} cm^{-3} 。需要注意的是, 这种线性关系的假设实际上会随体系的不同而变化, 因此在具体材料的研究中应进行适当的调整和验证。在这种假设条件下, 当迁移率提升 2 倍时, 可以获得不同晶格热导率体系下 ZT 提升幅度作为载流子浓度的函数关系, 如图4所示。结果表明, 随着载流子迁移率的提升, 载流子浓度的减小能够显著增强电-声解耦程度。在晶格热导率较高的体系中, 这种电-声解耦的优化尤为明显, 进而有利于提高 ZT 。这也说明, 通过调控载流子浓度和优化迁移率, 可以有效提升热电材料的热电性能, 为新型热电材料的设计和 optimization 提供了重要的理论依据。

简化的电-声解耦参数模型是为了更直观地探讨在近室温条件下提升热电材料载流子迁移率的电-

声解耦规律。除此之外,使用单能带 Kane 模型做出假设也可以模拟出更贴近实际情况的电-声解耦规律。在不考虑电-声耦合情况下,假设迁移率的提升不来源于有效质量、形变势和杨氏模量。通过式 (13) 可以得出,改变迁移率的大小实际上相当于 Fermi 能级的重新定位,此时 ZT 仅会向低载流子浓度方向发生平移,而无法实现增幅。然而,在考虑电-声耦合的情况下,由于迁移率提升和电-声解耦程度增强(形变势减小, B 参数增大), ZT 不仅向低载流子浓度方向移动,同时也实现了较大程度的增幅,从而形成了热电性能优化的潜在优化区域,如图 5 所示。

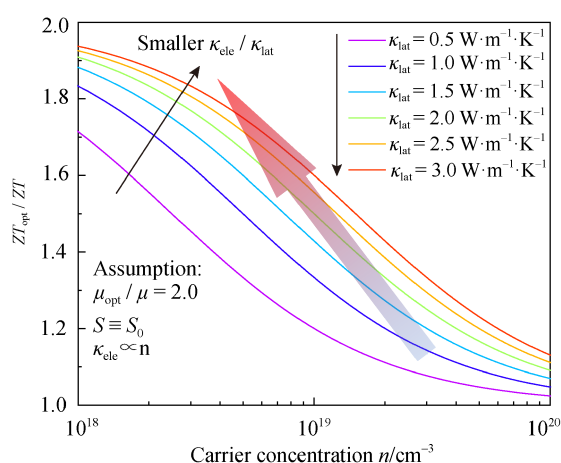


图 4 在不同晶格热导率的条件下, ZT 提升幅度作为载流子浓度的函数关系

Fig. 4 Enhancement of ZT as a function of carrier concentration under different lattice thermal conductivity

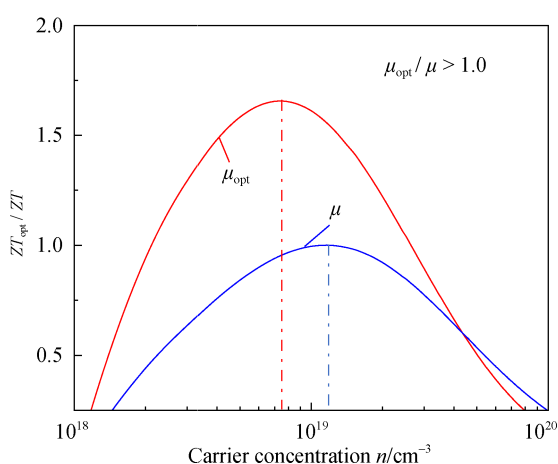


图 5 考虑电-声耦合情况下, ZT 提升幅度作为载流子浓度的函数变化示意图

Fig. 5 Schematic diagram of the ZT improvement as a function of carrier concentration when carrier mobility is improved with considering electron-phonon coupling

2.3 迁移率提升对于近室温热电性能的影响

材料的近室温热电性能对于热电制冷技术至关重要,开发宽温域热电材料的迫切性则进一步突显了这一需求。因此,通过实现较低的载流子浓度、较高的迁移率以及较大的 Seebeck 系数,成为提升近室温热电性能的一种有效策略。先前的讨论表明,当电子热导率和晶格热导率分别作为主导因素时, ZT 的提升范围会因迁移率的提高而产生上限和下限。然而,在实际情况下,当 ZT 作为载流子浓度的函数达到最优时,电子热导率与晶格热导率的比值通常会被限制在区间[0.1, 10]。这也表明 ZT 提升范围在实际情况中会形成新的上限和下限,如图 4 所示。当迁移率提升 2 倍时,通过电-声解耦优化材料

的热电性能的上限和下限分别为 $ZT_{\text{opt}} = \frac{11}{6} ZT$ 和

$$ZT_{\text{opt}} = \frac{22}{21} ZT$$

。这表明在迁移率显著提高的情况下,材料的热电性能受限于电子和晶格热导率之间的相互作用,从而影响 ZT 提升的最终表现。

近些年,一些热电材料通过调制掺杂、固溶体合金化和晶格素化等策略实现了电-声解耦,显著提高了载流子迁移率,并有效提升了室温热电性^[18, 23-25]。在本工作中,通过简化模型(假设迁移率提升 2 倍),评估了若干已报道热电材料在当前电-声解耦水平下所对应的理论 ZT 增幅,如图 6 所示。对于 p 型体系,包括 SnS-Se^[22]、PbSe-Cu^[25]、SnSe-Na-Cu^[24]和 GeTe-Pb-Bi^[40]; 对于 n 型体系,包括 PbSe-Cu^[18]、PbSnS₂-Ni^[41]、Bi₂Te₃-Cu^[19]以及 SnSe-Cl-Pb^[31]。结果表明, n 型 PbSnS₂ 体系通过引入 Ni 元素实现晶格素化,同时达到最大的电-声解耦程度,因此理论 ZT 增幅最大。此外, n 型 SnSe-Cl 除了具有三维电荷和二维声子输运的结构特征,实验上还通过固溶 Pb 元素降低了形变势,从而实现了较大程度的电-声解耦^[32]。因此,相较于 p 型 SnSe-Na-Cu 体系, n 型 SnSe-Cl-Pb 具有更大的理论 ZT 增幅。这一结果不仅进一步证明了电-声解耦对于各向异性材料 ZT 增幅的重要性,还表明未来通过电-声解耦策略进一步提升 p 型 SnSe 性能的巨大潜力。尽管一些材料通过栅格法设计(n 型和 p 型 PbSe-Cu)、晶格素化(p 型 SnSe-Na-Cu 和 n 型 Bi₂Te₃-Cu)和改良退火工艺(p 型 GeTe-Pb-Bi)提升了迁移率,以优化近室温热电性能,但由于其电-声解耦程度较弱,这些材料的 ZT 增幅仍与理论预期水平相差较远。因此,如何在提高迁移率的同时

有效操纵电-声解耦, 以实现近室温热电性能的优化, 将成为未来热电研究领域的一项关键挑战。

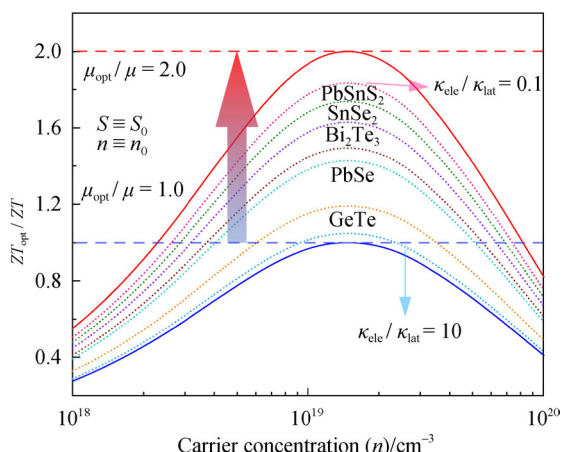


图6 载流子迁移率提升时, 电-声解耦对于 ZT 提升的理论关系

Fig. 6 Theoretical relationship between electron-phonon decoupling and ZT improvement when increasing carrier mobility

3 结论与展望

基于简化的电-声解耦参数模型和 Kane 热电参数模型, 系统探讨了迁移率提升对近室温电-声解耦的规律。结果表明, 通过提升载流子迁移率优化热电性能时, 必须重视电子热导率与晶格热导率的比值, 即电-声解耦程度。通过进一步的公式推导和计算分析, 得出了以下主要结论: 1) 温度通常和电子热导率的晶格热导率的比值呈正相关, 这证明载流子迁移率在提升近室温热电性能更具有潜力; 2) 对于具有较高晶格热导率的体系, 协同解耦电-声输运矛盾优化其热电性能则更显著; 3) 通过模型理论评估一些热电材料在迁移率提升时的 ZT 增幅, 发现它们的增幅与理论预期相差较远, 这反映了解耦电-声输运矛盾的重要性。理论上, 在考虑电-声耦合情况下, 由于迁移率提升和电-声解耦程度增强(表现为形变势减小, B 参数增大), 协同优化会共同推动 ZT 峰值朝着低载流子浓度方向移动并实现了显著的增幅, 这也揭示了近室温热电性能的潜在优化区间 ($10^{18} \sim 10^{19} \text{ cm}^{-3}$)。综上所述, 如何在提升迁移率的同时有效操控电-声解耦, 以实现材料近室温热电性能的优化, 将成为未来热电研究领域的一项关键挑战。

对此, 给出以下展望以供参考。首先, 本工作简化的电-声解耦参数模型处理是基于迁移率提升不改变 Seebeck 系数, 目的是凸显制备晶体、晶格

素化、多晶织构化等不显著改变 Seebeck 系数而提升迁移率的策略的显著优势。然而, 在实际情况下, 当迁移率提升来源于载流子浓度下降或有效质量降低等常见因素时, 由于电导率会随之降低, 最终 ZT 值的提升幅度在一定程度上要小于本工作的计算预估。其次, 针对不同材料体系, 由于本征电子热导率与晶格热导率的比值存在较大差异, 应考虑不同的载流子迁移率提升策略。在较低比值下, 除使用上述策略外, 还可通过提高晶体对称性、降低形变势、能带锐化和能带对齐等方式有效提升 ZT 值; 而在较高比值下, 需要考虑如何在提升迁移率的同时保持或降低这一比值。采用痕量掺杂、点缺陷调控和本征元素自掺杂等方式适当降低载流子浓度提高载流子迁移率, 可能会在解耦电-声传输矛盾以提升 ZT 值中实现更显著的效果。此外, 对于不同体系, 本工作的讨论中只给出了迁移率提升 2 倍条件下的结果。若能与用于提升载流子迁移率的各种关键策略相结合, 如同时开展晶格素化和降低形变势等策略协同实现载流子迁移率更大幅度的提升, 有望实现更大的 ZT 值增幅, 特别是在低载流子浓度和近室温区域, 这有望促进热电技术尤其是热电制冷技术在更多关键领域的大规模应用。

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Role of Carrier Mobility in Decoupling Electron–Phonon Transport Contradiction

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Extend Abstract

Introduction Thermoelectric materials, capable of directly converting heat to electricity, have a significant potential in sustainable power generation and thermoelectric cooling. Research in this area focuses on optimizing multiple interdependent and competing thermoelectric parameters to maximize the dimensionless figure-of-merit (ZT). Achieving an optimal ZT value requires materials with a large Seebeck coefficient, an excellent electrical conductivity, and a low thermal conductivity. However, these transport properties are interdependent and often in competition, necessitating a balance between the related parameters. A critical aspect of this optimization involves the trade-off between the Seebeck coefficient and electrical conductivity, and both of which are strongly affected by carrier concentration. Lower carrier concentrations generally enhance the Seebeck coefficient, but reduce the conductivity, whereas higher carrier concentrations favor the conductivity at the cost of a lower Seebeck coefficient. This competition also extends to the effective mass, where an increased effective mass can boost the Seebeck coefficient, but often reduce the conductivity due to the decreased carrier mobility. Effective thermoelectric optimization thus requires balancing enhanced effective mass with a high mobility. Furthermore, the coupling between electronic and lattice thermal conductivities significantly impacts the overall performance, positioning a thermal transport as a pivotal element in this optimization. To improve the ZT at low carrier concentrations, achieving electron-phonon decoupling while enhancing carrier mobility are an effective strategy. Based on some simplified thermoelectric models, this work demonstrated that electron-phonon decoupling could improve the thermoelectric performance at near room temperature under the condition of enhanced carrier mobility. In the narrow region of a low carrier concentration where the Seebeck coefficient could change minimally, the effect of the ratio of electronic conductivity to lattice thermal conductivity on the enhancement of ZT was evaluated. Finally, we emphasized the important role of electron-phonon decoupling in enhancing carrier mobility to optimize the thermoelectric performance.

Methods In this work, a simplified theoretical model was proposed to evaluate a relationship between the ZT enhancement and the ratio of electronic conductivity to lattice thermal conductivity (*i.e.*, the degree of electron-phonon decoupling). A simplified phonon-electron decoupling parameter model was designed *via* assuming that the Seebeck coefficient and carrier concentration could remain constant. In this model, the increase in electronic thermal conductivity was considered to be consistent with the increase in mobility. The lattice thermal conductivity was primarily affected by some complex factors such as crystal structure, defects, and anisotropy, and was therefore treated as a constant term without detailed consideration. In addition, the single-band Kane model was also utilized under approximate conditions, effectively simulating the impact of electron-phonon decoupling on the thermoelectric performance at near room temperature when enhancing the carrier mobility.

Results and discussion Electronic conductivity and lattice thermal conductivity are two important thermal conductivity parameters in semiconductors, and their difference lies in the mechanism and main carrier of heat conduction. The enhancement of carrier mobility can significantly affect the electronic thermal conductivity without changing the lattice thermal conductivity. Therefore, the improvement of mobility can achieve the enhancement of ZT while unchanging the lattice thermal conductivity, and the improvement effect becomes dominant as the carrier mobility increases when using the electron-phonon decoupling parameter model. In addition, for systems with a lower lattice thermal conductivity, the electronic thermal conductivity can be a low level in order to achieve optimal optimization when using optimization strategies to increase carrier mobility. This indicates that the ratio of electronic conductivity to lattice thermal conductivity (*i.e.*, the degree of electron-phonon decoupling) must be concerned when optimizing ZT by increasing carrier mobility in different systems because this ratio directly determines the extent of ZT improvement. Since the ratio of electronic conductivity to lattice thermal conductivity is usually limited in the range of [0.1, 10] when the ZT value reaches its peak as a function of carrier concentration, this range ensures that the material can achieve the optimal performance. Also, the ratio of electronic conductivity to lattice thermal conductivity increases with increasing temperature. This indicates that optimizing carrier mobility can have a more significant effect on the improvement of near-room temperature thermoelectric performance. Since the carrier concentration is directly proportional to the electronic thermal conductivity, and the lattice thermal conductivity does not depend on the carrier concentration, there is a positive correlation between the carrier concentration and the ratio of electronic conductivity to lattice thermal conductivity. This means that the electronic thermal conductivity increases quickly as the carrier concentration increases, resulting in an increase in the ratio. Therefore, the decrease in carrier concentration can significantly enhance the degree of electron-phonon decoupling as the carrier mobility increases. The thermoelectric performance can be effectively improved *via* regulating carrier concentration and optimizing carrier mobility, providing an important theoretical basis for the design and optimization of novel thermoelectric materials. In practical situations, the ratio of electronic conductivity to lattice thermal conductivity is usually limited to the interval [0.1, 10] when the ZT reaches an optimum value as a function of carrier concentration. Therefore, the improvement range of ZT value can also form different upper and lower limits, thereby restricting the improvement of

thermoelectric performance. Although the improvement of carrier mobility can effectively improve the thermoelectric performance, there are differences in the electron-phonon coupling strength of different thermoelectric materials, which can make it difficult to improve the ZT to the theoretical optimal level. The single-band Kane model used is combined with some assumptions to simulate the electron-phonon decoupling discipline that is closer to the actual situation. For instance, the peak of ZT moves in the direction of lower carrier concentration, and achieves a larger increase in amplitude, thus forming a potential optimization area due to the increase in carrier mobility and the enhancement of electroacoustic decoupling (*i.e.*, the deformation potential decreases and the B parameter increases).

Conclusions This study systematically explored the discipline of electron-phonon decoupling at near room temperature when enhancing the carrier mobility based on the simplified electron-phonon decoupling model and single-band Kane model. The results showed that the ratio of electronic conductivity to lattice thermal conductivity could be concerned when optimizing the thermoelectric performance by increasing the carrier mobility, that is, the electron-phonon decoupling strength. The increase in this ratio with increasing temperature further verified the importance of optimizing the carrier mobility for improving the room-temperature thermoelectric performance. Meanwhile, the enhanced ZT of some thermoelectric materials was evaluated by the model, and the increase was far from the theoretical expectation. For the electron-phonon coupling, this synergistically promoted the shift of the ZT peak toward lower carrier concentrations and achieved significant improvements due to the increase in mobility and electron-phonon decoupling (*i.e.*, the reduction of deformation potential and the improvement of B parameter), revealing a potential optimization range for the near room temperature thermoelectric performance. In summary, how to effectively manipulate electron-phonon decoupling while improving mobility to optimize the near room temperature thermoelectric performance could become a challenge in the field of future thermoelectric cooling.

Keywords thermoelectric performance; carrier mobility; electronic thermal conductivity; lattice thermal conductivity; electron-phonon transport