



碲化锡基热电材料的研究进展

庞慧梅, 王华才*

中国原子能科学研究院, 北京 102413

* 联系人, E-mail: wanghc1986@163.com

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摘要 热电材料能够实现热能与电能直接相互转换, 展现出在极端环境条件下的出色性能, 是重要的新型能源材料之一. 传统的PbTe以其卓越的电子和声子输运特性在中温区热电转换领域占据着主导地位, 然而铅毒性涉及的环境问题正促使热电材料向无铅路线发展. 作为PbTe的潜在替代者, SnTe近年来引起了热电领域研究者的广泛关注. 众多新技术与策略被应用于改善SnTe材料电输运与热输运性能, 使SnTe热电性能实现了大幅提高. 尽管距离替代PbTe并实现工业化应用仍有较大差距, 但SnTe依然显示出作为卓越中温区热电材料的巨大潜力. 本文介绍了SnTe材料的内在非化学计量特点以及热电输运特性, 综述了在p型SnTe半导体中成功应用的载流子浓度优化、能带工程、能量过滤和声子工程等性能优化策略, 并总结了近年来对n型SnTe材料和全SnTe基热电器件的探索工作. 最后, 对SnTe热电材料的研究进展进行了总结, 并对其今后的研究方向提出了展望.

关键词 热电材料, SnTe, Seebeck系数, 晶格热导率, 热电优值(ZT)

科技的进步促进了深空探测技术的快速发展, 各航天国家和组织加快了探索太阳系其他天体和宇宙空间的步伐. 由于距离太阳过远, 光照强度极弱, 太阳能电池已经无法满足深空探测器的工作需求. 同位素温差电池(radioisotope thermoelectric generator, RTG)不受太阳光和其他环境的影响, 在恶劣乃至极端环境下也可以工作数十年, 对于空间探测、深海高压等特殊应用环境是一种理想的电源选择^[1]. RTG中的换能器件是关键部件, 常由热电材料构成, 通过Seebeck效应可将放射性同位素衰变产生的热能直接转换成电能^[2]. 目前受限于热电材料与器件的性能, RTG的系统效率并不高(约6%左右). 优化热电材料的性能, 推动热电转换技术的进步, 对RTG的产业化应用以及深空探测等关键领域的发展具有重要作用.

热电材料的性能可通过无量纲热电优值ZT来量化评价, 其定义式为 $ZT = (S^2 \sigma / \kappa_{\text{tot}}) T$, 其中 S 、 σ 和 κ_{tot} 分别代

表Seebeck系数、电导率和总热导率, T 为绝对温度. Seebeck系数也叫温差电动势, 其定义为材料上单位温度梯度所产生的电压差, 其平方与电导率的乘积 $S^2 \sigma$ 也被称为功率因子(power factor, PF)^[3]. 作为能够实现热能与电能之间直接转换的新型能源材料, 热电材料的发电与制冷效率都与ZT值有关, ZT值越高, 其能量转换效率就越高. 结合公式可知, 若要获得理想的ZT值, 则意味着材料需要具有高的Seebeck系数和电导率, 以及低的热导率. 然而, 材料的电输运性能与热输运性能之间往往相互耦合, 因此如何将参数解耦, 实现材料性能的有效提高, 是热电材料领域的关键问题.

热电材料服役温度范围可分为低温(< 500 K)、中温(500~900 K)和高温(> 900 K). 中温区热电材料中发展最为成熟的是PbTe基金属, 其最高ZT值已达到2以上^[4,5], 然而铅的毒性限制了PbTe更广泛的应用. SnTe因其环境友好性以及与PbTe相似的晶体结构与双价带

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结构, 被视为PbTe的潜在替代材料^[6]. 然而, SnTe较低的Seebeck系数和较高的热导率导致其本征热电性能较低, 大量阳离子空位的存在也使得SnTe难以由p型半导体向n型半导体转变. 众多研究者为了优化p型SnTe材料的热电输运性能以及开发高性能n型SnTe热电材料进行了广泛而深入的研究, 并取得了一系列重要成果. 本文将简述SnTe热电材料的晶体结构和能带特点, 总结归纳对其热电性能的优化策略以及相应的进展, 介绍对n型SnTe的研究现状, 结合热电器件的发展需求, 讨论SnTe热电材料未来发展方向.

1 SnTe热电材料晶体结构和能带结构

SnTe有3种不同的相: α -SnTe、 β -SnTe和 γ -SnTe, 分别为三方结构、立方结构和正交结构. 其中, α -SnTe是低温相, 只能在低于100 K的温度下稳定存在; γ -SnTe则属于高压相, 可由 β -SnTe在18 kbar下转变而成^[7]; β 相是SnTe最为常见的形态, 其晶体结构为立方结构, 如图1(a)所示, 空间群为Fm $\bar{3}$ m, 晶格参数为 $a=6.32$ Å, $\alpha=90^\circ$. 在电负性、原子 p 轨道和非化学计量的综合作用下, SnTe表现出复杂的离子-共价-金属键结合方式. 半导体化合物在相图中一般存在均相区域, 即成分可以在一定范围内变化而保持单相结构. SnTe化合物的均相区域较宽, 如图1(b)所示, 其稳定成分范围为50.1 at% ~50.9 at% Te, 即Sn_{0.996}Te~Sn_{0.965}Te^[8]. 大量的本征锡空位引起高空穴载流子浓度, 使SnTe呈现出显著的p型简并半导体特征, 并导致SnTe的本征Seebeck系数较低, 电子导热系数较高, 热电性能较差($ZT\sim 0.4$).

SnTe的电子能带结构的密度泛函理论(density functional theory, DFT)计算结果如图1(c)所示^[9], 价带

顶(valance band maximum, VBM)和导带底(conduction band minimum, CBM)均位于L点, 直接带隙较小, 计算值约为0.108 eV, 光学实验测量值约为0.18 eV^[10]. 由于双极扩散效应, 过窄的带隙会导致高温Seebeck系数降低和热导率上升, 不利于热电性能的提高. 此外, Σ 点存在另一个价带, 其载流子有效质量明显重于L点轻价带, 轻价带L和重价带 Σ 之间的能量差计算值约为0.254 eV^[9], 实验测量值约为0.3 eV^[10]. 对于双价带结构而言, 通过调控轻重价带能量差和费米能级位置, 使费米能级进入重价带, 使重空穴价参与载流子输运, 有助于增加Seebeck系数提高SnTe材料热电性能. 但与PbTe相比, SnTe中的轻重价带能量差相对较大(PbTe中仅为0.15 eV^[11]), 使得SnTe中对价带的调控也相对困难.

2 p型SnTe热电性能优化策略

如前所述, 由于本征锡空位的存在, SnTe材料一般为p型半导体, 且本征 ZT 值十分有限. 为优化材料的热电性能, 需要尽可能提高材料的电导率和Seebeck系数, 降低材料的热导率. 然而, 这些热电参数之间存在大量耦合关系, 如电导率 σ 和Seebeck系数 S 分别可表达为^[12]

$$\sigma = ne\mu = \frac{ne^2\tau}{m^*}, \quad (1)$$

$$S = \frac{8\pi^2 k_B^2}{3 eh^2 m^*} T \left(\frac{\pi}{3n} \right)^{\frac{2}{3}}, \quad (2)$$

其中, n 为载流子浓度, e 为电子电荷, μ 为载流子迁移率, τ 为弛豫时间, m^* 为载流子有效质量, k_B 和 h 分别为玻尔兹曼常数和普朗克常数. 可以看出, 电导率与Seebeck系数之间通过载流子浓度和有效质量联系在一起. 在特

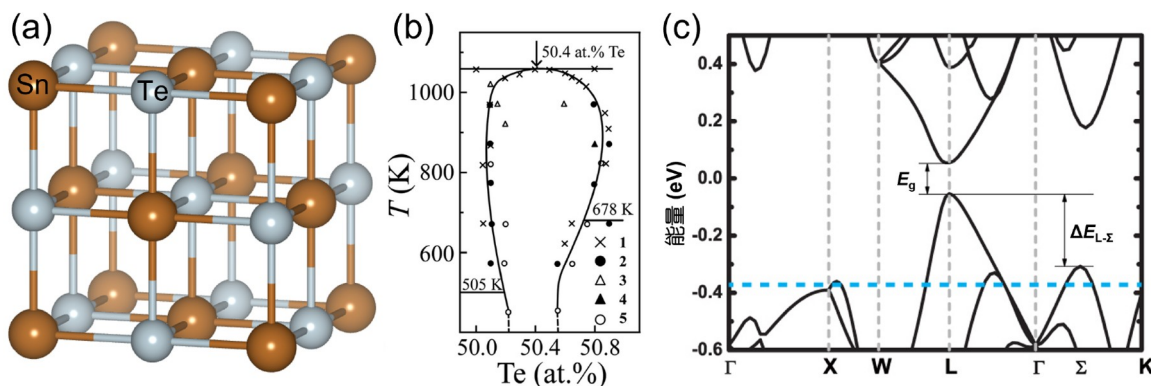


图1 (网络版彩色)SnTe晶体性质. (a) 晶体结构; (b) 局部相图^[8]; (c) 能带结构^[9], 其中 E_g 表示带隙, $\Delta E_{L-\Sigma}$ 表示L带与 Σ 带之间能量差

Figure 1 (Color online) Properties of SnTe crystal. (a) Crystal structure; (b) local phase diagram^[8]; (c) band structure^[9], where E_g represents the band gap, and $\Delta E_{L-\Sigma}$ represents the energy difference between the L band and the Σ band

定有效质量下, 载流子浓度越大, 电导率越高, 但会损害Seebeck系数; 载流子有效质量的影响则相反. 此外, 由Wiedemann-Franz关系可知热输运性能与电输运性能之间也存在耦合关系, 即^[12]

$$\kappa_{\text{tot}} = \kappa_{\text{ele}} + \kappa_{\text{lat}}, \quad (3)$$

$$\kappa_{\text{ele}} = L\sigma T, \quad (4)$$

其中, κ_{ele} 和 κ_{lat} 分别代表电子热导率和晶格热导率, L 表示洛伦兹常数. 电子热导率与电导率成正比, 难以在不损失电输运性能的情况下对其进行抑制, 只有晶格热导率可相对独立地进行调控. 这些参数之间的耦合关系使得热电材料 ZT 值的提高困难重重.

近几十年来, 热电材料领域发展出一系列的性能优化策略, 很多方法已应用在SnTe体系中并取得了良好的效果, 如载流子浓度调控、能带工程和能量滤波等策略可提高SnTe材料电性能; 点缺陷、位错、晶界、纳米结构的引入可降低SnTe材料晶格热导率等. 本章将对这些优化策略进行详细介绍.

2.1 提升电输运性能

评价热电材料电性能优劣的指标为功率因子 $PF = S^2\sigma$, 取决于材料的电导率和Seebeck系数. 由式(1)和(2)可知, 电导率和Seebeck系数均与载流子特性有关, 因此对载流子和能带结构的调控是优化p型SnTe电输运性能的有效途径, 主要包括载流子浓度优化、能带工程和能量过滤策略.

2.1.1 载流子浓度优化

电导率、Seebeck系数和电子热导率等多项热电参数都与载流子浓度有紧密关联, 其中电导率和电子热导率正比于载流子浓度, 而Seebeck系数则与载流子浓度呈负相关. 为达到最高的 ZT 值, 需要将材料的载流子浓度保持在一个适当范围内, 称为最优载流子浓度. 最优载流子浓度与材料特性和温度有关, 通常正比于 $(m_d^*T)^{3/2}$, 其中 m_d^* 为态密度有效质量^[13], 这意味着随着温度升高, 材料的最优载流子浓度也会随之提高. 研究表明, p型SnTe的理论最优载流子浓度在300 K时约为 10^{18} cm^{-3} , 773 K时约为 10^{19} cm^{-3} ^[14]. 而SnTe的本征空穴浓度常温下为 $2 \times 10^{20} \sim 1.5 \times 10^{21} \text{ cm}^{-3}$ ^[15], 远远高于最优范围. 过高的载流子浓度虽然使p型SnTe具有出色的电导率, 但也导致其Seebeck系数较小, 电子热导率较大, 从而限制了最终的 ZT 值. 为改善p型SnTe的热电性能, 首要的挑战便是降低其载流子浓度.

Sn自补偿是降低空穴浓度的一种有效方法. Tan等人^[16]在合成SnTe时加入过量的Sn, 以补偿Sn空位从而降低载流子浓度, 结果表明当Sn补偿量为0.03时, 载流子浓度从原始SnTe的 $4.7 \times 10^{20} \text{ cm}^{-3}$ 降低至 $\text{Sn}_{1.03}\text{Te}$ 的 $2 \times 10^{20} \text{ cm}^{-3}$, ZT 峰值也得到了50%的显著提高. 而当Sn补偿量超过0.03后, 载流子浓度则变化不大, 表明存在自补偿极限.

自补偿对降低载流子浓度作用有限, 为使SnTe的载流子浓度达到最佳范围, 通常会使用外源性掺杂的方法. 常用的施主掺杂剂为周期表中Sn和Te相邻列的异价元素. 阳离子位常用掺杂元素有Sb、Bi、In等^[17-19]. Yang等人^[20]通过In掺杂, 使常温载流子浓度从SnTe的 $2.83 \times 10^{20} \text{ cm}^{-3}$ 降低至 $\text{In}_{0.0125}\text{Sn}_{0.9875}\text{Te}$ 的 $3.19 \times 10^{19} \text{ cm}^{-3}$. 阴离子位常用卤素掺杂, 其中I的掺杂效果最为显著, 可使SnTe载流子浓度降低至 $\sim 3 \times 10^{19} \text{ cm}^{-3}$ ^[14,21]. 此外, 掺杂Cd、Pb、Ca等同价元素会减少Sn空位浓度, 因此也能降低SnTe的空穴载流子浓度^[22-24]. 除单一掺杂外, 共掺杂和复合掺杂也能有效调节载流子浓度. Zhou等人^[25]使用 BiCl_3 化合物进行掺杂, 其中Bi和Cl分别取代Sn和Te, $\text{Sn}_{0.96}\text{Bi}_{0.04}\text{Te}_{0.88}\text{Cl}_{0.12}$ 常温载流子浓度降低至 $\sim 4 \times 10^{19} \text{ cm}^{-3}$, 在873 K下得到了 ~ 1.27 的 ZT 值. Ma等人^[26]在p型SnTe中复合n型 $\text{Mg}_{3.2}\text{Sb}_{0.6}\text{Bi}_{1.4}$ 纳米颗粒, 使 $\text{Sn}_{1.03}\text{Te}$ 载流子浓度降低至 $\sim 3 \times 10^{19} \text{ cm}^{-3}$.

2.1.2 能带工程

由式(1)可知, 除了降低载流子浓度, 增大载流子有效质量也有利于Seebeck系数的优化. 载流子有效质量 m^* 可表达为^[27]

$$m^* = (N_v)^{2/3} m_b^*, \quad (5)$$

其中, N_v 为能谷简并度, m_b^* 为单带的载流子有效质量. 因此, 通过调控SnTe能带结构, 改善 N_v 和 m_b^* , 能够实现p型SnTe的Seebeck系数和功率因子的有效提高.

能带钝化, 即提高单个价带的平坦度, 能够增大单带载流子有效质量从而提高Seebeck系数. 一般来说, 能带钝化虽然能提升 m_b^* , 但会在一定程度上降低载流子迁移率, 因此对PbTe等热电材料收效甚微甚至会造成功率因子的下降^[28]. 但在SnTe中, 更高的 m_b^* 意味着更高的最优载流子浓度, 更接近于SnTe实际使用中的载流子浓度范围, 因此能带钝化能够有效改进其功率因子. Ma等人^[9]报道了Pd掺杂的SnTe表现出更平坦的价带, 800 K下的功率因子也从 $\text{Sn}_{1.03}\text{Te}$ 的 $80 \mu\text{V K}^{-1}$ 提高至 $\text{Sn}_{1.02}\text{Pd}_{0.01}\text{Te}$ 的 $100 \mu\text{V K}^{-1}$. Orabi等人^[24]通过在

$\text{Sn}_{1.03}\text{Te}$ 中掺杂9%Ca, 促进了能带钝化, 将载流子有效质量从 $0.133 m_e$ 提高至 $0.35 m_e$, 从而使873 K下的功率因子从 $16 \mu\text{W cm}^{-1} \text{K}^{-2}$ 改善至 $26 \mu\text{W cm}^{-1} \text{K}^{-2}$.

价带收敛策略即通过促进SnTe的双价带在能量上的汇聚以增大 N_v , 在不显著改变 m_b^* 即不明显牺牲电导率的情况下, 提高载流子有效质量, 从而改善热电性能. 加入合适的掺杂剂或者提高温度, 能够减小SnTe中重空穴价带和轻空穴价带之间的能量差, 使重价带更多参与到载流子输运中, 增加载流子有效质量, 从而提高Seebeck系数和功率因子^[27,29]. Pd、Ca、Mg、Mn、Sr、Cd等已被证明是有效促进价带收敛的掺杂剂^[9,30-33]. 最近, Li等人^[34]通过在SnTe中合金化三元 MnCdTe_2 , 激活了 Λ 价带, 实现了SnTe中三价带(L、 Λ 和 Σ 价带)的收敛, 如图2(a)所示. 进一步的Ce掺杂促进了 Λ 和L价带的对齐, 提高了Seebeck系数, 同时调整了 MnCdTe_2 在SnTe中的溶解度, 形成全尺度声子散射结构降低了晶格热导率. 如图2(b)和(c)所示, $(\text{SnTe})_{0.92}(\text{MnCd}_{0.6}\text{Ge}_{0.4}\text{Te}_2)_{0.08}$ 在900 K时的功率因子达到 $\sim 29.3 \mu\text{W cm}^{-1} \text{K}^{-2}$, 并获得了 ~ 1.97 的极高ZT值.

共振能级概念最早是于20世纪50年代在固体物理领域提出^[35]. 当杂质能级位于基体导带或价带内, 并且与基体扩展态的能量相匹配时, 基体能带在杂质能级附近会产生畸变形成额外的态密度, 由于态密度的畸变和共振散射, 掺杂引入的共振态对Seebeck系数有增强作用. Zhang等人^[36]通过In掺杂首次在SnTe中引入共振能级, 实现了ZT值的显著增强. 后来, 在Zn^[37]、Bi^[38-41]和Sb^[42]掺杂SnTe体系中也观察到了类似的增强

效果. Shenoy等人^[39]报道, 得益于Bi-Zn共掺杂实现的共振能级效应, $\text{Sn}_{0.92}\text{Bi}_{0.04}\text{Zn}_{0.04}\text{Te}$ 在300~840 K的温度范围内实现了0.86的高平均ZT. 共振掺杂能够显著改善热电材料室温附近性能, 而在较高温度下, 由于费米能级会逐渐偏离共振能级, 以及弛豫时间更短的声子散射成为载流子主要散射机制, 共振掺杂的优化作用会逐渐减弱^[43].

2.1.3 能量过滤策略

基于玻尔兹曼输运理论的计算结果表明, Seebeck系数主要来源于能量较高的载流子, 而低能载流子则会造成Seebeck系数降低^[44]. 在热电材料中引入异质结构或纳米颗粒, 使界面处形成势垒, 能够实现对载流子的能量过滤, 筛选出能量较高的载流子, 提升载流子平均能量, 进而增加Seebeck系数. Zhou等人^[45]在SnTe中复合ZnO, 通过弯曲能带产生能量过滤效果(图3), 873 K时复合0.8 wt% ZnO的样品ZT值达到 ~ 0.9 . 相较于单势垒, 多势垒结构能进一步增强能量过滤效果. Ma等人^[46]通过复合BiCuSeO纳米颗粒, 在SnTe基体中构建BiCuSeO@SnO₂核壳纳米结构, 在SnTe基体与壳层、壳层与核层以及核层内部产生非均质界面, 形成多重势垒, 显著降低了载流子浓度并提高了霍尔迁移率, 含5% BiCuSeO的样品835 K时的Seebeck系数提高至 $\sim 176.05 \mu\text{V K}^{-1}$.

2.2 降低晶格热导率

热电材料的热导率由电子热导率和晶格热导率组成. 如前所述, 电子热导率与电导率之间存在耦合关系,

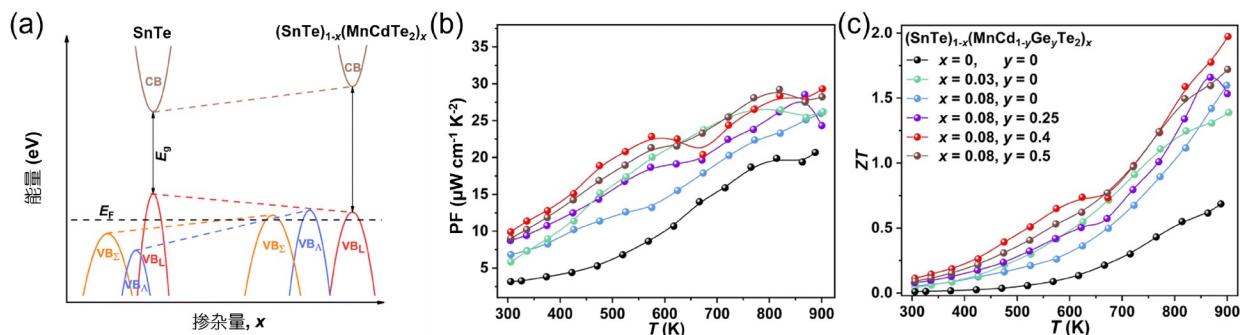


图2 (网络版彩色)三价带收敛策略优化p型SnTe热电性能^[34]. (a) SnTe中多价带随掺杂浓度变化的演化示意图. E_F 表示费米能级, VB和CB分别表示价带和导带, VB下标L、 Λ 和 Σ 分别表示价带处于倒易空间的L、 Λ 和 Σ 对称点, 其 N_v 值分别为4、8和12. $(\text{SnTe})_{1-x}(\text{MnCd}_{1-y}\text{Ge}_y\text{Te}_2)_x$ 样品的功率因子(b)和ZT(c)随温度的变化关系

Figure 2 (Color online) Three-valence-band convergence strategy optimizes the thermoelectric performance of p-type SnTe^[34]. (a) Schematic diagram of the multivalence band evolution in SnTe as the dopant concentration varies. E_F represents the Fermi level. VB and CB represent the valence band and the conduction band respectively, and the subscripts L, Λ and Σ of VB represent the valence bands are at L, Λ and Σ symmetric points in the reciprocal space respectively. Their N_v values are 4, 8 and 12, respectively. PF (b) and ZT (c) for the $(\text{SnTe})_{1-x}(\text{MnCd}_{1-y}\text{Ge}_y\text{Te}_2)_x$ samples as a function of temperature

互相牵制, 优化效果往往受限, 只有晶格热导率可以相对独立地控制, 因此对热电材料热输运性能的优化通常是围绕晶格热导率进行的. 晶格热导率取决于声子输运, 因此可通过声子工程来改善. 如图4所示, 点缺陷、位错、晶界、纳米结构等晶体缺陷能够散射不同频率的声子, 通过引入各种晶体缺陷增强声子散射, 能够实现对晶格热导率的降低, 从而改善SnTe热电材料的ZT值.

点缺陷和位错会导致晶格质量场和应变场的波动, 通过散射高频和中频声子降低晶格热导率, 如图4(a), (b)所示. 在热电材料中, 点缺陷可以是本征点缺陷(空位), 也可以是由掺杂元素(取代原子或间隙原子)引起的外来点缺陷. Pei等人^[47]通过在SnTe中固溶Cu₂Te引入间隙Cu原子, 将850 K的晶格热导率降低至 $\sim 0.5 \text{ W m}^{-1} \text{ K}^{-1}$. 此外, Tan等人^[48]发现AgSbTe₂合金化可以显著增加SnTe中阳离子空位浓度, 增强声子散射,

样品AgSn₅SbTe₇在800 K时的晶格热导率降低至 $\sim 0.4 \text{ W m}^{-1} \text{ K}^{-1}$, 接近SnTe的非晶态极限. In₂Te₃^[49]、NaSbTe₂^[50]、MnSb₂Se₄^[51]等也有类似的效果. 位错也是有效增强中长波声子散射的一种方法, 位错的密度和位置对声子输运有显著影响. Wu等人^[52]利用球磨和火花等离子烧结在SnTe晶界处形成高密度的位错网络, 显著增强了声子散射, 使其室温晶格热导率从 $\sim 4.7 \text{ W m}^{-1} \text{ K}^{-1}$ 降低至 $\sim 2.8 \text{ W m}^{-1} \text{ K}^{-1}$.

纳米结构设计通过在材料中引入具有特定尺寸和形状的第二相粒子, 为中长波声子提供了有效的散射中心, 如图4(c)所示. 纳米结构的尺寸应该足够小(通常是几十纳米或更小), 且需要均匀分布, 以尽可能高地增加界面密度, 提高声子散射效率. Ma等人^[26]通过掺杂MgAgSb在SnTe中形成直径几纳米到几微米的第二相纳米颗粒, 873 K下晶格热导率显著降低至 $\sim 1.046 \text{ W m}^{-1} \text{ K}^{-1}$. 若纳米沉淀相与基体的晶格完全一

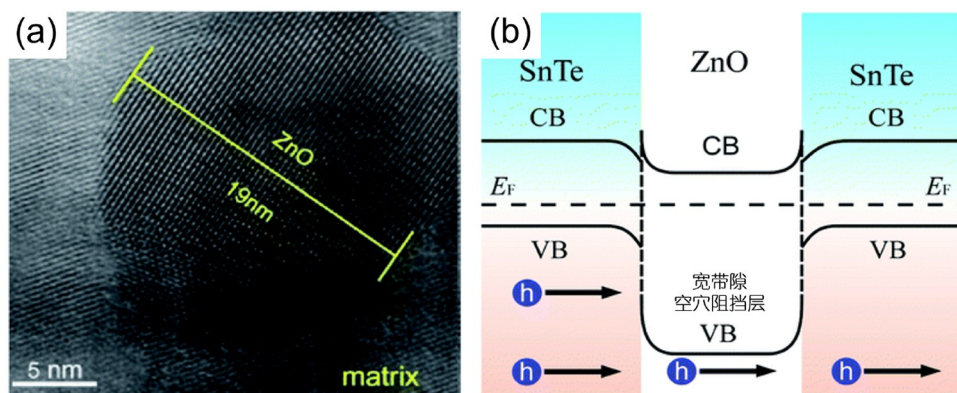


图3 (网络版彩色)在SnTe中引入ZnO纳米粒子实现能量过滤效应^[45]. (a) 含0.8 wt% ZnO的SnTe样品的低倍率透射电子显微镜(transmission electron microscope, TEM)图像; (b) ZnO与SnTe界面载流子能垒示意图

Figure 3 (Color online) Energy filtering effect is achieved by introducing ZnO into SnTe^[45]. (a) Low-magnification transmission electron microscope (TEM) image of the SnTe sample with 0.8 wt% ZnO; (b) schematic diagram of the carrier energy barrier at the interface between ZnO and SnTe

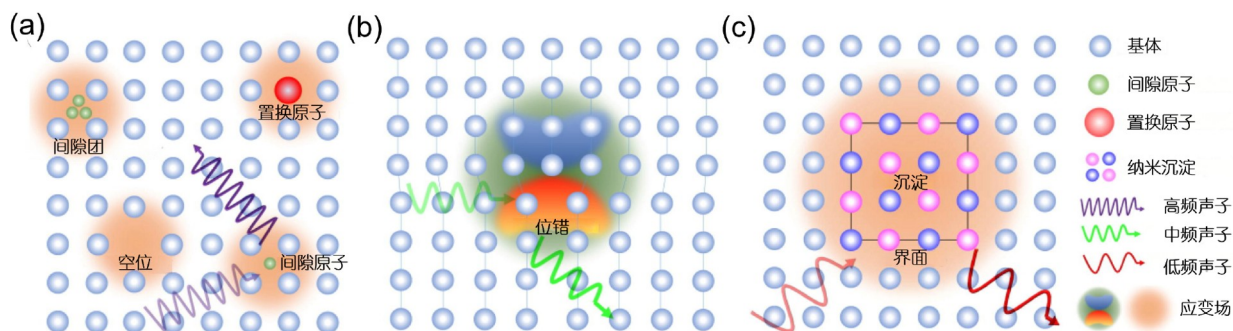


图4 (网络版彩色)声子工程示意图. (a) 点缺陷; (b) 位错; (c) 纳米沉淀

Figure 4 (Color online) Schematic diagram of phonon engineering. (a) Point defect; (b) dislocation; (c) nanoprecipitate

致, 则称为内延纳米结构, 能在不破坏材料整体晶体结构、不明显影响载流子迁移率的情况下, 通过纳米尺度的异质结构散射声子, 优化材料的热电性能^[53]. Zhao等人^[54]在SnTe中引入SrTe第二相, 形成应变内延纳米结构, 将823 K下的晶格热导率降低至 $\sim 0.70 \text{ W m}^{-1} \text{ K}^{-1}$. Li等人^[55]利用Cu₂Te内延纳米结构, 使样品Sn_{0.92}Ge_{0.04}Sb_{0.04}Te-5%Cu₂Te在873 K下获得了 $\sim 0.27 \text{ W m}^{-1} \text{ K}^{-1}$ 的超低晶格热导率与 ~ 1.5 的高ZT值.

多晶材料的晶界能够散射长波声子, 有助于降低晶格热导率. Zhang等人^[56]通过球磨和放电等离子烧结的方法减小晶粒尺寸, 发现随着球磨时间的延长, 样品晶格热导率明显降低. Yang等人^[18]通过掺杂MgB₂将晶界工程应用于SnTe, 形成的Mg-B化合物以特殊的“核壳”结构包覆SnTe晶粒, 显著降低了晶格热导率, Sn_{0.78}Sb_{0.16}Te(MgB₂)_{0.09}的平均ZT相比原始Sn_{1.03}Te提高了约117%. 然而, 晶界在散射声子的同时, 也会对载流子的输运造成阻碍, 导致迁移率损失. 因此, 适当的晶粒尺寸是平衡热电参数, 获得更优热电性能的必要条件.

不同尺度的晶格缺陷散射不同波长的声子. 为了尽可能减少声子弛豫时间, 可在单一热电材料中同时构建各种不同尺度的缺陷, 共同抑制声子输运, 这种多尺度微观结构的策略已成功地应用于SnTe热电材料. 如Li等人^[34]通过在SnTe中引入Ge和MnCdTe₂, 成功构建了全尺度分层结构, 在670 K时获得了 $\sim 0.26 \text{ W m}^{-1} \text{ K}^{-1}$ 的超低晶格热导率. Xu等人^[57]在SnTe-CuSbSe₂合金中观察到了Cu基纳米沉淀、位错和点缺陷等不同尺度缺陷, 晶格热导率在823 K下低至 $\sim 0.40 \text{ W m}^{-1} \text{ K}^{-1}$. Nan等人^[58]通过复合NaSbSe₂在SnTe中形成了Sn空位、取代点缺陷、密集位错和应变, 使得823 K时的晶格热导率大幅降低至 $\sim 0.38 \text{ W m}^{-1} \text{ K}^{-1}$.

3 对n型SnTe材料和SnTe基热电器件的探索

热电器件通常由多对p型和n型热电臂通过电极、导流片、导热绝缘基板等串并联连接组装而成. 考虑到热膨胀系数的匹配, 以及为了能量转换效率的最大化, 热电器件的p型与n型热电臂通常使用同种基体且性能相匹配的材料^[59]. 然而如前所述, SnTe由于含有高浓度的锡空位, 通常以p型半导体的形式存在, n型SnTe的实现非常困难. 虽然近几十年对p型SnTe的性能优化已取得众多进展, 但对n型SnTe的研究与开发则相对滞后, 限制了SnTe基热电器件的进一步发展.

Singh^[60]通过理论计算表明SnTe具有比PbTe更为

优异的导带结构, 考虑到两者具有相似的晶格热导率, 这意味着优化后的n型SnTe可能具有比n型PbTe更出色的热电性能. Xu等人^[61]用第一性原理研究了压力对SnTe等热电材料性能的影响, 结果表明n型SnTe常压下具有比p型SnTe更高的Seebeck系数和ZT值, 且其热电性能随压力增加先提高后降低, ZT最高出现在5 GPa左右.

2021年, Pang等人^[62]在实验上成功合成了性能优异的n型SnTe热电材料, 通过固溶PbTe抑制阳离子空位, 同时掺杂I提供电子, n型Sn_{0.6}Pb_{0.4}Te_{0.98}I_{0.02}在573 K时实现了 ~ 0.8 的高ZT值. 研究证明, 对于n型SnTe中的卤素掺杂, Br和I相比Cl具有更高的掺杂效率, 分别可将电子浓度优化至 1.03×10^{19} 和 $1.11 \times 10^{19} \text{ cm}^{-3}$ ^[63]. Guo等人^[64]通过实验深入验证了n型SnTe热电相变与拓扑相变之间的对应关系, 通过Pb合金化诱导拓扑平凡相转变为拓扑平凡相, 然后通过Br掺杂将费米能级推入导带, SnTe-Pb-Br多晶与单晶在573 K的ZT值分别达到了 ~ 0.7 和 ~ 0.8 . Hong等人^[65]基于PbSe固溶和I掺杂的n型SnTe, 搭配高性能p型SnTe, 制备了全SnTe基热电器件. 如图5所示, 该器件在350 K的温差下最大能量转换效率为 $\sim 2.7\%$, 显示了SnTe热电材料在中温发电领域的应用潜力.

然而, 目前对n型SnTe热电材料的优化手段还十分有限, 得到的最高ZT只有 ~ 0.8 ^[62,64], 相比p型SnTe的 ~ 1.97 ^[34]还存在较大差距, 有待进一步改善. 此外, 对n型SnTe的实验合成方法仍需用到大量的Pb元素, 不利于SnTe基热电材料与器件的商业化应用, 需要寻找更为环保的无铅n型SnTe热电材料制备方法. 最近, Mishra等人^[66]通过理论计算提出, 在富锡和无氧条件下, Sb、Bi以及卤素掺杂在能量上有望将SnTe转变为n型导电.

4 结语

SnTe作为一种极具潜力的中温区热电材料, 受到研究者广泛关注. 许多先进的技术被用于改善SnTe的热电性能, 在电输运性能方面, 能带钝化、价带收敛、共振能级和能量滤波等策略均取得了良好的效果; 在降低晶格热导率方面, 引入点缺陷、位错、纳米沉淀物、晶界和多尺度微观结构等被证明是有效的优化方法. 由于多种策略的协同作用, p型SnTe的热电性能已得到显著提高, 目前ZT最高值可达到 ~ 1.97 ^[34].

尽管如此, 该领域仍然存在许多问题有待进一步

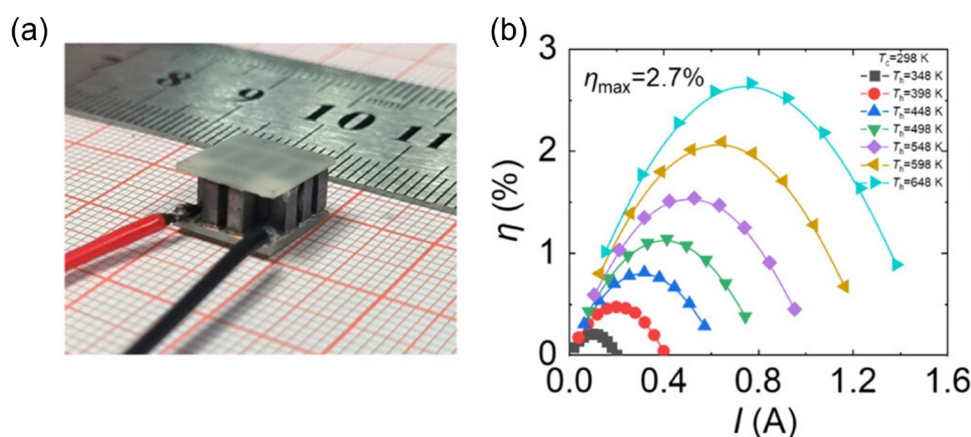


图5 (网络版彩色)全SnTe基热电器件^[65]. (a) 器件照片; (b) 器件在不同温差下的能量转换效率 η 与电流 I 的关系, 其中 T_c 为器件冷端温度, T_h 为器件热端温度

Figure 5 (Color online) All-SnTe-based thermoelectric device^[65]. (a) Photograph of the device; (b) measured conversion efficiency η for the device as a function of current I at different temperature differences, where T_c is the cold-end temperature of the device, and T_h is the hot-end temperature of the device

研究. 例如, 由于最优载流子浓度与温度有关, 探索如何精确控制不同温度下的最佳载流子浓度将有助于SnTe热电性能的进一步改善. SnTe作为拓扑晶体绝缘体, 其拓扑相变特性与热电性能的关系也有待进行更为深入的研究. 此外, 为促进SnTe的实际应用, 开发高

性能的n型SnTe材料显得尤为关键. 如何在现有研究基础上改善n型SnTe的热电性能, 以及寻找无铅n型SnTe制备方法, 将是SnTe热电材料领域的重要课题. 这不仅对实现SnTe基热电器件的商业化应用有重要意义, 也对推动先进能源技术的发展具有深远影响.

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Summary for “碲化锡基热电材料的研究进展”

Research progress of tin telluride based thermoelectric materials

Huimei Pang & Huacai Wang*

*China Institute of Atomic Energy, Beijing 102413, China** Corresponding author, E-mail: wanghc1986@163.com

The energy problem is a significant factor constraining the development of human society. Seeking cleaner and more sustainable new energy sources has become a crucial direction in contemporary academic research and industrial development. Thermoelectric materials, which can directly convert heat energy into electric energy and vice versa, have garnered widespread attention due to their simple structure, noiseless operation, pollution-free nature, and high reliability. Unlike solar and wind energy, which require specific external conditions, heat energy is ubiquitous, enabling thermoelectric devices to be applied in a wide range of fields, including extreme environments such as deep space, oceans, deep seas, and deserts, thus supporting energy supply in these areas. Among mid-temperature thermoelectric materials, PbTe boasts the best thermoelectric performance and the most mature development. However, the toxicity of lead limits its broader application. SnTe, with its environmental friendliness as well as the same crystal structure and similar band structure with PbTe, is considered a potential alternative. Nonetheless, the thermoelectric performance of pristine SnTe is inherently inferior to that of PbTe for some reasons. Initially, SnTe suffers from high hole carrier concentration due to its numerous Sn vacancies in the lattice, which leads to a low Seebeck coefficient and a high electronic thermal conductivity. Additionally, compared to PbTe, SnTe has a smaller band gap between the conduction and valence bands, and a larger energy offset between the light and heavy valence bands. The heavy valence band contributes minimally to electrical transport, which limits the Seebeck coefficient and negatively impacts the thermoelectric figure of merit (ZT). Many research efforts have been dedicated to addressing these issues and optimizing the thermoelectric properties of p-type SnTe, yielding a series of significant results. By regulating intrinsic defects or doping with external elements, the carrier concentration of p-type SnTe can be effectively reduced, improving various thermoelectric transport characteristics. To further enhance its electrical transport performance, band engineering methods such as band flattening, valence band convergence, and resonance levels have shown promising optimization effects, increasing the Seebeck coefficient and power factor of p-type SnTe materials. Moreover, introducing nanostructures to create barriers and achieve energy filtering of carriers has also proven to be an effective strategy for improving the Seebeck coefficient. In terms of thermal transport properties, the introduction of crystal defects such as point defects, dislocations, grain boundaries, and nanostructures can significantly enhance phonon scattering and reduce lattice thermal conductivity, thus improving the ZT value of p-type SnTe thermoelectric materials. In recent years, significant breakthroughs have also been made in the study of n-type SnTe. High-performance n-type SnTe has been successfully synthesized through the method of high-ratio PbTe alloying combined with halogen doping, and corresponding all-SnTe-based thermoelectric devices have been prepared. However, compared to p-type SnTe, the research progress of n-type SnTe still lags behind. Developing lead-free n-type SnTe thermoelectric materials and exploring more strategies to optimize the thermoelectric properties of n-type SnTe remain significant challenges in this field. This review pays attention to the crystal structure and band structure of SnTe materials, the research progress on optimization strategies for the thermoelectric performance of p-type SnTe, and recent explorations of n-type SnTe materials and all-SnTe-based thermoelectric devices. To promote the practical application of SnTe, more new technologies and strategies need to be employed, and further research is required to develop and optimize n-type SnTe materials.

thermoelectric materials, SnTe, Seebeck coefficient, lattice thermal conductivity, thermoelectric figure of merit (ZT)

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