



低成本高性能PbS基热电材料研究进展

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摘要 热电材料由于其高可靠性、长寿命等特点, 在废热回收及半导体制冷等领域有着广泛应用. 其中, 硫化铅(PbS)基热电材料因为原料储量丰富、价格低廉, 被研究人员所关注, 近些年逐渐成为研究热点. 受限于本身的低载流子浓度及高晶格热导率, PbS热电性能的提升较为困难. 本文从载流子浓度、迁移率、有效质量、晶格热导率等热电参数优化的角度介绍了具有代表性的PbS基热电材料研究工作. 具体而言, 能带结构调控以及生长晶体等方式对于电传输性能有很好的优化作用, 多尺度缺陷的引入则有助于晶格热导率的优化. 最后, 对PbS基热电材料未来可能的发展方向进行了展望.

关键词 热电材料, PbS, 载流子迁移率, 有效质量, 晶格热导率

热电材料作为可实现热电相互转换的新能源材料受到研究人员的广泛关注^[1-3]. 全球每年消耗的能源有超过60%以废热形式散失^[4], 热电材料可以回收部分余废热来发电以提高能源利用效率. 随着5G通讯以及物联网的快速发展, 电子产品的热管理成为热电制冷应用的重要方向^[5,6]. 衡量热电材料性能优劣的指标是热电优值 ZT , 其中 T 为热力学温度, $Z=\sigma S^2/\kappa$, 涉及3个热电材料特性参数: 电导率 σ 、塞贝克系数 S 以及热导率 κ ^[7-9]. 铅基硫族化合物, 包括PbTe、PbSe、PbS, 是一类传统的中温区热电材料, 其中PbTe热电性能优异, n型最高 ZT 达到~2.2^[10], p型 ZT 最高达到~2.8^[11]. 由于PbTe中Te元素原料稀缺, 与其同为岩盐结构的PbSe及PbS被认为是其潜在的备选材料^[12]. 目前实现商业化应用的Bi₂Te₃热电材料同样存在Te元素储量稀少且价格昂贵的问题^[13], 热电技术的可持续发展已成为一个急需解决的问题.

图1(a)中的数据展示了常见热电材料组成元素的地壳丰度以及相对Te元素的价格, PbS基热电材料的原料, 特别是S, 在地壳中储量丰富, 原料价格更为低廉^[1,12,14]. 此外, PbS相较于PbTe和PbSe, 机械性能更好, 工作温域更宽^[12]. 以上优点意味着PbS有着潜在的商业应用价值. 图1(b)展示了自2011年以来PbS基热电材料中具有代表性的工作及其报道的最大 ZT ^[14-42], 其中n型PbS基热电材料逐步成为研究热点, 最大 ZT 达到~1.7^[20,27], p型PbS基热电材料相对于n型发展滞后, 最大 ZT 达到~1.3^[17]. 本文将从载流子浓度、迁移率、有效质量、晶格热导率等热电参数优化的角度介绍PbS基热电材料性能的优化策略.

1 载流子浓度优化

热电材料的性能参数 σ 、 S 、 κ 随着载流子浓度 n 变化趋势不尽相同, 衡量电传输性能的功率因子PF以及

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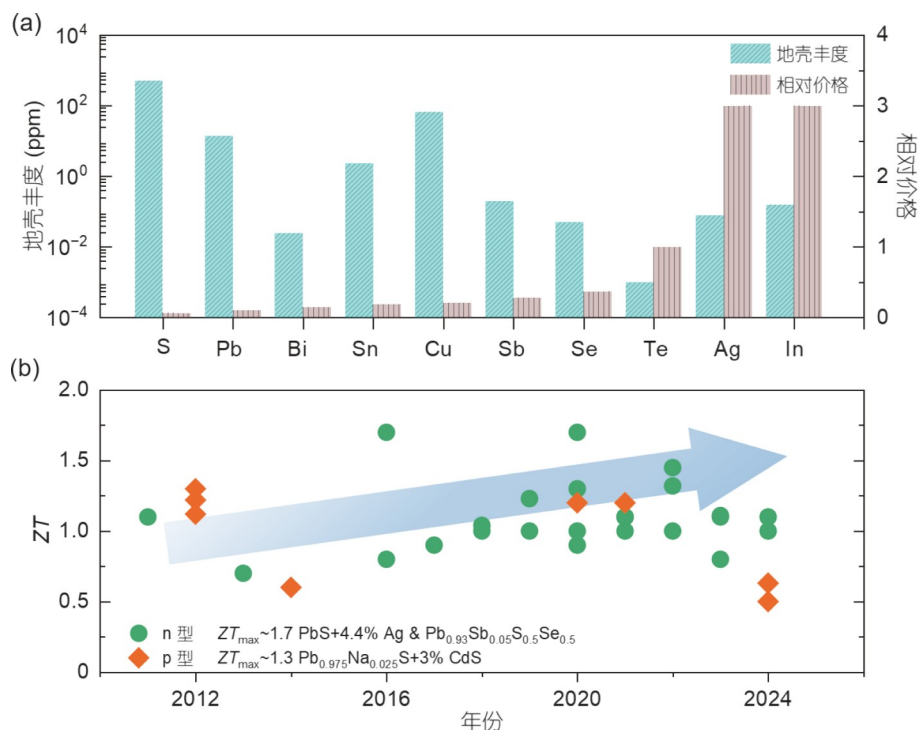


图1 (网络版彩色)PbS的原料成本优势和发展趋势。(a) 热电材料常见组成元素的地壳丰度及相对Te元素价格^[1,12,14]; (b) 具有代表性的PbS工作报道的时间以及最大 ZT ^[14-42]

Figure 1 (Color online) Raw material cost advantage and development tendency for PbS. (a) The earth abundance and relative price to Te of normal elements to form thermoelectric materials^[1,12,14]; (b) timeline and ZT maximum for typical research for PbS-based thermoelectric materials^[14-42]

ZT 会在一定载流子浓度范围内达到峰值^[43], 如图2(a)所示。

图2(b)为理论计算得到的PbS能带结构示意图^[34], 导带和价带都在L点与 Σ 点有简并的能带。L点带隙在300 K时为 ~ 0.41 eV, 带隙会随着温度变大, 因此在高温时受到双极扩散影响没有其他窄带半导体的大^[18]。

PbS是本征n型半导体, 通过异价掺杂可以有效提升PbS的载流子浓度。如图2(c)所示, n型掺杂剂相较于p型更为丰富, 在Pb位掺杂ⅢA族的Ga、In^[26,28,31,32]、VA族的Bi、Sb^[25,27,34,44], 以及在S位掺杂第七主族的Cl、Br等^[18,40]可以优化n型的载流子浓度。掺杂Ti等过渡金属元素^[37]以及额外加入Cu等小半径金属原子也被证明可以优化n型PbS的载流子浓度^[14,38]。在Pb位掺杂Li、Na、K等ⅠA族元素以及Ag元素可以优化p型PbS的载流子浓度^[41,42,45,46], 由图2(c)可以看出Cl相较于其他元素有着较高的掺杂效率。电导率定义为 $\sigma = ne\mu$, 其中 e 为元电荷, μ 为载流子迁移率。载流子浓度的提升可以提升电导率, 但是由于载流子与载流子间的相互作用, 随着载流子浓度的增加, 载流子间的散射加剧, 导致载流子迁移率 μ 下降^[43], 如图2(d)所

示^[18,25-28,31,32,34,40,44]。因此, 选取掺杂剂时, 应当综合考虑掺杂效率以及载流子浓度对迁移率的影响。

2 迁移率优化

载流子迁移率的优化有利于功率因子的提升, 对热电性能提升至关重要。在相对较低载流子浓度条件下, 通过高迁移率的方式来提升热电材料性能^[43]。载流子迁移率的优化策略包括能带锐化^[29]、能带对齐^[17,29,34]、晶格素化^[14]以及生长高质量晶体^[14]。

Xiao等人^[29]通过在掺杂2%的Sb优化载流子浓度后的PbS中固溶Sn, 达到使能带尖锐化的效果, 使得有效质量减小, 从而优化迁移率。如图3(a)内示意图所示, Sn固溶使得导带位置下移, 与引入的PbTe导带能量位置相近, 实现了导带对齐, 减少了载流子在PbS与PbTe带间的散射从而维持高迁移率。图3(a)中展示了300、623、923 K下的PbS、 $\text{Pb}_{0.94}\text{Sn}_{0.06}\text{S}$ 以及 $\text{Pb}_{0.94}\text{Sn}_{0.06}\text{S} + 8\% \text{ PbTe}$ 样品的热电品质因子 B , B 正比于加权迁移率和晶格热导率的比值, 也可以反映热电性能优劣^[29]。由于导带锐化与导带对齐策略维持了高迁移率, 品质因子 B 逐步提升, PbS的性能得到了逐步优化, 与图3(b)中

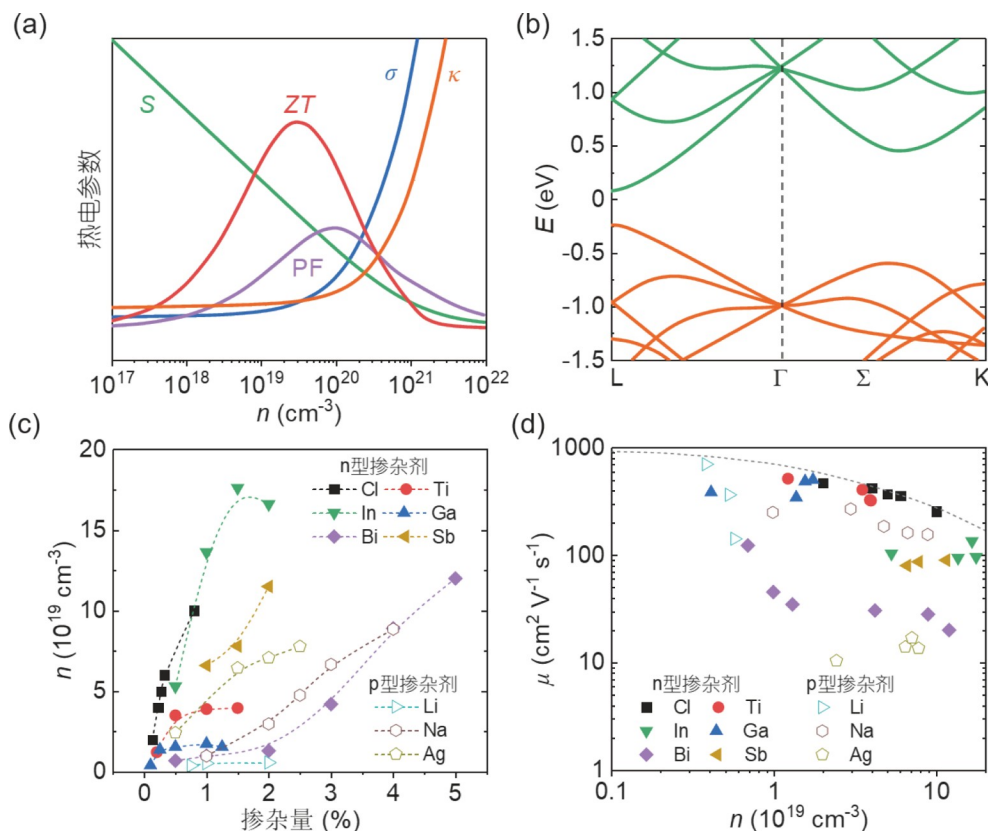


图 2 (网络版彩色)PbS的载流子浓度优化方法. (a) 热电参数随载流子浓度变化示意图^[43]; (b) 计算得到的PbS能带结构^[34]; (c) 不同掺杂剂条件下, PbS的掺杂量与载流子浓度关系^[18,25-28,31,32,34,40,44]; (d) 不同掺杂剂条件下, PbS的迁移率随载流子浓度变化关系^[18,25-28,31,32,34,40,44]

Figure 2 (Color online) Carrier concentration optimizing approach to PbS. (a) Thermoelectric parameters changing with carrier concentration^[43]; (b) calculated band structure for PbS^[34]; (c) carrier concentration as a function of doping amount for different dopants^[18,25-28,31,32,34,40,44]; (d) carrier mobility as a function of carrier concentration for different dopants^[18,25-28,31,32,34,40,44]

全温域内 ZT 的逐步提升趋势相符, 最终该工作的最高性能样品在300~923 K内的平均 ZT 达到~0.7, 923 K时获得~1.3的 ZT 峰值。

Luo等人^[34]在PbS中合金化GeS, 取代Pb位置的 Ge^{2+} 发生价态歧化生成 Ge^0 与 Ge^{4+} , 从而形成稳定的 $\text{Pb}_5\text{Ge}_5\text{S}_{12}$ 第二相。由于 $\text{Pb}_5\text{Ge}_5\text{S}_{12}$ 与PbS可以实现良好的导带对齐, 最终合金化14% GeS的样品在 $3 \times 10^{19} \text{ cm}^{-3}$ 的载流子浓度下获得高达 $\sim 121 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ 的迁移率, 400~923 K内的平均 ZT 达到~0.76, 923 K时获得~1.32的 ZT 峰值。

p型PbS同样可以通过基体与第二相的价带对齐策略维持高迁移率。Zhao等人^[17]在p型PbS中分别引入CdS、ZnS、CaS、SrS, 发现CdS、ZnS中化学键共价性比CaS、SrS更强且带隙更窄。理论计算结果表明, CdS与PbS基体之间价带能量差仅为0.13 eV, 由于价带对齐, 引入CdS的样品比与引入其他3种硫化物的样品

表现出更高的迁移率, 最终样品 $\text{Pb}_{0.975}\text{Na}_{0.025}\text{S}+3\% \text{ CdS}$ 的 ZT 在923 K达到~1.3。

晶格素化是一种通过减少材料基体的本征空位缺陷以提升载流子迁移率的策略, 最初由Liu等人^[47]在p型SnSe晶体的研究中提出。随后, 该策略成功应用于PbTe基以及PbSe基热电材料近室温性能的开发以及热电器件制冷温差的提升^[48,49]。Wang等人^[14]首先在PbS中固溶40% Se优化晶格热导率, 之后在PbS基体中额外加微量Pb, 填补本征存在的Pb空位, 降低阳离子空位对于载流子的散射, 使得载流子浓度与迁移率实现了协同优化。如图3(c)中插图所示, $\text{Pb}_{1.004}\text{S}_{0.6}\text{Se}_{0.4}$ 相比于基体载流子浓度提升了60%, 但是迁移率提升至 $\sim 614 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ 。最终, 额外补偿4% Pb的样品的 ZT 相较于基体 $\text{PbS}_{0.6}\text{Se}_{0.4}$ 在整个测试温域内得到了全面提升, 300~823 K的平均 ZT 提升了~31%。在该工作中, 研究人员通过布里奇曼法生长高质量PbS基晶体, 也使得

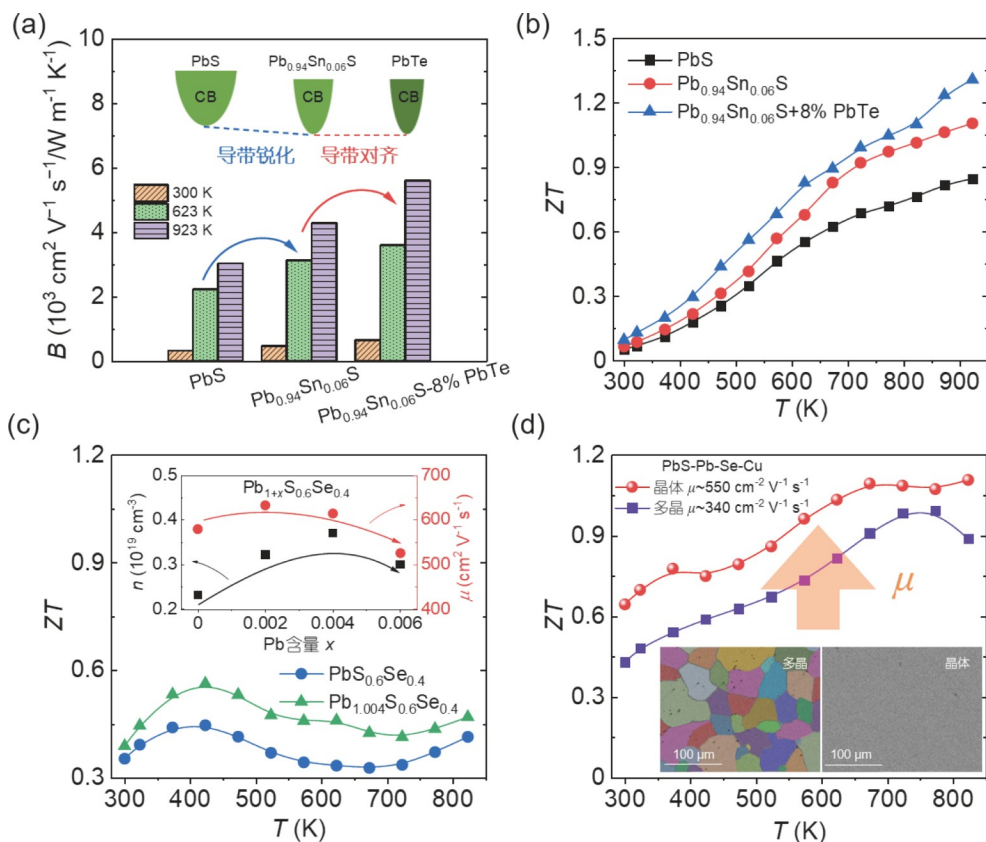


图3 (网络版彩色) PbS的载流子迁移率优化策略. 导带锐化以及导带对齐增强PbS的品质因子 B (a)以及 ZT (b)^[29]; (c) 补偿铅空位提升 $PbS_{0.6}Se_{0.4}$ 的 ZT , 插图: $Pb_{1+x}S_{0.6}Se_{0.4}$ 的载流子浓度和迁移率^[14]; (d) 生长晶体优化迁移率提升 $PbS-Pb-Se-Cu$ 的 ZT , 插图: 多晶与晶体样品扫描电子显微镜对比^[14]

Figure 3 (Color online) Carrier mobility enhancing strategies for PbS. Enhancing quality factor B (a) and ZT (b) of PbS through conduction band sharpening and conduction band alignment^[29]. (c) Enhancing ZT of $PbS_{0.6}Se_{0.4}$ through Pb compensation. Inset: Carrier concentration and carrier mobility for $Pb_{1+x}S_{0.6}Se_{0.4}$ ^[14]. (d) Optimizing carrier mobility to enhance the ZT of PbS-Pb-Se-Cu. Inset: Comparison of the scanning electron microscopes between crystal samples and polycrystal samples^[14]

迁移率得到明显提升. 通过生长晶体可以减少晶界对于载流子的散射. 从图3(d)中扫描电子显微镜结果可以看出, 同样的观测尺度下晶体样品未观察到晶界, 而多晶样品中则存在大量晶界以及烧结过程中产生的孔洞. 相同名义成分的晶体样品相较于SPS烧结得到的多晶样品迁移率提升了近60%, 如图3(d)所示. 晶体样品的热电性能在全温域内得到提升, 在300~823 K内平均 ZT 达到~0.92, 室温 ZT 达到~0.64, 均为目前PbS基热电材料体系中报道的最高值. 由于迁移率的提升带来的高室温性能, 该工作搭建了首个基于n型PbS基热电材料的制冷器件, 实现了36.9 K的室温制冷温差, 表明原料储量丰富的PbS基热电材料也有成为商用制冷材料的潜力.

3 有效质量优化

有效质量的提升可以提升塞贝克系数进而优化电

传输性能. 有效质量提升方法主要包括引入共振能级、实现能带收敛等. Hou等人^[32]在PbS中掺杂了少量的In, 计算结果表明In可以在PbS中引入穿越费米能级的新带, 提升了有效质量从而使得电传输性能得到提升. 该工作最终实现在423~823 K内获得~0.8的平均 ZT , 在723 K获得~1.1的峰值 ZT .

Chen等人^[39]在n型PbS中引入化合物GaSb, 使Ga与Sb占据Pb位置. 由于Ga的4s轨道以及Sb的5p轨道的共同作用, GaSb掺杂将n型PbS导带中L带和 Σ 带之间的能量差从0.34 eV降低到0.15 eV, 如图4(a)所示. 该工作通过化合物掺杂策略, 首次实现了n型铅基硫族化合物中的导带收敛. 从图4(b)中可以看出, 由于态密度有效质量的增强, 掺杂GaSb的样品在相同载流子浓度下, 与掺杂Sb以及Ga、In共掺杂的样品相比拥有更高的塞贝克系数. 由于GaSb掺杂在优化载流子浓度的同时通过导

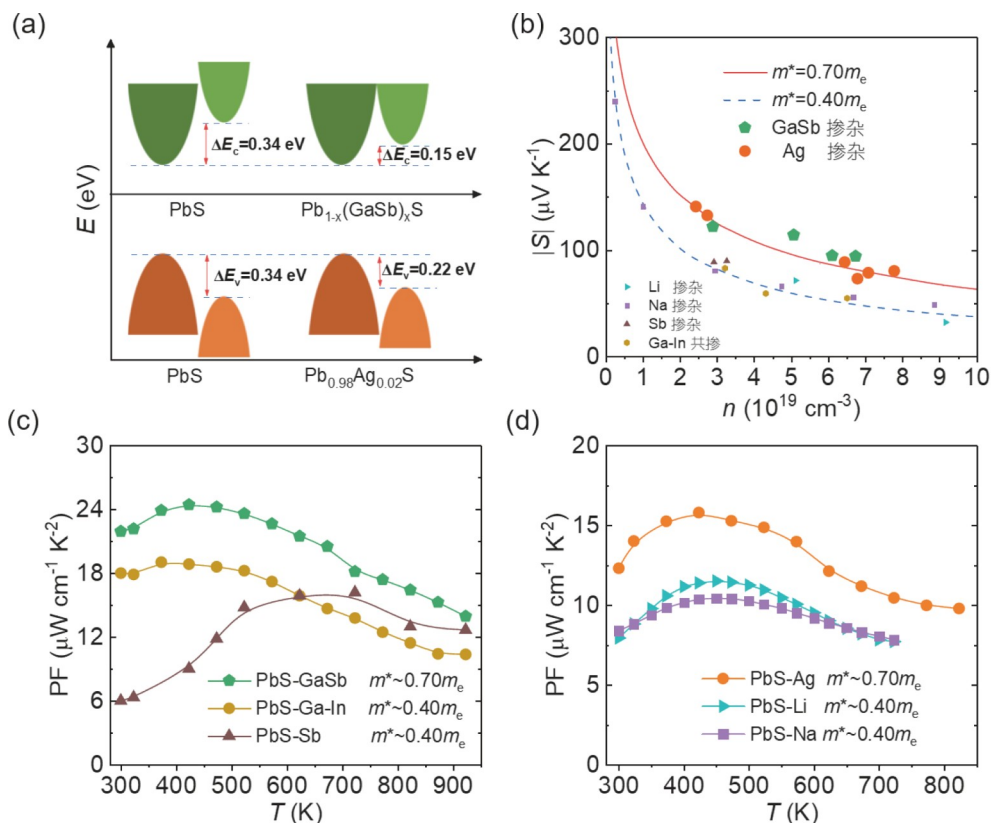


图4 (网络版彩色)能带收敛提升PbS热电性能. (a) PbS能带收敛示意图^[39,41]; (b) GaSb、Ag以及其他掺杂剂掺杂样品的Pisarenko曲线^[17,26,39,41,45]; (c) GaSb掺杂、Ga-In共掺杂以及Sb掺杂样品的PF^[26,39]; (d) Ag、Li、Na掺杂样品的PF^[17,41,45]

Figure 4 (Color online) Enhancing thermoelectric performance of PbS through band convergence. (a) Schematic of band convergence for PbS^[39,41]; (b) Pisarenko plot for samples doped by GaSb, Ag and other dopants^[17,26,39,41,45]; (c) PF for GaSb, Ga-In and Sb doped samples^[26,39]; (d) PF for Ag, Li and Na doped samples^[17,41,45]

带收敛使得有效质量增强, n型PbS的电传输性能得到了大幅度的改善. 功率因子PF在423 K达到 $\sim 24 \mu\text{W cm}^{-1} \text{K}^{-2}$ 的峰值, 在423~823 K内平均PF达到 $\sim 20.4 \mu\text{W cm}^{-1} \text{K}^{-2}$, 是目前PbS基热电材料中的最高值.

Wu等人^[41]通过在p型PbS中引入Ag, 首次实现了p型PbS中的价带收敛, 如图4(a)所示, Ag掺杂使得p型PbS中L带和 Σ 带之间的能量差从0.34 eV降低到0.22 eV. 由于价带收敛, 图4(b)中Ag掺杂的样品与Li掺杂及Na掺杂的样品相比有着更高的有效质量^[17,45], 使得最终掺杂Ag的p型PbS表现出更突出的电传输性能, 如图4(d)所示. Li等人^[42]的工作也印证了Ag在p型PbS中具有促进价带收敛从而增强有效质量的效果.

4 晶格热导率优化

本征高晶格热导率是限制PbS热电性能提升的重要因素. 晶格热导率是不受载流子浓度影响的热电参

数, 降低晶格热导率的关键是要在考虑载流子运输的同时尽量阻碍声子的传输^[9]. 从图5(a)可以看出, 不同的散射机制对不同频率的声子有着不同的散射率, 其中, 声子-声子相互作用是材料本征散射机制. 在众多散射机制中, 晶界对于声子的散射率独立于声子频率且在低频声子区域占据主导地位, 点缺陷对声子散射随声子频率变大而增强, 最终在高频声子区占据主导地位, 而纳米相对于声子的散射率与纳米相尺度有关^[50]. 图5(b)为通过引入点缺陷、晶界、第二相或析出物等缺陷散射声子, 从而降低晶格热导率的示意图^[9].

在引入微量掺杂剂时, 掺杂元素与本征元素尺寸不同会造成晶格畸变, 也可以利用合金化或者与Pb或S的同族元素形成大比例固溶体等手段, 通过尺寸及应力波动散射声子来大幅度降低晶格热导率. 图5(c), (d)分别列举了通过不同手段降低晶格热导率进而获得高ZT的代表性工作. Zhao等人^[25]在n型PbS中掺杂Sb调

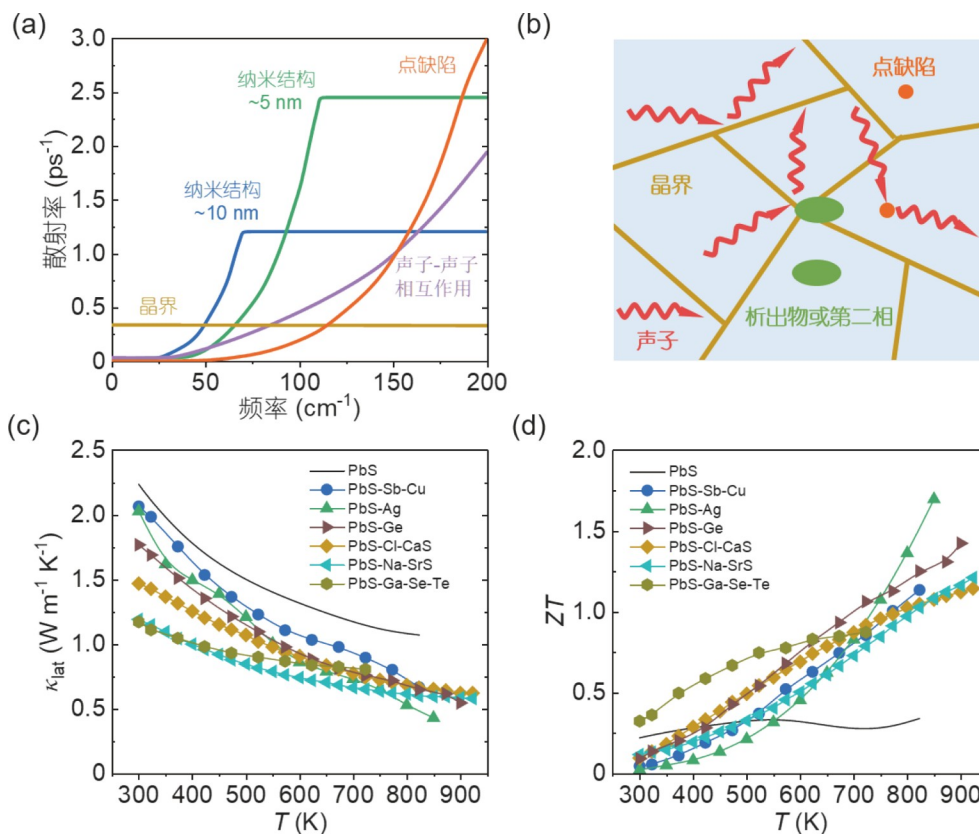


图5 (网络版彩色) PbS晶格热导率优化策略。(a) 不同散射机制频率与散射率关系^[50]; (b) 散射机制示意图^[9]; 代表性的降低热导率工作^[15-17,20,25,31,36]报道的晶格热导率(c)及ZT(d)

Figure 5 (Color online) Lattice thermal conductivity optimizing strategies for PbS. (a) Frequency dependent scattering rate for different scattering mechanisms^[50]; (b) schematic for scattering mechanisms^[9]; lattice thermal conductivity (c) and ZT (d) for some typical work related to lattice thermal conductivity reduction^[15-17,20,25,31,36]

节载流子浓度后引入不同形式的Cu, 研究发现位于晶格间隙的Cu相较于取代Pb位置的Cu有着更突出的降低晶格热导率的作用。同时, 引入两种形式Cu的样品 $\text{Pb}_{0.95}\text{Sb}_{0.02}\text{Cu}_{0.03}\text{S}$ -0.03Cu在923 K的晶格热导率降低至 $\sim 0.57 \text{ W m}^{-1} \text{ K}^{-1}$, 获得了 ~ 1.23 的最大ZT。

溶剂法合成的具有纳米结构的PbS基热电材料拥有显著低的热导率, 从而可以获得较高的ZT^[20,51]。Ibáñez等人^[20]通过溶剂法合成了PbS-Ag纳米复合材料, PbS的纳米结构以及晶界处Ag纳米相的存在有效阻碍了声子输运, 最终成分为PbS-4.4% Ag的纳米复合材料在850 K的晶格热导率降低至 $\sim 0.43 \text{ W m}^{-1} \text{ K}^{-1}$, ZT达到 ~ 1.7 , 是PbS基热电材料报道的最高ZT之一。Rathore等人^[36]在PbS中引入Ge, Ge在调整电子结构的同时在基体中生成了尺度5~20 nm的 Pb_2GeS_4 纳米第二相。由于平均自由程在20 nm以下的声子在PbS中占比 $\sim 90\%$ ^[52], Pb_2GeS_4 可以有效散射声子。此外, 非弹性中子散射测试表明该体系中存在超短的声子弛豫时间, 说明Ge掺

杂加强了该体系中的声子-声子相互作用。最终, 掺杂10% Ge的样品在900 K时获得了 $0.56 \text{ W m}^{-1} \text{ K}^{-1}$ 的超低热导率, 900 K获得 ~ 1.45 的高ZT。

合适的第二相的引入可以在适当保持电性能的同时有效降低热导率, 如CaS、SrS等硫化物第二相在n型和p型PbS中都有良好的降低热导率的效果^[15-17]。在PbS中固溶PbSe、PbTe可以形成单相化合物, 在保持载流子传输性能的同时显著降低热导率, 其中PbSe与PbS可以形成任意比例的固溶体, 而PbTe在PbS中的固溶度只有 $\sim 4\%$ ^[31]。Cheng等人^[31]通过固溶30% Se, 消除PbTe与PbS间的混溶间隙, 使得PbTe在PbS中的固溶度达到16%, 最终最高性能的样品在300~723 K内的平均ZT达到 ~ 0.73 , 723 K时ZT达到 ~ 1.1 。

5 总结

本文从归纳载流子浓度、迁移率、有效质量、晶格热导率等参数强化方法的角度介绍了针对PbS近些

年取得的代表性工作。需要强调的是, 这些强化方法彼此之间有一定关联, 不同的强化方法可以结合使用。如间隙Cu的引入不仅可以优化载流子浓度, 也可以有效散射声子降低晶格热导率^[14]。在优化个别物理参数时, 也要考虑其他参数的影响。比如, 载流子浓度提升虽然可以提升电导率, 但是电子热导率也会大幅度提升, 塞贝克系数和迁移率也会下降, 因此需要控制在合适范围内。目前PbS基热电材料体系的室温 ZT 达到~0.64, 最大 ZT 达到~1.7, 充分表明原料储量丰富、价格低廉的

PbS材料具有广阔的制冷与发电的潜力。

目前针对n型PbS的研究取得了许多创新性成果, 而p型PbS的开发稍显落后。对于PbS基制冷器件的应用, 需要开发与n型PbS室温性能相匹配的p型PbS热电材料, 还需要开发与PbS相匹配的接触材料以降低接触电阻从而提升制冷温差。理论计算表明, 二维PbS材料由于量子限域效应的存在会有很高的室温 ZT , 可能具有潜在的制冷能力^[53]。对于温差发电器件, 提升宽温域的平均 ZT 相较于追求最高 ZT 对于提升发电效率更有实用意义。

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Summary for “低成本高性能PbS基热电材料研究进展”

Progress in PbS-based thermoelectric materials with low cost and high performance

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Thermoelectric materials are widely used in the fields of waste heat harvest and electrified refrigeration because of their high reliability and long life. Among them, PbS-based thermoelectric materials have attracted much attention because of the earth abundance and low price of raw materials, and have been a research hotspot in recent years. Due to its low carrier concentration and high lattice thermal conductivity, it is difficult to improve the thermoelectric performance of PbS. In this paper, the representative research work of PbS-based thermoelectric materials is introduced from the perspective of the optimization of thermoelectric parameters including carrier concentration, carrier mobility, effective mass and lattice thermal conductivity. The energy band structure engineering such as band sharpening and band alignment maintains high carrier mobility while reducing lattice thermal conductivity. High quality crystal growth has a crucial effect on the optimization of thermoelectric performance in near room temperature, and high carrier mobility enables PbS-based materials to realize thermoelectric cooling. Recently, an approach to optimize the effective mass through band convergence has also been achieved both in n- and p-type PbS successfully. Appropriate doping (GaSb in n-type and Ag in p-type PbS) minimizes the energy difference between L band and Σ band to optimize the effective mass. The introduction of multi-scale defects optimizes the lattice thermal conductivity, because the combination of different kinds of phonon scattering mechanism could hinder the transport of phonon with a wide range of frequency. We also emphasize that the influence on other parameters should also be taken into account when optimizing individual thermoelectric physical parameters. For example, although increasing carrier concentration could improve the electrical conductivity, the electronic thermal conductivity will also be greatly increased, and the Seebeck coefficient and carrier mobility will also decrease, so it needs to be controlled within the appropriate range. The scattering mechanism introduced to slow down the phonon transport also needs to be taken into consideration. At present, the room temperature ZT of the PbS-based thermoelectric material system reaches ~ 0.64 , and the maximum ZT reaches ~ 1.7 , which indicates that the PbS-based material with abundant raw material reserves and low price has broad potential for refrigeration and power generation. However, some challenges still need to be addressed. For example, the research of n-type PbS has achieved many innovative results, while the development of p-type PbS is slightly left behind. For the application of PbS-based refrigeration devices, it is necessary to develop p-type PbS thermoelectric materials that match the room temperature performance of n-type PbS. Moreover, it is also necessary to develop contact materials that match PbS to reduce the contact resistance and thereby increase the cooling performance. Quantum confinement in PbS with low dimension also deserves attention because it may have the potential of thermoelectric cooling. For power generation, it is more practical to increase the average ZT of wide temperature range than to pursue the highest ZT value for improving the power generation efficiency.

thermoelectric materials, PbS, carrier mobility, effective mass, lattice thermal conductivity

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