

Bi₂Te₃ 基热电材料中的声子工程

刘志愿^{1,2}, 管希成¹, 李 周³, 马 妮⁴, 马俊杰¹, 巴 倩¹, 夏爱林¹, 晋传贵¹

(1. 安徽工业大学材料科学与工程学院, 安徽 马鞍山 243002; 2. 安徽工业大学 先进金属材料绿色制备与表面技术教育部重点实验室, 安徽 马鞍山 243002; 3. 安徽大学材料科学与工程学院, 合肥 230601; 4. 中国科学技术大学化学与材料科学学院, 合肥 230026)

摘 要: Bi₂Te₃ 基合金因其优异的电输运性能和较低热导率在低温区热电材料中备受关注。然而由 Bi₂Te₃ 基合金制造的热电发电或制冷器件转化效率仍较低, 因此进一步提升 Bi₂Te₃ 基材料的热电优值 zT 是关键。由于晶格热导率与电性能参数关联较少, 在热电性能参数中较为独立, 因此, 在不影响电性能的前提下, 通过声子工程降低晶格热导率成为提升 zT 值的重要方法。本文主要综述了近年来通过纳米改性、超晶格结构、纳米复合、掺杂和引入位错阵列等声子工程优化 Bi₂Te₃ 基材料热电性能的主要研究进展。通过这些优化手段可以显著降低材料的比热容、声子群速度或声子平均自由程, Bi₂Te₃ 基材料的晶格热导率显著降低, 热电性能大幅提升, 为热电器件的应用提供科学和技术支撑。

关键词: 碲化铋基热电材料; 声子工程; 晶格热导率; 热电性能

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热电材料作为一种新型能源材料因可以实现热能和电能直接相互转化而备受关注^[1-4]。相比于传统热机, 热电材料制成的器件具有结构简单、体积小、无机械运动部件等优点^[5-7], 且热电发电或制冷器件转换效率逐步提高, 有望在未来能源利用和管理方面发挥重要作用^[8-11]。热电材料的转换效率主要由无量纲优值(zT)来决定, $zT = S^2 \sigma T / \kappa$, 其中: σ 为电导率; S 为 Seebeck 系数; T 为绝对温度; κ 为热导率, 由载流子热导率(κ_e)和晶格热导率(κ_L)组成^[9, 12]。对热电材料而言, zT 值越大, 器件的转换效率就越高。由于影响 zT 值大小的 3 个核心参数 σ 、 S 和 κ 相互之间强耦合, 难以单独改变某一参数而不影响其它 2 个参数, 因此需要在优化功率因子($S^2 \sigma$)基础上尽可能降低热导率, 以实现热电性能的协同优化^[13]。载流子热导率服从 Wiedemann-Franz 定律:

$$\kappa_e = L \sigma T \quad (1)$$

式中: L 是 Lorentz 数。载流子热导率与电导率成线性相关, 难以单独调控, 所以通过声子工程调控 κ_L 就成为降低总热导率的主要手段^[7, 14-18]。根据理想

气体模型假设, κ_L 可表示为:

$$\kappa_L = \frac{1}{3} C_v v_g l = \frac{1}{3} C_v v_g^2 \tau \quad (2)$$

式中: C_v 是比热容; v_g 是声子振动模的群速度; l 是声子平均自由程; τ 是声子弛豫时间。因为弛豫时间 τ 和散射概率 τ^{-1} 成反比, 所以调控 κ_L 本质上是对比热容、声子群速度和声子散射的调控^[19]。

热电材料体系较多, 如 SiGe 合金^[20]、笼状化合物^[21-23]、方钴矿^[24-25]、Heusler 热电半导体^[26-29] 等。Bi₂Te₃ 是硫族化合物材料体系中研究最早的热电材料之一。由于较窄带隙($E_g = 0.14$ eV)和独特的晶体结构(菱方层状结构, 沿 c 轴以 $-\text{Te}^{(1)}-\text{Bi}-\text{Te}^{(2)}-\text{Bi}-\text{Te}^{(1)}$ 顺序堆叠 5 个交替排列的 Te 层和 Bi 层^[30]) 使得其具有较大 Seebeck 系数和较低热导率, 是当前公认最好的近室温热电材料, 在热电制冷领域获得应用。经过近几十年的发展, Bi₂Te₃ 基材料的 zT 值已获得较大提升。近年来通过声子工程优化热电材料的输运性能已有报道^[19, 29], 但针对近室温 Bi₂Te₃ 基合金通过声子工程优化热电性能的总结报道较少。本文讨论了影响材料比热容、声子群速度和声

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第一作者: 刘志愿(1982—), 男, 博士, 副教授。

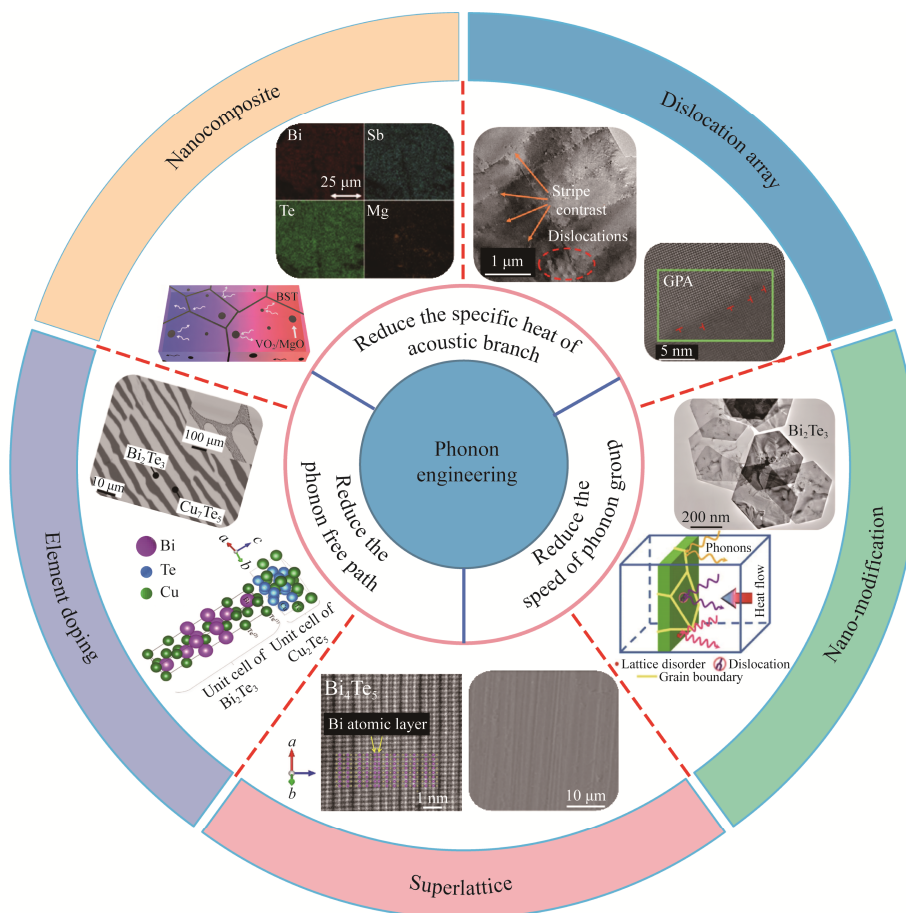
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First author: LIU Zhiyuan (1982—), male, Ph.D., Associate Professor.

E-mail: zhiyuanliu826@ahut.edu.cn

子散射的因素, 综述了近年来通过一些声子工程方法^[11, 31–34]优化 Bi_2Te_3 基材料热电性能的主要研究进展(图 1), 通过这些优化手段调控比热容、声子群速

率或声子平均自由程, Bi_2Te_3 基材料的晶格热导率显著降低, 热电性能大幅提升, 为热电器件的应用提供科学和技术支撑。



BST represents Bi-Sb-Te alloy thermoelectric material.

图 1 Bi_2Te_3 基热电材料中的声子工程^[11, 31–34]

Fig. 1 Phonon engineering in Bi_2Te_3 base thermoelectric materials^[11, 31–34]

1 比热容、声子群速度和声子散射

1.1 比热容

根据 Debye 模型, 晶格导热由相向运动的声学支声子导热和相对运动的光学支声子导热组成, 由于光学支声子速率接近于 0, 对晶格导热贡献可以忽略不计, 所以晶格热导率以声学声子导热为主^[35]。在多原子体系中, 假设每个原胞的原子数为 n , 总原胞数为 N , 则体系总自由度为 $3Nn$, 其中声学支有 $3N$ 个, 光学支有 $3(n-1)N$ 个, 根据能量均分定理, 声学支贡献的比热为 C_V/n 。所以原胞中原子数目越多, 晶胞越复杂, 声学支贡献比热越小, 晶格热导率也就越小。在 Bi_2Te_3 基热电材料的改性方法中, 掺杂合金化^[36]和超晶格结构^[33]无疑是获得复杂晶胞的有效方法。Zhu 等^[33]制备的 $(\text{Bi})_m(\text{Bi}_2\text{Te}_3)_n$ 超晶

格结构就具备复杂的晶体结构, 该超晶格结构由于声子在界面的强烈散射和层间较低的穿透系数也具有较低的晶格热导率。

1.2 声子群速度

声子速度(V_s)在 Brillouin 区表示为

$$V_s \approx (K / \bar{m})^{\frac{1}{2}} \quad (3)$$

式中: $\bar{m}$ 是平均原子质量; K 是表征原子键强度的恢复力常数。根据式(3), 通常弱化学键和重组分的材料具备低声速^[37–40]。而 Bi_2Te_3 基热电材料也是因为其弱化学键和非谐动力学获得低晶格热导率, 从而在众多近室温热电材料中脱颖而出^[41–43]。在不改变其它本征参数的基础上调节 Bi_2Te_3 的键合来优化晶格热导率也是获取优异热电性能的一种方法。研究发现超晶格结构能通过区域折叠和组成层之间的

质量失配来改变声子色散, 促使超晶格结构形成弱化学键和晶格非谐性, 从而具备较低的声子群速度^[33, 44]。除了直接调节材料键合以外, 纳米改性也是降低声子群速度的有效途径之一^[45-48]。纳米改性减小晶粒尺寸会导致界面密度增大, 增强长波声子的散射强度, 根据 Miyazaki^[48]和 Bessas 等^[49]的报道, 长波声子被散射后, 平均声子群速度会显著降低。

1.3 声子散射

相比于改变热电材料的本征性质, 增强对声子的散射强度实施起来更加简单直接, 这也是 Bi₂Te₃ 基合金降低晶格热导率的主要途径。根据 Matthiessen 定则^[50-51], 如果材料具备多种散射机制, 各种散射之间的关系可用弛豫时间 τ 来表示

$$\tau^{-1} = \tau_R^{-1} = \tau_U^{-1} + \tau_{PD}^{-1} + \tau_B^{-1} + \tau_S^{-1} + \tau_D^{-1} + \tau_P^{-1} + \tau_{BP}^{-1} \quad (4)$$

式中: τ^{-1} 是声子散射概率; τ_U^{-1} 是非弹性声子-声子散射; τ_{PD}^{-1} 是点缺陷散射; τ_B^{-1} 是边界散射; τ_S^{-1} 是应力散射; τ_D^{-1} 是位错散射; τ_P^{-1} 是杂质散射; τ_{BP}^{-1} 是双极化散射。声子-声子散射和边界散射是造成 Bi₂Te₃ 基热电材料在室温低晶格热导率的主要散射机制。然而, 当温度升高时, 双极化散射逐渐增强, 其它散射机制对热导率影响逐渐减小, 且电输运性能显著降低, 最终会导致 zT 值减小。此外, 杂质散射以低频声子为散射目标, 位错以中频声子为散射目标, 而点缺陷散射则是以高频声子为散射目标。因此, 降低晶格热导率的优化方法往往不只是依靠单一的散射机制, 而是多种散射机制共同作用。甚至有可能不仅有声子自由程降低, 有时往往会导致声子群速度和声学支贡献比热降低。增强声子散射降低晶格热导率的声子工程根据其造成的微观结构不同, 主要分为纳米改性^[52]、第二相纳米复合^[53]、超晶格、元素掺杂^[54]以及引入位错阵列^[55]等 5 种优化方法。

2 纳米改性

纳米化是提升热电材料性能的重要方法之一。利用声子和电子平均自由程的差异, 当 Bi₂Te₃ 基热电材料晶粒尺寸大于电子平均自由程但小于声子平均自由程时, 就能实现对 Bi₂Te₃ 基合金电-热输运性能的解耦^[56]。在热输运性能的研究中, 人们主要利用纳米改性的方法来增强 Bi₂Te₃ 基热电材料的界面散射。随晶粒尺寸的减小, 界面体积比增大, 导致声子在晶界处的散射增强并降低晶格热导率^[57-62]。已报道的纳米改性途径主要有低维化、引入异质纳米结构和细化晶粒等, 其制备工艺主要有球磨^[63-65]、

熔融旋甩^[66-68]、水热合成^[69-71]、湿化学反应^[72]、金属有机化学气相沉积^[73]、分子束外延^[74]、喷墨打印^[75]、脉冲激光沉积^[76]和真空蒸发^[77]等。

2.1 低维化

近年来, 低维化已被证实是提高热电材料性能的最有效的途径之一^[11, 78], 维数和晶粒尺寸的降低会导致费米能级附近的态密度增加并增强声子散射, 导致 Seebeck 系数提高的同时降低晶格热导率。

2.1.1 二维结构 由于其菱形层状结构, 使得 Bi₂Te₃ 基合金的二维化相比于其他近室温热电材料更简单。在声子输运性能优化方面, 二维化通过细化晶粒来提高晶界密度和对声子的边界散射, 使二维结构 Bi₂Te₃ 基合金表现出小的声子群速度和较短的本征平均自由程, 导致其晶格热导率比其 Bi₂Te₃ 铸块显著降低^[79-80]。

1) 二维纳米片及含有纳米片结构的块状材料

纳米片的引入, 使 Bi₂Te₃ 基材料内部界面和晶格缺陷密度增加, 同时纳米片的晶粒尺寸越小, 声子在边界和晶格缺陷处的散射越强, 有效阻碍声子在材料中的传播^[81]。近年来报道的 Bi₂Te₃ 基纳米片的制备工艺主要有机械铣削法、分子束外延(MBE)^[79]、水热法和溶剂热法^[82-84]以及湿化学法^[85]。

MBE 法是制备二维纳米结构最常用的方法。该制备技术中, 衬底和外延界面之间的晶格失配和界面粗糙度会显著影响成品的形貌以及热电性能。此外, 衬底温度和是否存在籽晶层也影响纳米片的生长行为和晶体质量。Wu 等^[79]就凭借籽晶层对晶粒生长的促进作用和 Si (111)衬底表面饱和的悬空键, 通过调节衬底表面和籽晶层改变 Bi₂Te₃ 基材料中堆叠纳米片和交叉纳米片的比例和尺寸。较多高密度晶界的交叉纳米片会显著增强能量过滤效应和声子的界面散射, 进而优化 Bi₂Te₃ 基材料的热电性能。

水热法和溶剂热法制备 Bi₂Te₃ 基纳米片过程中, 其晶粒生长与唯象学机制(PM)有关。在初始反应阶段, 存在的初生晶核形成之后, 由于还原剂会选择性地吸附到某一晶面上, 使初生晶核聚集导致产物重力增加。当大于 van der Waals 力时, 会破坏 Te^(II)原子层之间的结合, 阻碍 Bi₂Te₃ 基材料的晶体沿长轴继续生长^[84]。与其他制备工艺相比, 唯象学机制的存在使该工艺能够很好控制晶粒尺寸、相的形成和形貌的生长, 容易在减小晶粒尺寸的同时增加位错密度, 增强对中频声子的散射强度并降低声子自由程, 进一步改善 Bi₂Te₃ 基合金的热输运性能。Yang 等^[86]利用水热法结合放电等离子体烧结(SPS)

工艺制备的 Bi_2Te_3 纳米片具有较小晶粒尺寸并含有高密度位错的小角度晶界。导致平均自由程为几百纳米或更大的中低频声子在位错和晶界处强烈散射，材料的晶格热导率显著降低。在 400 K 时获得了 0.88 的最大 zT 值。该值是当时 n 型二元 Bi_2Te_3 所能获得的最高 zT 值之一。

此外，湿化学法和机械铣削法也能够制备片状 Bi_2Te_3 基热电材料。相比于自上而下的机械铣削法，自下而上的湿化学法因为表面活性剂的加入不仅能够更简单地获得纳米和异质结构，还能将纳米晶粒尺寸控制在较窄的范围^[87]。但任何参与合成的表面活性剂都会明显降低烧结铸块的电输运性能，所以表面活性剂的选择和去除就成为改进湿化学法工艺的关键^[88]。Son 等^[89]就利用湿化学法合成了 1 nm 厚的超薄 Bi_2Te_3 纳米片，通过表面活性剂与油酸交换，然后与氨反应有效去除表面活性剂。最后通过 SPS 烧结制备了致密的具有丰富纳米结构的块体材料，相比其它方法制备的块体材料，热导率显著降低，最低热导率仅为 $0.44 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ 。在 250 °C 烧结温度下固结的 Bi_2Te_3 材料在 400 K 具备 0.62 的最大 zT 值，是当时纯 n 型碲化铋最高 zT 值之一。

2) 纳米薄膜结构

在 Bi_2Te_3 基热电材料的声子工程中，薄膜热电材料降低热导率的方法主要是制备薄膜超晶格结构，利用声子散射和超晶格层之间的声学失配来降低晶格热导率^[90]。其详细内容将在薄膜超晶格部分讨论。此外，对 Bi_2Te_3 基纳米薄膜进行一定的应变工程或者引入缺陷诱导结构无序也能够有效降低薄膜的晶格热导率^[91–93]。Yu 等^[91]发现，向 Bi_2Te_3 薄膜施加 6% 的拉伸应变， Bi_2Te_3 纳米薄膜热导率能够降低约 50%，这归因于拉伸应力下 Bi_2Te_3 纳米薄膜内原子间的非谐性增强，导致声子-声子散射增强，声子群速度降低，压缩应力则相反。与之相比，在 Bi_2Te_3 薄膜中增加晶格缺陷的情况则比较复杂，不同的界面缺陷对热导率的影响也不同。Lai 等^[93]通过分子动力学模拟研究得知， Bi_2Te_3 薄膜界面缺陷的高度和宽度增加均会导致晶体结构无序并导致声子散射，热导率降低。

2.1.2 一维结构 纳米线一维结构作为经典的纳米结构之一，其平均声速比块体材料要低 7% 左右。一维结构的声子散射主要由声子-声子散射和边界散射为主导，使得声子倾向于沿纳米线中心传输，晶格热导率显著降低。Rojo 等^[94]通过电位脉冲化学沉积在阳极氧化铝模板上生长具有相同组成和晶体

取向但直径大小不一的纳米线，发现 Bi_2Te_3 纳米线的直径越小，总热导率和晶格热导率越低，这主要源于声子的边界散射促使声子平均自由程减小。此外，制备的纳米线直径一般小于声子的平均自由程，但大于电子的平均自由程，使 Bi_2Te_3 纳米线的声子输运受到阻碍，但电子输运几乎不受影响，呈现类似“声子玻璃-电子晶体” (PGEC) 的特征^[95]。但因为低尺寸对低频声子抑制不完全，即使在极小的尺寸下，也不能完全阻止热传导。根据分子动力学研究发现，室温下 Bi_2Te_3 纳米线收敛长度无关热导率仅为 $0.89 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ ，比 Bi_2Te_3 铸块的热导率降低约 2 倍。此外，又因为强边界散射效应，一维结构的 Bi_2Te_3 基纳米线的热导率对温度的依赖性不强^[96]。与 Bi_2Te_3 纳米薄膜相比， Bi_2Te_3 纳米线的最大热导率和最小热导率比 Bi_2Te_3 纳米薄膜分别降低 23% 和 77%^[94]。凭借优异的热电输运性能和柔性，一维结构在穿戴式热电元器件的应用方面具备巨大竞争力^[97]。 Bi_2Te_3 基纳米线的制备工艺主要有电位脉冲化学沉积^[94, 96, 98]和液相法^[99–101]。液相法因为操作简单，生产效率高得到广泛应用。但现有液相法制备的纳米线基本都有数纳米厚的碳层，且对纳米结构形态的控制较差。然而液相法合成纳米线结构大多使用肼或羟胺等高危化学品作为还原剂，反应后的废液处理成本较为高昂。Yang 等^[99]设计了一种用无害的抗坏血酸作为还原剂来制备碲化物纳米线，并成功获得平均直径为 10.0~14.6 nm 的碲化物纳米结构。若能进一步精确控制纳米线织构， Bi_2Te_3 纳米线在商业上的应用有望得到推广。要想实现 zT 值的最大化，必须精确控制纳米线的织构和材料的化学计量比，这归因于 Bi_2Te_3 基合金的各向异性和热电性能对载流子浓度的强烈依赖性。而电位脉冲化学沉积法制备的纳米线能够将化学计量比的偏差控制在 6%~7%，可以使热导率降低至同体积块体材料热导率的 1/3^[102]。同时制备的纳米线具备较高的结晶度，有利于其电性能的提高，是生长高度织构 Bi_2Te_3 纳米线的有效方法^[96]。

除了 Bi_2Te_3 基纳米线外，同时具备低维形态和多孔结构的准一维 Bi_2Te_3 基纳米管也是阻碍声子输运并降低晶格热导率的有效优化手段。 Bi_2Te_3 基纳米管由于其中空的通道使材料晶界密度增加，对长波声子的散射增强，使得其具有较低的热导率^[103]。此外，纳米管壁的低维性质造成的声子阻塞效应，使 Bi_2Te_3 基纳米管的晶格热导率进一步降低^[104]。

2.1.3 异质纳米结构 随着 Bi_2Te_3 基纳米结构研

究的不断深入, 研究人员发现单一的低维化或者细化晶粒对 zT 值的提升已经达到瓶颈。因此, 人们开始将多种纳米结构组合形成异质纳米结构^[105–106]。不同纳米结构的相组合在一起产生的异质界面能够强烈散射由晶格失配和晶格振动导致的长波声子。此外, 不同纳米结构具备不同的功函数, 使相界面存在接触电势差, 导致低能载流子被散射, 产生能量过滤效应, Seebeck 系数明显增加, 实现了热电性能的协同优化^[107]。Hong 等^[106]就通过合理的结构设计, 以 Te 纳米管作为外延模板, 利用微波辅助溶剂热法将 Bi_2Te_3 纳米片有序地依附在 Te 纳米管上, 形成 Te/ Bi_2Te_3 异质纳米结构。与纯 Bi_2Te_3 纳米片相比, 有序排列的纳米板能够增强声子散射, 降低晶格热导率。同时因为 Te 和 Bi_2Te_3 之间的带隙差异导致 Te/ Bi_2Te_3 导带和价带之间存在能量偏移, 使双极热导率降低, 最终总热导率比无序的纯 Bi_2Te_3 组成的热电材料减小约 20%。

2.2 细化晶粒

在相同温度下, 30 nm 的 Bi_2Te_3 晶粒 zT 值最高能达到 0.92, 而 150 nm 的 Bi_2Te_3 晶粒最大 zT 值仅为 0.45, 相比之下晶粒细化后的热电性能明显提升。在 Bi_2Te_3 基热电材料中, 声子输运性能主要由非弹性声子-声子散射和界面散射主导, 随晶粒尺寸的减小, 界面体积比增大, 声子的界面散射增强^[108–109]。此外, 在小尺寸 Bi_2Te_3 晶粒制备过程中也会引入晶格缺陷, 缺陷散射使晶格热导率进一步降低。Chiritescu 等^[110]发现 $(\text{Bi}, \text{Sb})_2\text{Te}_3$ 纳米颗粒的晶粒尺寸在小于 10 nm 的极限状态下, 晶格热导率仅为 $0.3 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ 。Yu 等^[111]使用球磨结合热压烧结技术来制备纳米尺寸的 Bi_2Te_3 合金, 与区熔法制备的 Bi_2Te_3 相比, 晶粒细化后的 Bi_2Te_3 合金存在声子的晶界散射和点缺陷散射机制, 在 300 K 获得的晶格热导率仅为区熔样品的 40%, zT 值提高了 40%, 在 403 K 时达到 1.03。

2.3 引入特殊纳米结构

除了低维化和细化晶粒外, 在 Bi_2Te_3 基热电材料引入孪晶和纳米孔等特殊结构也是增加晶格缺陷降低热导率的有效方法^[92, 98, 112]。对 Bi_2Te_3 基块体材料而言, 从 Miyazaki 等^[48]对 $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_{36}$ 多孔材料的声子输运机制进行声子 Boltzman 输运和分子动力学模拟研究可知, 在 Bi_2Te_3 基块体材料引入纳米孔隙后, 孔隙对长波声子散射强度增加, 导致平均声子群速度降低, 声子平均自由程减小。若是纳米孔呈周期性有序排列, 则还会对材料的弹道声子产生强烈散射, 热导率会大幅降低。Qiu 等^[112]在 Bi_2Te_3

薄膜中引入了纳米孔, 在声子输运过程中, 除了同样具备声子-声子散射机制和边界散射机制使晶格热导率降低, 对声子强烈的孔散射还会减小热导率对温度的依赖性。之后 Fang 等^[92]在此基础上添加应力改变孔径大小后发现随着孔径增大, 热导率随之减小, 这主要归因于大孔径的多孔 Bi_2Te_3 较为脆弱, 增加应力会使孔隙附近的 Bi_2Te_3 晶格变形, 产生大量晶格畸变, 阻碍声子输运。但纳米孔隙的引入也会对载流子进行强散射, 使得多孔材料电导率有所降低。

3 Bi_2Te_3 基超晶格结构

超晶格作为一种人为设计制造的纳米结构, 对载流子输运表现出微弱阻挡而对声子输运表现为强散射, 被认为是能够实现“声子玻璃-电子晶体”热电材料标准的最佳候选者之一^[80]。Broide 等^[113]从理论上证明, 当量子阱宽度约 3 nm 时, 具有无限势的 Bi_2Te_3 超晶格 zT 值达到了 3, 而在不完全量子限域的结构中, 量子阱宽度为 2 nm 的 Bi_2Te_3 超晶格最大 zT 值也能达到 2.5。Venkatasubramania 等^[90]预测 p 型 $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$ 超晶格的 zT 值在 300 K 可以达到 2.4, 这是第一种 zT 值超过 2.0 的热电材料。超晶格结构之所以能够显著降低热导率原因主要有以下 3 个方面: 1) 超晶格强的声子边界散射缩短了声子平均自由程^[74]; 2) 量子限域效应导致声学声子色散曲线扁平化, 降低了垂直于超晶格原子层的声子群速度^[44, 114]; 3) 超晶格中存在低频声子类局域化行为(localization-like behavior)^[90, 115]。

3.1 薄膜超晶格结构

Bi_2Te_3 基超晶格结构主要出现在其薄膜热电材料中。在超晶格薄膜中, 由于量子阱结构的存在, 载流子被限制在平行于 Bi_2Te_3 层的二维平面移动, 不和界面发生散射, 而声子不局限于在二维平面移动, 可以从界面散射出薄膜, 进而拥有高的载流子迁移率和低晶格热导率^[116]。获得 Bi_2Te_3 薄膜的方法有很多, 其中适用于合成高质量超晶格结构的制备工艺主要有有机金属化学气相沉积(MOCVD)^[117–119]、MBE 法^[120–121]和机械剥离^[122–123]等。

MBE 生长的薄膜因具有更高的纯度和更好的化学计量比而备受关注^[124]。获得高质量超晶格的重点在于衬底的选择。MBE 的生长机制遵循 TLK 模型。在阶地边缘和 Bi_2Te_3 基合金界面之间会同时存在原子尺度的粗糙度和平坦区域, 不同衬底拥有不同粗糙度是超晶格热导率降低的主要原因之一^[80]。此

外, 由衬底和超晶格薄膜层之间失配导致的螺纹位错显著影响超晶格的微观结构和电-热输运性能。这种失配主要取决于选择的衬底, 不同衬底会产生不同位错量的超晶格。MBE 法在制备超晶格结构的过程中同样要求调控衬底温度, 既需要足够高的温度提供能量促使共蒸发元素中形成超晶格单晶, 又不能有过高的温度提供多余能量促使各元素在体系内扩散丧失超晶格结构, 形成多元化合物^[121]。

MOCVD 法是把反应物全部用有机金属化合物的气体分子形式以氢气作为携带气体送到反应室, 进行热分解反应形成目标化合物半导体, 它是如今沉积薄膜的主要技术之一。早在 1997 年, Venkatasubramanian 等^[125]就利用 MOCVD 法在 GaAs 衬底上制备 $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$ 超晶格, 因其周期性结构导致 U 散射过程所需的最小声子能量降低, 且随周期厚度减小持续降低。当 Sb_2Te_3 和 Bi_2Te_3 尺寸接近晶胞尺寸($\sim 30 \text{ \AA}$)时具有最小的热导率 $0.2 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ 。比 p 型(BiSb)Te 固溶体低 4 到 5 倍, 预估该薄膜样品可能在平行于超晶格界面方向上获得 2.0 的室温 zT 值。然而由于有机金属和氢化物前驱体热解所需要的温度较高, 会导致组成超晶格结构的 Bi 和 Sb 原子在内部产生层间扩散, 破坏超晶格结构; 同时加剧异质外延中不可逆的晶格失配问题^[126]。为此, 研究人员采用光诱导解离^[127]、源气体裂解^[128]和低温有机金属外延^[126]等方法来解决超晶格结构的高温解理。

无论是通过能带还是声子工程, 要充分发挥超晶格的低维约束效应, 都需要制造出具备少原子层厚度和高质量界面的准二维结构。这是化学气相沉积、电化学或者其他方法都无法满足的条件。MBE 法制备的超晶格薄膜虽然能够获得符合条件的厚度和界面, 但因为晶格失配等因素, 会产生晶格位错阻碍量子阱中载流子的量子限域效应, 无法使超晶格结构的 zT 值获得显著提升。受石墨烯机械剥离法的启发, Teweldebrhan^[122–123]等利用 Bi_2Te_3 晶体结构中的范德华间隙将 Bi_2Te_3 大块晶体机械解理成 1 nm 厚的 $\text{Te}^{(1)}\text{--Bi--Te}^{(2)}\text{--Bi--Te}^{(1)}$ 五元层薄膜。这种准二维薄膜能够对声学声子和载流子进行完全量子限制。但因为本身较低的热导率, 热量进入准二维薄膜后难以逸出, 容易发生局部熔化和氧化, 所以将多个五元层的 Bi_2Te_3 准二维晶体堆叠在一起形成堆叠超晶格。因其声子在粗糙界面的散射和量子限域效应导致堆叠超晶格结构的热导率和准二维晶体薄膜完全相当, 拥有 $0.1\sim 0.3 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ 的面外热导率和

$1.1 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ 的面内热导率, 与 Bi_2Te_3 基铸块相比显著下降。导致其 zT 值相比于 Bi_2Te_3 铸块提升 30%~40%。

3.2 块体超晶格结构

与薄膜超晶格结构能够依靠强边界散射效应降低晶格热导率不同, 块状超晶格结构则是依赖其复杂的晶体结构来减小 Brillouin 区体积, 促使声子模的截止频率减小。同时块体超晶格材料中热携带的声学声子和低频光学声子之间存在声光耦合效应, 使超晶格内部产生强的声子共振散射, 导致其本征热导率较低^[129–130]。此外, 化学键软化和晶格非谐导致的低声子群速度也是块体超晶格本征热导率较低的原因之一^[121]。 Bi_2Te_3 基超晶格铸块虽然在电-热输运性能方面与超晶格薄膜之间还有所差距, 但其制备工艺相比于薄膜超晶格的制备成本更低且制备周期更短, 在商业上的应用潜力更高。Zhu 等^[33]利用简单的粉末冶金法结合热压烧结工艺制备得到 $(\text{Bi})_m(\text{Bi}_2\text{Te}_3)_n$ ($m:n=3:9, 2:7$ 和 $1:5$) 天然块体超晶格, 样品在 423 K 的温度下获得 $0.21 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ 的超低晶格热导率。

4 纳米复合

将纳米颗粒引入热电材料中作为第二相形成具有微-纳米结构的复合材料是 Bi_2Te_3 基热电材料提升热电性能最主要的途径之一。在纳米复合工艺中, 分散到热电基体材料中的纳米颗粒不会进入基体晶格内部而是附着在基体晶粒表面(甚至嵌入晶粒中), 并且与基体形成新的异质界面。同时, 纳米颗粒的引入增加了晶界密度, 导致长波声子得到进一步散射。此外, 第二相的加入也增加了更多的散射中心, 包括位错、基体中的原位沉积物和点缺陷, 是增强多尺度声子散射的有效途径^[34, 131–134]。

4.1 复合金属元素或金属氧化物

近年来, 金属或金属氧化物纳米颗粒是制备 Bi_2Te_3 基纳米复合材料常用的纳米第二相。除了能够增强声子在晶界和其它晶格缺陷的散射强度降低热导率外, 这些纳米第二相和半导体主界面处的能带弯曲也会导致电子的能量依赖性散射, 增加 Seebeck 系数, 实现声子散射和量子限域的结合。此外, 导电性较好的金属纳米包含物还能提升基体材料的电导率。与 Bi_2Te_3 基基体相比, 适量的金属或金属氧化物纳米颗粒的引入可以显著优化基体的相关热电参数。表 1 列出了以金属或金属氧化物作为第二相合成 Bi_2Te_3 基纳米复合热电材料的制备工

艺和相关热电性能参数^[34, 87, 131, 135–138]。

4.2 复合磁性纳米材料

受 Zhao 等^[25, 139]将磁性纳米颗粒引入 Ba_{0.3}In_{0.3}Co₄Sb₁₂ 中制备磁性纳米复合热电材料的启发, 人们开始尝试将硬磁性或软磁性纳米颗粒与 Bi₂Te₃ 基热电材料复合, 期望通过磁性纳米粒子磁转变产生的热电磁耦合效应在抑制 Bi₂Te₃ 基金本征激发的同时提升其热电性能。在声子输运性能方面, 磁性纳米颗粒的引入导致界面和晶界密度的增加, 强烈散射低频声子。同时在温度高于居里温度后作为 Bi₂Te₃ 基金第二相的磁性纳米颗粒大都具备顺磁性特征^[25, 140–144], 甚至超顺磁特征, 超顺磁纳米颗粒造成的磁矩波动能强烈散射声子, 进一步降低晶格热导率^[25, 140–145]。与 Bi₂Te₃ 基基体相比, 适量的磁性纳米颗粒的引入可以显著优化基体的相关热电性能参数。表 2 列出了以磁性纳米粒子作为第二相合成 Bi₂Te₃ 基纳米复合热电材料的制备工艺和相关热电性能参数。

4.3 复合碳的同素异形体

碳的同素异形体如石墨、石墨烯量子点(GODs)

和纳米结构的碳大都具备高的电导率^[146–151], 与 Bi₂Te₃ 基热电材料复合后能构建载流子通道, 实现电导率和 Seebeck 系数的解耦, 优化材料的电输运性能^[145]。同时由于纳米夹杂物抑制基体晶粒生长以及夹杂物本身的纳米尺寸导致复合材料界面和晶界密度增加, 使低频声子的边界散射增强, 导致晶格热导率显著降低, 因此协同提升了 Bi₂Te₃ 基纳米复合热电材料的 zT 值。如表 3 是碳的同素异形体复合 Bi₂Te₃ 基材料的制备工艺和热电性能相关参数。

4.4 复合导电聚合物

导电聚合物因其非常低的热导率和较好的电输运性能而被选择与 Bi₂Te₃ 基金复合制备复合材料^[152–154]。Kim 等^[152–153]将聚吡咯与 Bi₂Te₃ 进行复合获得 Bi₂Te₃-聚吡咯块状复合材料。因为声子在 Bi₂Te₃ 和聚吡咯界面处强烈散射, 使含有 5.0% (质量分数) 聚吡咯的复合材料的晶格热导率比原始 Bi₂Te₃ 铸锭要低 40%~69%。不过, 导电聚合物本身不耐高温, 随温度升高, 导电聚合物会发生降解, 此时界面散射效果会减弱, 导致晶格热导率升高, 并伴随电输运性能降低。

表 1 Bi₂Te₃ 基金属纳米复合材料的制备工艺和热电性能

Table 1 Preparation process and thermoelectric properties of Bi₂Te₃-based metal nanocomposites

Sample	Preparation method	T/K	$\sigma \times 10^4 / (\text{S} \cdot \text{m}^{-1})$	$S / (\mu\text{V} \cdot \text{K}^{-1})$	$\kappa_L / (\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1})$	$\kappa / (\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1})$	zT
5 mol MgO/Bi _{0.5} Sb _{1.5} Te ₃ ^[34]	Melting+hot-pressing sintering	375	5.93	185	0.87	1.25	0.62
5% (in mole) VO ₂ /Bi _{0.5} Sb _{1.5} Te ₃ ^[34]	Melting+hot-pressing sintering	375	6.94	186	0.87	1.29	0.69
2% (in mole) Au-ND/Bi ₂ Te ₃ NT ^[87]	Solution phase reaction+SPS	480	8.46	-164	0.50	1.15	0.95
2% (in volume) Ag/Bi ₂ Te ₃ ^[131]	Hydrothermal method+SPS	475	5.35	-137	0.16	0.62	0.77
1.5% (in volume) Ag-NW/Bi ₂ Te ₃ ^[135]	Hydrothermal method+SPS	475	6.06	-136	0.29	0.75	0.71
5% (in volume) ZnO/Bi _{1.5} Sb _{0.5} Te ₃ ^[136]	Ball milling+SPS	337	4.67	242	0.30	0.71	1.30
5% (in volume) ZnO/Bi ₂ Te _{2.7} Se _{0.3} ^[136]	Ball milling+SPS	423	8.97	-161	0.30	1.20	0.82
1% (in volume) γ -Al ₂ O ₃ /Bi ₂ Se _{0.3} Te _{2.7} ^[137]	Melting+SPS	405	1.15	-155	0.43	1.13	0.99
Al ₂ O ₃ /Bi ₂ Se _{0.3} Te _{2.7} ^[138]	Polyol reduction process+SPS	300	2.50	-128	0.56	0.85	0.20

T is absolute temperature; σ is electrical conductivity; S is Seebeck coefficient; κ_L is lattice thermal conductivity; κ is thermal conductivity; zT is dimensionless figure of merit.

表 2 Bi₂Te₃ 基磁性纳米复合热电材料的制备工艺和热电性能

Table 2 Preparation method and thermoelectric properties of Bi₂Te₃-based magnetic nanocomposites

Sample	Preparation method	T/K	$\sigma \times 10^4 / (\text{S} \cdot \text{m}^{-1})$	$S / (\mu\text{V} \cdot \text{K}^{-1})$	$\kappa_L / (\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1})$	$\kappa / (\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1})$	zT
0.15% (in mass) Fe ₃ O ₄ /Bi _{0.5} Sb _{1.5} Te ₃ ^[140]	Hydrothermal method+SPS	340	6.23	251	0.56	0.89	1.50
1% (in volume) NiTe/Bi ₂ Te ₃ ^[141]	Solvothermal method+ball milling	368	16.58	-125		2.01	0.12
0.3% (in mass) Ni/Bi ₂ Te _{2.7} Se _{0.3} ^[142]	Solvothermal method+SPS	360	7.84	-207	0.66	1.10	1.10
0.4% (in mole) Ni/Bi ₂ Te _{2.7} Se _{0.3} ^[143]	Solvothermal and thermal decomposition+SPS	425	2.56	-165	0.25	0.45	0.66
0.2% (in mass) Bi ₂ Fe ₄ O ₉ /Bi _{0.4} Sb _{1.6} Te ₃ ^[144]	Hydrothermal method+SPS	393	7.99	205	0.68	1.20	1.10

表 3 碳的同素异形体复合 Bi_2Te_3 基纳米材料的制备工艺和热电性能Table 3 Preparation method and thermoelectric properties of Bi_2Te_3 -based nanomaterials composed of allotropy of carbon

Samples	Preparation method	T/K	$\sigma \times 10^4 / (\text{S} \cdot \text{m}^{-1})$	$S / (\mu\text{V} \cdot \text{K}^{-1})$	$\kappa_1 / (\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1})$	$\kappa' / (\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1})$	zT
1% (in mass) graphite/ Bi_2Te_3 ^[146]	Solid-state reaction+ball milling	315			0.77	0.81	
1.5% (in volume) GQDs/ Bi_2Te_3 ^[147]	Ball milling+hot-pressing sintering	494	7.57	-126	0.3136	1.08	0.55
MWCNT/ Bi_2Te_3 ^[148]	Hydrothermal method	333	5.75	-134	0.456	0.93	0.37
1% (in volume) $\text{Bi}_2\text{Te}_3/\text{CNT}/\text{PEDOT}$ ^[149]	Hydrothermal method+ball milling	327	9.12	-123	0.22	0.94	0.48
20 nm-GQDs-ND/ Bi_2Te_3 ^[150]	Solution phase reaction	425	3.85	-150	0.44	0.67	0.55
0.7% (in mass) CNT/ Bi_2Te_3 ^[151]	CVD+solution phase reaction	473	6.69	-128	0.13	0.61	0.85

5 掺杂改性

Bi_2Te_3 是由多个通过 van der Waals 力链接的五元层组成, 使得外部原子很容易在各层之间扩散, 再加上 Bi_2Te_3 作为 A_2B_3 类化合物可以形成无限固溶体, 导致 Bi_2Te_3 基热电材料在掺杂改性方面具备优势。 Bi_2Te_3 基合金的掺杂主要是对 Bi 位(或 Te 位)进行取代, 进而改变其空穴(或电子)浓度, 形成 p 型(或 n 型) Bi_2Te_3 基热电材料。选择合适的元素对 Bi_2Te_3 基热电材料进行掺杂能够有效对电和热输运性能进行解耦, 显著改善热电器件的转换效率。因其制备工艺简单, 掺杂元素选择范围广, 因而是提升 Bi_2Te_3 基热电材料 zT 值的重要方法。对 Bi_2Te_3 基热电材料进行掺杂改性导致晶格热导率降低的主要原因有以下 3 个方面: 1) 引入其他元素导致的杂质散射; 2) 晶粒尺寸减小导致的声子边界散射增强^[155–156]; 3) 晶格内部明显增加的点缺陷浓度、位错密度和晶

格应变导致的多尺度散射效应^[157–158]。除掺杂元素种类不同会对晶格热导率产生影响外, 合适的掺杂工艺也能有效降低材料的晶格热导率。尤其是机械球磨法, 随球磨时间增加, 粉末的晶粒尺寸减小, 声子在晶体表面的散射增强^[159]。在此基础上结合 SPS 烧结过程中某些杂质相(如 Bi_2TeO_5 杂相或原位析出的 Te 杂相等)会在高温环境和大等离子体电流下被升华, 产生均匀分布的孔隙, 从而制备出具有高孔隙率的 Bi_2Te_3 材料^[59, 160–161], 这些微纳米级的孔结构可以阻碍长波声子的输运, 显著降低材料的热导率。表 4 是近年来不同元素掺杂的 Bi_2Te_3 基热电材料的制备工艺、热导率和最优 zT 值。

除了对 Bi 位或 Te 位取代掺杂外, 还有层间间隙掺杂。掺杂原子进入 Bi_2Te_3 五元层之间的 van der Waals 间隙^[78, 169–170], Liu 等^[82]就是利用简单的溶剂热法制备出较低热导率($0.8 \sim 1.2 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ @300 K)的单晶 $\text{Cu}_x\text{Bi}_2\text{Te}_3$ 纳米板, 研究发现当 $x < 0.05$ 时, 掺

表 4 不同元素掺杂 Bi_2Te_3 基热电材料的制备方法、热导率、晶格热导率和 zT 值Table 4 Preparation method, lattice thermal conductivity and zT values of Bi_2Te_3 thermoelectric materials doped with different elements

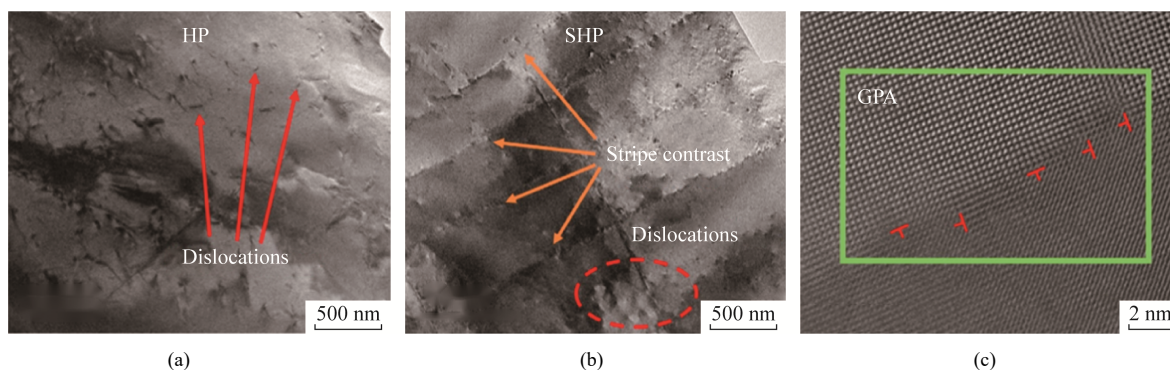
Sample	Preparation method	T/K	$\kappa_1 / (\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1})$	$\kappa' / (\text{W} \cdot \text{m}^{-1} \cdot \text{K}^{-1})$	zT
$\text{Bi}_{39}\text{Ge}_1\text{Te}_{60}$ ^[145]	Solid state melt-grown method	325	0.74	1.63	0.90
$\text{Ce}_{0.2}\text{Bi}_{1.8}\text{Te}_3$ ^[155]	Hydrothermal method+hot-pressing sintering	398		0.51	1.29
$\text{Bi}_{1.95}\text{Ge}_{0.05}\text{Te}_3$ ^[156]	Solid state melt-grown method	320	0.46	0.81	0.95
$\text{Bi}_2\text{Te}_{2.9}\text{I}_{0.1}$ ^[157]	Hydrothermal method+hot-pressing sintering	448	0.09	0.79	1.10
$\text{Bi}_2\text{Te}_2\text{S}$ ^[158]	Solid state reaction	413	0.53		1.20
$\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ ^[159]	Oxide reduction process+mechanical milling	373	0.52	1.05	1.05
$\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ ^[162]	Hydrothermal method+SPS	300	0.56	0.97	0.42
$\text{Bi}_2\text{Te}_{2.85}\text{Se}_{0.15}$ ^[163]	Gas atomization+SPS	623	0.93	1.31	0.76
$\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ ^[164]	Zone melting method	350	0.56	0.90	1.15
$\text{Cu}_{0.87}\text{Bi}_2\text{Te}_{2.69}$ ^[165]	Disproportionation redox reaction+SPS	415	0.30	0.87	0.67
$\text{Bi}_{1.9}\text{TM}_{0.1}\text{Te}_3$ ^[166]	Microwave-solvothermal method+SPS	432		0.70	0.70
$\text{Bi}_{1.9}\text{Lu}_{0.1}\text{Te}_3$ ^[166]	Microwave-solvothermal method+SPS	432		0.62	0.85
$\text{Bi}_{1.9}\text{Lu}_{0.1}\text{Te}_3$ ^[167]	Hydrothermal method+hot-pressing sintering	373		0.62	1.70
$\text{Mg}_{0.01}\text{Bi}_{1.99}\text{Te}_3$ ^[168]	Solid state reaction+SPS	350	1.01	1.59	0.80

入的 Cu 会首先嵌入 van der Waals 间隙, 不会对 Bi 位进行取代, 并在 $x=0.02$ 时取得最大 zT 值(0.33), 是未掺杂 Cu 元素的 Bi_2Te_3 粉末 zT 值的 3.3 倍。

6 引入位错阵列

在其它声子工程中, 掺杂改性能够优化载流子浓度并降低热导率。纳米改性增加的晶界密度以及纳米复合引入的第二相均可有效增强声子散射。但传统声子工程优化工艺多是增强对低频和低频声子的散射, 对中频声子散射强度较低。为此, 研究发

现在 Bi_2Te_3 基热电材料中引入位错阵列能够有效散射中频声子。因此, 结合掺杂、纳米改性及纳米复合可以实现声子的多尺度散射。 Bi_2Te_3 基热电材料中的位错阵列密度主要是通过合金化和改进烧结工艺等途径来增加^[18, 31, 55, 171]。Zhang 等^[31]通过简单的热压烧结在 $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ 热电材料中引入小角度晶界, 小角度晶界是由位错阵列组成(图 2a、图 2b 和图 2c), 对中频声子和载流子都有着强烈散射作用, 在提升 Seebeck 系数的同时显著降低晶格热导率。最终烧结后的 $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ 样品在室温获得 0.94 的高 zT 值。



Transmission electron microscope (TEM) images of $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ treated by (a) traditional hot pressing (HP) and (b) step-hot-pressing (SHP), (c) the high-angle annular dark field (HAADF) image of $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ treated by SHP.

图 2 分步热压工艺对 $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ 微观结构和晶格热导率的影响^[31]

Fig. 2 Effects on microstructure and lattice thermal conductivity of $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ by step-hot-pressing^[31]

7 总结与展望

本文综述了近年来通过一些声子工程方法优化 Bi_2Te_3 基材料热电性能的主要研究进展。通过纳米改性增加界面密度和减小声子群速度, 导致晶格热导率显著降低, 同时结合掺杂合金化和纳米复合在 Bi_2Te_3 基合金中引入多种散射中心, 增强声子的多尺度散射, 进一步降低晶格热导率。此外, 通过人为调控 Bi_2Te_3 基材料的原子层有序排列产生超晶格结构, 通过减小声子平均自由程、降低声子群速度和增加晶胞结构复杂性大幅度降低 Bi_2Te_3 基热电材料的热导率。在此基础上, 结合载流子工程和能带工程优化电输运性能, 实现电和热输运性能的协同调控, 最终使得 Bi_2Te_3 基合金的热电性能大幅提升。为热电器件的应用提供科学和技术支撑。然而, Bi_2Te_3 基热电材料的声子工程的研究仍存在一些需要进一步研究。1) 进一步筛选合适的衬底减小和 Bi_2Te_3 基合金原子层之间的失配是合成具有高质量界面和原子层厚度超晶格碲化铋薄膜的关键; 2) 进一步筛选合适的掺杂元素、纳米第二相实现声子

多重散射大幅降低声子平均自由程是再次提升 Bi_2Te_3 基材料热电性能的关键; 3) 进一步探索新工艺快速制备具有丰富的可显著增强多尺度声子晶粒结构的 Bi_2Te_3 基热电材料也尤为关键。

总之, 要进一步通过声子工程甚至载流子工程或能带工程改善 Bi_2Te_3 基材料的热电性能还有很多工作要做。尽管挑战无处不在, 但 Bi_2Te_3 基合金大规模的商业化仍吸引了众多研究人员加入热电材料的研究领域。同时随着各行业的联系越发紧密, 热电领域和其他学科的交叉研究也愈加频繁, 相信未来 Bi_2Te_3 基热电材料的研究和大规模应用必将持续快速增长。

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Phonon Engineering in Bi_2Te_3 -Based Thermoelectric Materials

LIU Zhiyuan^{1,2}, GUAN Xicheng¹, LI Zhou³, MA Ni⁴, MA Junjie¹, BA Qian¹, XIA Ailin¹, JIN Chuangui¹

(1. School of Materials Science and Engineering, Anhui University of Technology, Ma'anshan 243002, Anhui, China; 2. Key Laboratory of Green Fabrication and Surface Technology of Advanced Metal Materials, Ministry of Education, Anhui University of Technology, Ma'anshan 243002, Anhui, China; 3. School of Materials Science and Engineering, Anhui University, Hefei 230601, China; 4. School of Chemistry and Materials Science, University of Science and Technology of China, Hefei 230026, China)

Extended Abstract

Bi_2Te_3 based alloys have attracted considerable attention in low-temperature thermoelectric materials due to their superior electrical transport properties and low thermal conductivity. However, the conversion efficiency of thermoelectric power generation or refrigeration devices made of Bi_2Te_3 -based alloys is still low. It is thus crucial to further improve the thermoelectric figure of merit zT of Bi_2Te_3 based materials. There are some correlations between lattice thermal conductivity and electrical performance parameter. Reducing the lattice thermal conductivity by phonon engineering becomes an important method to increase zT without deteriorating the electrical performance. This review summarized the main research progress in recent years to optimize the thermoelectric properties of Bi_2Te_3 based materials by phonon engineering, such as nano-modification, superlattice structure, nanocomposing, doping and adding dislocation arrays. The effect of the optimization method on the specific heat capacity, phonon group velocity and phonon mean free path was discussed. The specific heat capacity, phonon group velocity or phonon mean free path of Bi_2Te_3 based materials can be significantly reduced by the optimization methods. As a result, the lattice thermal conductivity of Bi_2Te_3 based materials is significantly reduced, leading to a significant increase in the thermoelectric properties.

Nano-modification: The interface density is increased *via* low dimensionalization and grain refinement, resulting in an enhanced scattering of low-frequency phonons, reduced phonon mean free path and phonon group velocity, significantly reducing the lattice

thermal conductivity. Nowadays, the grain size and morphology of Bi_2Te_3 -based alloys can be precisely controlled by mechanical milling, MBE method, hydrothermal method, chemical vapour deposition and wet chemical method. Bi_2Te_3 nanostructures with a ultra-low grain size can be prepared. However, heat conduction cannot be completely prevented even at rather small sizes due to the incomplete suppression of low-frequency phonons. Therefore, it is difficult to improve zT by a single low-dimensionalisation and grain refinement method. The specific surface area can be increased either by combining the phases of different nanostructures to form a heterogeneous interface or by introducing special nanostructures such as twins and nanopores, which can strongly scatter the low-frequency phonons caused by lattice mismatch and lattice vibration, and further reduce the lattice thermal conductivity.

Bi_2Te_3 -based superlattice structure: Furthermore, in the microscopic and mesoscopic scales, the superlattice structure generated by artificially controlling the ordered arrangement of atomic layers of Bi_2Te_3 -based materials is considered as the optimum candidate material to achieve the ‘phonon glass-electron crystal’ thermoelectric material standard. Especially, the quantum well structure in the thin film superlattice produces an intense boundary scattering effect and a quantum confinement effect on phonons, resulting in a decrease in the mean free path and group velocity of phonons, greatly reducing the thermal conductivity of Bi_2Te_3 -based thermoelectric materials. The bulk superlattice structure of the Bi_2Te_3 -based alloy relies on its complex crystal structure and acousto-optic coupling effect, causing a low cut-off frequency of phonon mode and an intense phonon resonance scattering, and resulting in a low intrinsic thermal conductivity. In addition, the low phonon group velocity caused by chemical bond softening and lattice anharmonicity is also a reason for the low intrinsic thermal conductivity of the bulk superlattice structure of Bi_2Te_3 -based alloy.

Nanocomposites, doping modification and dislocation arrays: Nanocomposite and doping modification are the main approaches to improve the thermoelectric properties of Bi_2Te_3 -based materials. In the nanocomposite process, the nanoparticles dispersed in the thermoelectric material do not enter the matrix lattice, but attach onto the surface of the matrix grain, forming a heterogeneous interface with the matrix. Also, introducing nanoparticles increases the grain boundary density, resulting in a further scattering of low frequency phonons. Doping modification is achieved by doping elements entering the Bi_2Te_3 lattice, replacing Bi site (or Te site) or entering the van der Waals gap for interstitial doping. This process can introduce multiple scattering centers such as grain boundaries, point defects, *in-situ* precipitates and dislocations into Bi_2Te_3 -based alloy, enhancing a multi-scale scattering of phonons and effectively reducing the mean free path of phonons. Combined with the preparation process such as sintering, the dislocation array is increased, which leads to a higher scattering intensity of intermediate frequency phonons, further reducing the lattice thermal conductivity.

Summary and prospects The phonon specific heat capacity, phonon group velocity and mean free path of the Bi_2Te_3 -based alloy could be effectively controlled by phonon engineering including nano-modification, superlattice structure, nanocomposite, doping and introduction of the dislocation array to achieve a sufficiently low lattice thermal conductivity. The electrical transport properties were optimized by the carrier engineering and energy band engineering techniques, and the synergistic regulation of the electrical and thermal transport properties was realized. As a result, the thermoelectric properties of Bi_2Te_3 -based alloys were significantly improved. This provided a scientific and technical support for the application of thermoelectric devices. However, a lot of work remained in improving the thermoelectric properties of Bi_2Te_3 materials by phonon, carrier and energy band engineering. Nevertheless, the large-scale commercialization of Bi_2Te_3 -based alloys as thermoelectric materials still attracts much attention. Also, interdisciplinary research in thermoelectricity and other disciplines becomes popular. The future research and large-scale application of Bi_2Te_3 thermoelectric materials are expected.

Keywords bismuth telluride based thermoelectric materials; phonon engineering; lattice thermal conductivity; thermoelectric properties