



Sn_xSe_y : 一类具有发展潜力的新型热电材料

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摘要 热电材料是一种通过声子和载流子定向运输实现热能和电能相互转化的新型能源材料, 具有可靠性高、无传动组件等优势, 被广泛应用于航空航天及5G通讯等领域. 在寻找理想的热电材料过程中, 研究人员将目光转向了地壳中包含丰富元素的材料, 如锡硒化合物(Sn_xSe_y). 其中一个被广泛研究的化合物是硒化锡(SnSe), 其被认为是迄今为止最有前景的热电材料之一. 此外, 二硒化锡(SnSe_2)也是一种具有发展潜力的热电材料. 本文首先简要介绍了 SnSe 和 SnSe_2 的研究成果, 然后对 $\text{SnSe}/\text{SnSe}_2$ 复合材料以及新型 Sn_2Se_3 的热电性能进行了总结, 最后指出了 Sn_2Se_3 热电材料领域的一些研究挑战及发展前景.

关键词 热电材料, SnSe , SnSe_2 , Sn_2Se_3

煤炭、石油等传统化石燃料是全球生活生产的重要能源供给, 但是其储量有限. 由于传统化石能源有近60%的热量损耗, 因此开发和利用一种能进行废热回收的新型能源材料具有重要的现实意义^[1]. 近几十年来, 热电材料一直是备受关注的新能源材料, 因为其能通过热能与电能的相互转换实现温差发电和通电制冷, 并且其具有可模块化、无噪声、低损耗等特点^[2]. 第一代商用热电材料开发于20世纪50年代, 随着材料在更低维度和尺度方面的研究突破, 热电材料也得到快速发展^[3,4]. 热电器件能量转化效率主要由器件两端温差以及热电材料的无量纲性能优值(ZT)决定, $ZT=(S^2\sigma/\kappa)T$. ZT 值越高, 则其发电或者制冷的效率就越高. 定义 ZT 值的几个参数分别为材料的温度 T 、塞贝克系数 S 、热导率 κ 和电导率 σ , $S^2\sigma$ 称为功率因子. 高 ZT 值的热电材料需要同时拥有低导热和高导电性能. 通常来说, 只要降低热导率的同时提高塞贝克系数和电导率, 就能得到高的热电优值. 但是金属和陶瓷材料很难同时满足这两点, 因为金属材料的热导率普遍过高, 而陶瓷材

料的电性能过低. 热电半导体材料能够很好平衡导电和导热之间的关系, 因此具有更加优异的热电性能^[5,6]. 目前唯一商用的热电材料是 Bi_2Te_3 , 从近年来热电制冷材料研究取得的显著成果来看, 基于 Bi_2Te_3 化合物的材料体系仍是一类最具竞争力的热电材料. 但从目前材料研究的大趋势来看, 需要兼顾矿产资源储量和环境兼容性. Te 元素在地球上的丰度只有0.005 ppm, Bi_2Te_3 热电器件的大规模应用会导致原料成本的大幅攀升, 制约了热电制冷器件的推广应用^[7,8].

1 Sn_xSe_y 复合材料

锡和硒元素在地壳中含量丰富^[9], 而且 SnSe 一直是近10年来热电材料研究的热点. 锡和硒反应能够合成多种二元化合物, 如图1(a)所示^[10]. 在固溶 S 之后, 其化合物种类更是大幅增加, 如图1(b)所示^[11]. 在众多锡硒化合物中, SnSe 和 SnSe_2 的热电性能被研究得最为充分. SnSe 为本征 p 型半导体, 室温下空间群为 $Pnma$. 之前受限于多晶极大的电阻率, SnSe 一直以来不被认为是一

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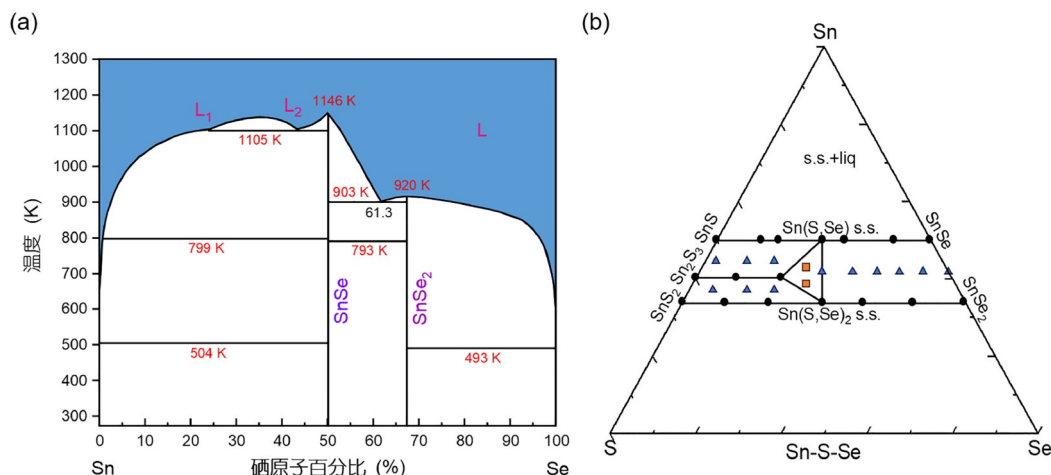


图1 (网络版彩色)Sn-S-Se之间的相组分关系。(a) Sn-Se的二元相图^[10]; (b) Sn-S-Se的三元相图^[11]

Figure 1 (Color online) The phase constituent relationship between Sn-S-Se. (a) Binary phase diagram of Sn-Se^[10]; (b) ternary phase diagram of Sn-S-Se^[11]

种高性能的热电材料^[12]。但2014年, Zhao等人^[13]发现, 其面内沿 b 轴方向(SnSe平面内垂直方向为 a 轴)具备优异的低热导性能以及高载流子迁移率, ZT 值在923 K时高达2.6。后续Qin等人^[14]通过对Sn位进行固溶Sr的合金化处理有效改变了p型SnSe的晶体结构, 促进了多带输运, 提高了晶体对称性和载流子迁移率, 最终使得SnSe单臂器件在温差300 K的情况下发电效率达到9%。另外, Chang等人^[15]通过阴离子位卤素掺杂实现了高热电优值n型SnSe, 通过卤素Br的掺杂制备了层间电荷密度高度重叠的n型SnSe晶体材料, 除连续相变增加对称性之外, 原先收敛的导带在高温发散(高温下两导带能量差增大, 导带退简并, 使得迁移率提高, 从而在高温下获得高热电性能), 从而得到了材料的高性能。

虽然SnSe₂和SnSe由相同的元素组成, 但是SnSe₂为本征n型半导体, 室温下空间群为 $P-3m1$ 。相对于SnSe, SnSe₂的热电性能研究较少。Shu等人^[16]通过6 at%的卤素Cl掺杂使n型SnSe₂多晶的最大 ZT 值在773 K下达到了0.56。Li等人^[17]通过插层Cu同样提高了SnSe₂的热电性能。Cu的引入一方面可以提供额外的电子, 提升层间与层内的电荷传输, 另一方面能够减轻对载流子的散射作用, 最终最大 ZT 值在773 K下达到了0.8。

由于锡硒化合物之间具有相似的层状结构, 因此SnSe与SnSe₂可以形成复合材料, 并且也被众多研究人员关注^[18-20]。Li等人^[21]通过SnSe₂和少量SnSe复合并掺杂Cl, SnSe和SnSe₂的两相散射可以大幅度降低SnSe₂的热导率, Cl掺杂优化了载流子浓度, 提升了其原先较差的电传输性能, 最终在773 K时, SnSe₂-2 at%SnSe-5 at%

Cl在平行于放电等离子烧结压力方向(SPS-211Lx, 日本富士电波)的 ZT 值达到了0.6。Gowthamaraju等人^[22]按不同比例制备了SnSe/SnSe₂复合材料并研究了其热电性能。SnSe/SnSe₂复合材料中载流子浓度和迁移率如图2(a)所示^[22]。随着SnSe₂掺杂量的提升, 载流子浓度呈先上升后下降的趋势, 并在掺杂23 at%左右的SnSe₂时达到峰值。迁移率的变化与载流子浓度的变化呈相反趋势, 随着掺杂量的提升先降低后上升, 在23 at% SnSe₂时达到最小值。如图2(b)所示^[22]为其复合材料的总热导率随温度的变化, 因为SnSe极强的非谐振效应, 在室温下掺杂11 at%左右的SnSe₂时总热导率约为 $0.8 \text{ W m}^{-1} \text{ K}^{-1}$, 与其他多晶p型SnSe相当。Sassi等人^[23]发现其在823 K时获得最大 ZT 值为0.5, 室温下总热导率约为 $0.6 \text{ W m}^{-1} \text{ K}^{-1}$ 。Gowthamaraju等人^[24]通过Sn位掺杂Cu, 发现最大载流子浓度超过 10^{18} cm^{-3} , 室温下总热导率约为 $0.5 \text{ W m}^{-1} \text{ K}^{-1}$ 。在0~300 K的温度区间内, 复合11 at%SnSe₂的SnSe的总热导率低于SnSe, 这归因于两相复合引起的第二相散射。但随着SnSe₂复合量的进一步提升, 总热导率显著提升。这是因为SnSe₂具有更高的热导率, 当复合的SnSe₂超过一定范围时, 高热导基体的复合效应超过了两相的声子散射效应。综合考虑SnSe₂对于导电和导热性能的影响, 掺杂11 at% SnSe₂是最优复合成分。

2 Sn₂Se₃热电性能

Sn₂Se₃从成分上来看是SnSe和SnSe₂按照1:1的比例混合而成的。有些研究指出Sn₂Se₃相是SnSe和SnSe₂

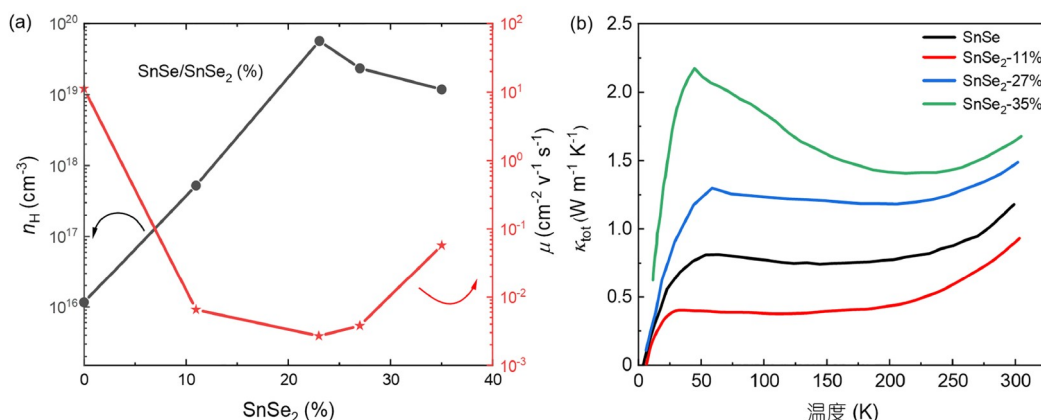


图2 (网络版彩色) SnSe₂的掺杂量提升对复合材料热电性能的影响. (a) SnSe/SnSe₂复合材料载流子浓度和迁移率随SnSe₂ (%)复合量的变化^[22], (b) SnSe/SnSe₂复合材料的总热导率随温度的变化^[22]
 Figure 2 (Color online) The increase in SnSe₂ doping levels affects the thermoelectric performance of composite materials. (a) Variation of carrier concentration and mobility for SnSe/SnSe₂ composites^[22]; (b) total thermal conductivity of SnSe/SnSe₂ composites^[22]

的两相叠加^[25~27], 并利用密度泛函理论进行了第一性原理电子结构计算^[28~30]. Sen等人^[31]对1D-Sn₂Se₃和3D-Sn₂Se₃的电子、输运、热学性质进行了计算模拟, 与Sn₂S₃进行了对比^[32,33].

利用Vesta程序模拟出的 $Pnma$ 相Sn₂Se₃和SnSe与 $P-3m1$ 相SnSe₂的优化模型如图3(a)所示^[31,34,35], 其中灰色球体为Sn, 绿色球体为Se. 由模型可分析其对应的XRD数据, 将其与SnSe和SnSe₂的标准卡片进行对比, 发现Sn₂Se₃部分峰与SnSe和SnSe₂标准卡片重合, 但仍有部分强峰并没有与SnSe和SnSe₂一一对应, 如图3(b)所示^[31,34~36]. 这些结果表明Sn₂Se₃是一种不同于两相混合的新相. 图3(c)为Sn₂Se₃的电子能带结构示意图^[31]. 不同于opt-PBE泛函计算结果的0.22 eV, 通过HSE06+D3泛函计算得出的间接带隙为0.64 eV, 小于SnSe的0.9 eV^[11]和SnSe₂的1.1 eV^[21]间接带隙, 这同样证明了Sn₂Se₃是一种全新的化合物. Lee等人^[32]通过模拟计算出Sn₂S₃的间接带隙为1.09 eV, David等人^[33]模拟计算出Sn₂S₃的间接带隙为0.97 eV.

通过比较新的物相, 对Sn和Se原子的形成焓可以评估Sn-Se不同相下的热力学稳定性^[26,37]. 图4(a)为Sn_xSe_y相的相对形成焓^[26]. 以SnSe和SnSe₂作为参考的基态结构, 基于计算结构所得Sn₂Se₃相位于SnSe和SnSe₂的连线上方, 但相对能量也仅比 $Pnma$ 相的SnSe和 $P-3m1$ 相的SnSe₂组成的相分离基态高9 meV/atom^[26]. 这意味着它在0 K温度下处于热力学不稳定状态, 但仍有可能以非稳态的形式存在, 例如高压或存在晶格应力的情况下. 对Sn_xSe_y相的相对形成焓进行分析

发现, $Pnma$ 相的Sn₂S₃同样位于折线的上方, 如图4(b)所示^[31], 与 $Pnma$ 相的Sn₂Se₃类似.

Sen等人^[31]利用第一性原理对Sn₂Se₃在300 K时3D和1D状态下的电子热导率、电导率、塞贝克系数和 ZT 值与化学势(μ)的依赖关系进行了计算评估. $\mu > 0$, 化学势为正, 体现n型导电性; $\mu < 0$, 化学势为负, 体现p型导电性. 塞贝克系数在化学势绝对值趋近于0时呈现极值, 随着载流子浓度不断变大总体呈下降的趋势, 如图4(c)所示^[31]. Sn₂Se₃的电导率随着p型载流子浓度的增大而升高. 而n型半导体的电运输性能不如p型半导体. Sn₂Se₃的热导率与电导率的变化趋势相似, 都呈现先增后减的趋势, 如图4(d), (e)所示^[31]. 最终, 3D-Sn₂Se₃的计算最大 ZT 值为0.9, 而1D-Sn₂Se₃的计算最大 ZT 值为1.0, 如图4(f)所示^[31].

3 Sn₂Se₃中的相变

Zhu等人^[38~40]发现Sn₂Se₃能够实现晶态-非晶态相变, 而且能量转变阈值较低, 其非晶态和导电晶相间体现极高的电阻对比度. 他们通过实验和分子动力学模拟研究了Ti掺杂对Sn₂Se₃薄膜相变性质的影响^[41]. Ti掺杂的Sn₂Se₃薄膜电阻与温度关系如图5(a)所示^[41]. 样品在加热过程中出现电阻的急剧下降现象称为晶化, 可以看出, 当温度即将达到晶化所需的温度时, 电阻会发生急剧下降. Ti掺杂后材料的晶态和非晶态下的电阻均高于未掺杂的Sn₂Se₃薄膜, 并且晶化电阻为10⁹ Ω时的转变温度同样随着Ti元素的掺杂提升, 如图5(b)所示^[41]. Hu等人^[42]选取了Al元素作为Sn₂Se₃的

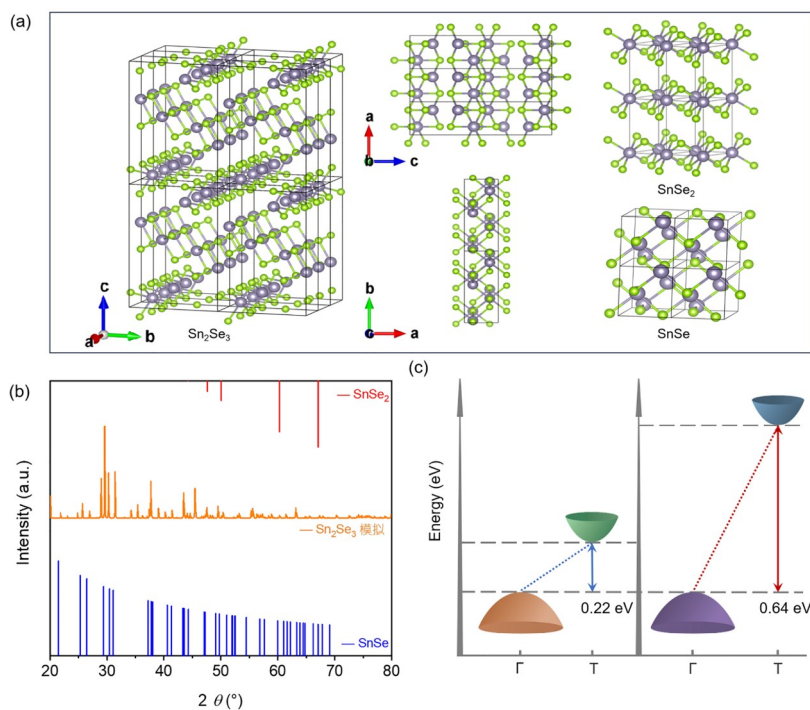


图 3 (网络版彩色) Sn-Se 基的球棍模型、对应的 XRD 数据以及 Sn_2Se_3 的带隙数据. (a) Sn_2Se_3 、 SnSe 、 SnSe_2 的晶体结构^[31,34,35], (b) 根据 Sn_2Se_3 晶体结构得到的 XRD 数据、 SnSe 和 SnSe_2 的 XRD 标准卡片^[31,34-36], (c) 通过第一性原理计算得到的 Sn_2Se_3 间接带隙^[31]

Figure 3 (Color online) Ball-and-stick model of the Sn-Se based compound, its corresponding XRD data, and the band gap data of Sn_2Se_3 . (a) Ball-and-stick models of Sn_2Se_3 , SnSe , and SnSe_2 ^[31,34,35], (b) XRD data obtained after simulating the ball-and-stick model for Sn_2Se_3 , SnSe and SnSe_2 ^[31,34-36], (c) indirect band gap of Sn_2Se_3 calculated by DFT calculations^[31]

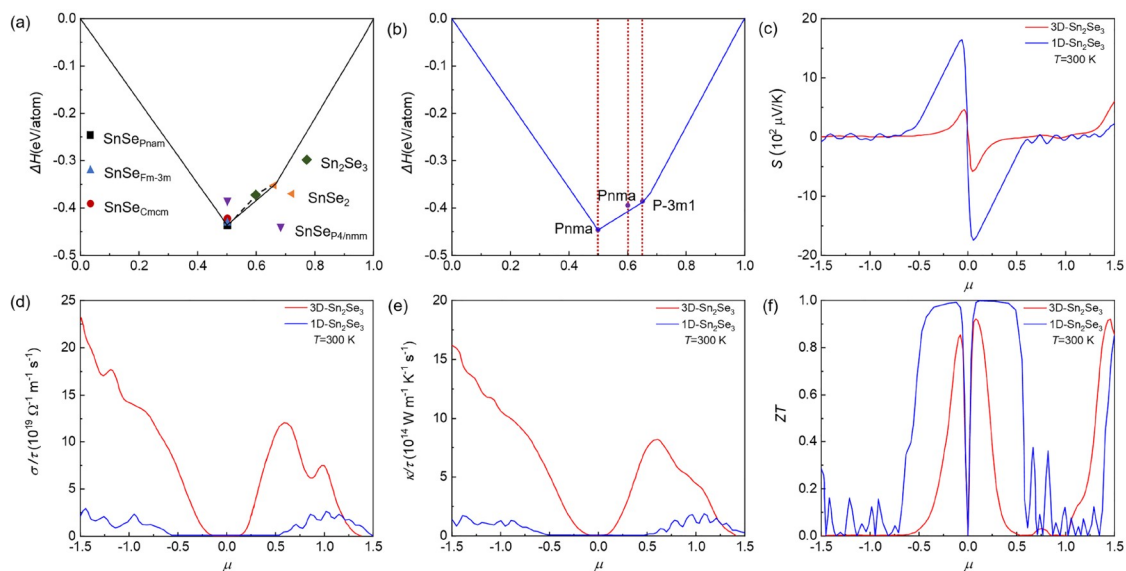


图 4 (网络版彩色) Sn-S-Se 间的相对形成焓以及 Sn_2Se_3 的热电性能. (a) Sn-Se 的相对形成焓^[26], (b) Sn-S 的相对形成焓^[31], (c) 300 K 时 1D- Sn_2Se_3 和 3D- Sn_2Se_3 的塞贝克系数与化学势的变化关系^[31], (d) 300 K 时 1D- Sn_2Se_3 和 3D- Sn_2Se_3 的电导率与化学势的变化关系^[31], (e) 300 K 时 1D- Sn_2Se_3 和 3D- Sn_2Se_3 的热导率与化学势的变化关系^[31], (f) 300 K 时 1D- Sn_2Se_3 和 3D- Sn_2Se_3 的 ZT 值与化学势的变化关系^[31]

Figure 4 (Color online) The relative formation enthalpy of the Sn-S-Se system and the thermoelectric performance of Sn_2Se_3 . (a) Relative formation enthalpy of Sn-Se^[26], (b) relative formation enthalpy of Sn-S^[31], (c) Seebeck coefficient of 1D- Sn_2Se_3 and 3D- Sn_2Se_3 as a function of μ at 300 K^[31], (d) electrical conductivity of 1D- Sn_2Se_3 and 3D- Sn_2Se_3 as a function of μ at 300 K^[31], (e) thermal conductivity of 1D- Sn_2Se_3 and 3D- Sn_2Se_3 as a function of μ at 300 K^[31], (f) ZT value of 1D- Sn_2Se_3 and 3D- Sn_2Se_3 as a function of μ at 300 K^[31]

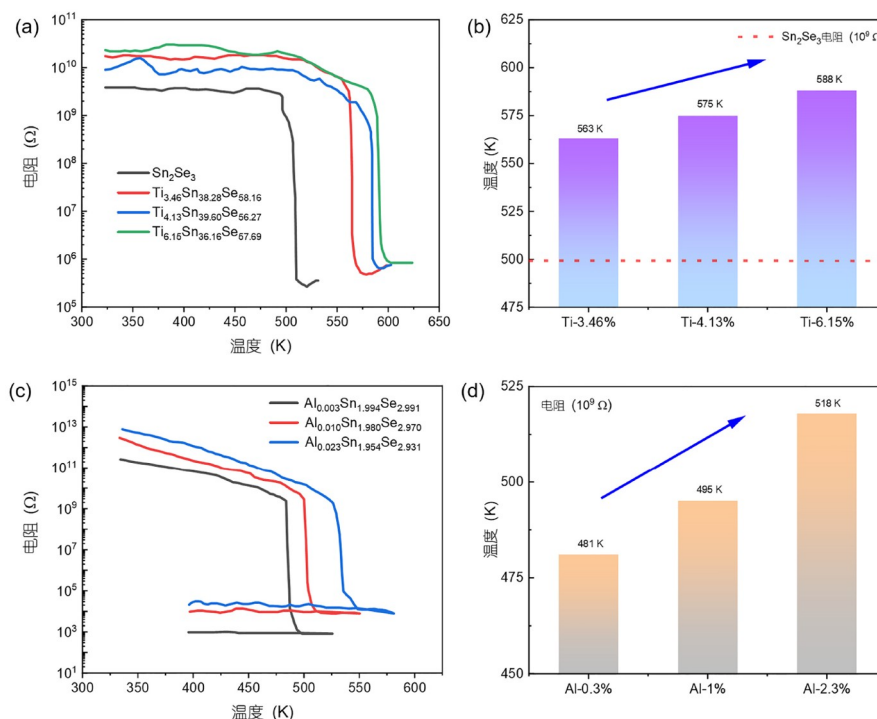


图5 (网络版彩色) 掺杂对 Sn_2Se_3 热稳定性能的影响. (a) Ti掺杂后 Sn_2Se_3 电阻随温度变化图^[41]; (b) Ti掺杂对 Sn_2Se_3 晶化反应的影响对比^[41]; (c) Al掺杂后 Sn_2Se_3 电阻随温度变化图^[42]; (d) Al掺杂对 Sn_2Se_3 晶化反应的影响对比^[42]

Figure 5 (Color online) The influence of doping on the thermal stability of Sn_2Se_3 . (a) Electrical resistance of Sn_2Se_3 changes with temperature after Ti doping^[41]; (b) crystallization temperature comparison of Sn_2Se_3 after Ti doping^[41]; (c) electrical resistance of Sn_2Se_3 changes with temperature after Al doping^[42]; (d) crystallization temperature comparison of Sn_2Se_3 after Al doping^[42]

掺杂元素, 采用射频溅射法成功制备了 $\text{Al}_x(\text{Sn}_2\text{Se}_3)_{1-x}$ 薄膜, $\text{Al}_x(\text{Sn}_2\text{Se}_3)_{1-x}$ ($x=0.003, 0.010, 0.023$)薄膜在10 K/min升温速率下的电阻随温度的变化关系如图5(c)所示^[42]. 随着Al含量增多, 在相同退火温度的情况下, 其非晶态和晶态的电阻不断升高, 并且Al元素在一定程度上提高了晶化所需要的温度, 在 $10^9 \Omega$ 左右的晶化电阻处, 温度同样随着Al元素的掺杂而提升, 如图5(d)所示^[42].

4 总结

Sn_xSe_y 是一类低成本且具有高性能潜力的热电材料.

本文总结了常见的 SnSe 、 SnSe_2 、 SnSe/SnSe_2 复合材料以及 Sn_2Se_3 的热电性能研究. 一方面, SnSe 与 SnSe_2 复合能够优化基体的电输运和热输运性能, 从而实现热电性能优化. 另一方面, 第一性原理计算表明 Sn_2Se_3 有可能以不同于 SnSe 和 SnSe_2 的新的物相存在, 并且其近室温ZT值有望达到1.0. 此外, 相关的实验结果表明通过Al、Ti等元素的引入能够提升 Sn_2Se_3 晶态-非晶态转变的温度. 但值得注意的是, 目前 Sn_2Se_3 材料在制备与合成中仍存在一些问题, 例如不易合成、低温退火后易分相、稳定性一般等问题, 相关问题在未来 Sn_2Se_3 的相关研究中需要重点关注.

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Summary for “ Sn_xSe_y : 一类具有发展潜力的新型热电材料”

Sn_xSe_y : New promising thermoelectric materials

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Traditional fossil fuels, which are finite and have high thermal losses, necessitate the development of new energy materials for waste heat recovery. As the world continues to grapple with energy shortages and environmental concerns, finding sustainable and efficient energy solutions has become a priority. Among these solutions, thermoelectric materials have gained significant attention over the past few decades due to their unique properties. These materials stand out because of their modularity and noiseless operation, making them promising candidates for power generation and refrigeration. The efficiency of thermoelectric materials is primarily determined by the dimensionless figure of merit (ZT), which is a measure of a material's ability to convert heat into electricity. ZT depends on three key parameters: The Seebeck coefficient, electrical conductivity, and thermal conductivity. Achieving high ZT values is essential for the practical application of thermoelectric materials. High ZT values require materials that exhibit both low thermal conductivity and high electrical conductivity. However, this is a challenging issue to achieve. Metals, which typically have high electrical conductivity, also have high thermal conductivity, making them less efficient for thermoelectric applications. On the other hand, ceramics, which have low thermal conductivity, generally suffer from poor electrical performance. In the search for ideal thermoelectric materials, researchers have turned their attention to elements that are abundant in the Earth's crust, such as tin (Sn) and selenium (Se). These elements not only are plentiful but also exhibit properties that are conducive to thermoelectric applications. One compound that has been extensively studied is tin selenide (SnSe). SnSe has garnered interest due to its remarkable thermoelectric performance, particularly in its p-type semiconductor form. It has been reported to have a high ZT value of 2.6 at 923 K, making it one of the most promising thermoelectric materials discovered to date. In addition to SnSe , tin diselenide (SnSe_2) is an n-type semiconductor that has shown potential for thermoelectric applications. Recent research indicates that SnSe_2 has achieved ZT values of up to 0.8. Moreover, the combination of SnSe and SnSe_2 in the form of SnSe-SnSe_2 composites has been explored as a way to optimize thermoelectric performance. These composites leverage the advantages of both materials, achieving lower thermal conductivity and enhanced electrical transport properties. Another compound that has emerged as a potential thermoelectric material is Sn_2Se_3 , which consists of a 1:1 ratio of SnSe and SnSe_2 . Both computational and experimental studies suggest that Sn_2Se_3 is a unique phase distinct from a simple mixture of SnSe and SnSe_2 . The band structure and thermoelectric properties of Sn_2Se_3 have been analyzed, revealing potential ZT values of around 1.0 for both three-dimensional (3D) and one-dimensional (1D) forms. These findings indicate that Sn_2Se_3 could be a valuable addition to the family of thermoelectric materials. Furthermore, researchers investigated the effects of doping Sn_2Se_3 with elements such as titanium (Ti) and aluminum (Al) to enhance its properties. Doping can improve the stability and electrical resistance of Sn_2Se_3 , making it more suitable for practical applications. Relative research has shown that Ti and Al doping can enhance the phase change properties of Sn_2Se_3 , potentially leading to higher performance and greater stability. Despite the significant progress made in the development of Sn_xSe_y compounds for thermoelectric applications, several challenges remain. One of the primary challenges is the synthesis of these materials with consistent properties. Ensuring the stability of the materials is also crucial. Future research should focus on addressing these challenges to unlock the full potential of Sn_2Se_3 and other Sn_xSe_y compounds as low-cost, high-performance thermoelectric materials.

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