

Dy 和 Nb 双掺杂优化 CaTiO_3 材料热电性能

蒋全伟, 田 震, 李建波, 史晓伟, 康慧君, 王同敏

(大连理工大学材料科学与工程学院, 辽宁省凝固控制与数字化制备技术重点实验室, 辽宁 大连 116024)

摘 要: CaTiO_3 热电材料因具有环境友好、良好的热稳定性和成本低等优点而受到广泛关注和研究。本征 CaTiO_3 具有大的能带带隙, 表现出不良的载流子输运性能。通过采用固相烧结结合热压烧结工艺制备了 n 型 Dy 和 Nb 双掺杂 CaTiO_3 基热电材料 $\text{Ca}_{1-x}\text{Dy}_x\text{Ti}_{0.95}\text{Nb}_{0.05}\text{O}_3$ ($x=0\sim0.15$), 并对样品的组成、微观形貌、热电性能进行了表征与分析。Dy 和 Nb 掺杂不仅可以显著增加载流子浓度, 提高电输运性能, 同时由于引入大的质量场和应力场波动, 显著散射高频声子, 体系的晶格热导率大幅度降低。由于电性能和热性能的协同优化, 在 1073 K 时, $\text{Ca}_{0.85}\text{Dy}_{0.15}\text{Ti}_{0.95}\text{Nb}_{0.05}\text{O}_3$ 获得最大 zT 值约 0.29, 表明 CaTiO_3 氧化物热电材料具有很大的应用潜力。

关键词: 钛酸钙热电材料; 电导率; 晶格热导率; 热电优值

中图分类号: TB34 文献标志码: A 文章编号: 0454-5648(2025)04-0742-06

网络出版时间: 2025-02-18



热电材料可以实现热能与电能直接相互转化, 在应对全球能源危机中扮演着关键角色^[1-2]。热电器件的转换效率通常用材料的无量纲参数热电优值 zT 决定。理想的热电材料应具有大的 Seebeck 系数以产生大的温差电动势, 应具有高的电导率减少材料发热导致的内部损耗, 并且热导率尽可能低以保持大的温差^[3-4]。但是由于 Seebeck 系数、电导率和电子热导率之间相互耦合制约, 难以单独依靠提升某个参数来综合提高热电性能^[5-6]。目前, 主要通过能带工程和声子工程来综合提高电性能和热性能。能带工程通过改变材料的能带结构, 影响电子或空穴的运动, 从而改变材料的电输运性能, 主要包括能带锐化^[7], 能带简并^[8-9]和共振能级^[10]等; 声子工程通过在材料内部构建多尺度散射中心以降低声子平均自由程来降低晶格热导率, 如共格纳米析出相^[11-12]、共振化学键^[13-14]以及位错^[15-16]等。通过不断的研究和探索, 热电材料的性能得到了显著提升, 例如 IV-VI 族化合物 SnTe 的最大热电优值在 773 K 达到了 1.9^[17], GeTe 的最大热电优值已经超过 2.0^[18-19]。然而, 由于热稳定性差、化学稳定性不

佳以及成本高昂等因素, 大大限制了这些材料的广泛工业化应用。

CaTiO_3 热电材料因其出色的热稳定性和化学稳定性, 在高温和恶劣环境下仍能维持较大的温度梯度, 具有高的发电效率或制冷能力, 因此受到广泛的关注和研究。由于具有大的能带带隙($\sim 2.55\text{ eV}$)^[20], 虽然可以显著抑制高温下材料的双极热扩散效应, 但是大的能带带隙使得电子的跃迁尤为困难, 因此通常认为本征 CaTiO_3 是一种绝缘体材料, 电输运性能差, 使 CaTiO_3 的热电性能调控尤为困难。Li 等^[21]通过 La 掺杂和引入氧空位使 CaTiO_3 热电性能从无到有。Li 等^[13]通过 Nb 掺杂在材料内部构建了均匀的异质结构, 晶格导热系数显著降低。Li 等^[22]发现 Nb 第二相可以在不牺牲电输运性质的情况下增强声子散射。由于 CaTiO_3 是由高硬度键组成的简单晶体, 实现有效掺杂较为困难。目前对 CaTiO_3 热电材料掺杂的研究主要集中在单元素掺杂上, 而利用多元掺杂效应协同调控热电性能的工作鲜有报道。本工作的切入点试图通过 Dy 和 Nb 的双掺杂协同调控 CaTiO_3 基材料的电性能和热性能并探究其内在机理。

收稿日期: 2024-10-07。 修订日期: 2024-10-28。

基金项目: 国家自然科学基金(52271025, 51927801)。

第一作者: 蒋全伟(1996—), 男, 博士研究生。

通信作者: 康慧君(1982—), 男, 博士, 教授。

Received date: 2024-10-07. Revised date: 2024-10-28.

First author: JIANG Quanwei (1996—), male, Doctoral candidate.

E-mail: jqw@mail.dlut.edu.cn

Correspondent author: KANG Huijun (1982—), male, Ph.D., Professor.

E-mail: kanghuijun@dlut.edu.cn

采用 $\text{CaTi}_{0.95}\text{Nb}_{0.05}\text{O}_3$ 为基体, 在 Ca 位掺杂不同含量的 Dy, 在调控载流子浓度的同时, 引入大的应力与质量场波动, 降低晶格热导率, 提高 CaTiO_3 基材料热电性能。

1 实验

以 CaCO_3 , Nb_2O_5 , Dy_2O_3 和 TiO_2 粉体为原料, 采用固相反应法和热压烧结合成 $\text{Ca}_{1-x}\text{Dy}_x\text{Ti}_{0.95}\text{Nb}_{0.05}\text{O}_3$ ($x=0\sim0.15$) 块体陶瓷。利用行星磨机将称量的粉体混合 12 h, 然后烘干、冷压成型, 在 1623 K, 保温 8 h 进行预烧。将预烧后的样品经过二次球磨 6 h, 将干燥粉末冷压成型。然后将成型样品放入直径为 13 mm 的石墨模具中进行热压烧结, 在 1573 K 保温 1.5 h, 得到厚度 2 mm 左右的致密圆片样品。

使用荷兰 PANalytical 公司生产的 EMPYREAN 型 X 射线衍射仪(XRD)对块体样品进行物相分析。样品的元素分布采用电子探针 X 射线微区分析仪(EPMA, 日本电子株式会社 JXA-8530F 型)进行分析。利用德国 Linseis 公司 LSR-3 型电性能综合测试系统同步测量样品的变温 Seebeck 系数和电阻率。测试所采用的样品均为长条状, 尺寸约为 $11.0\text{ mm} \times 2.0\text{ mm} \times 2.5\text{ mm}$ 。使用 Hall 测试系统(美国 Lake Shore 公司的 8400 型)测试体系的载流子浓度和 Hall 迁移率。使用激

光导热仪(德国 Netzsch 公司的 LFA-457 型)获得样品的导热系数, 使用 Dulong-Petit 律计算块体样品的比热容。

2 结果与讨论

图 1a 为 $\text{Ca}_{1-x}\text{Dy}_x\text{Ti}_{0.95}\text{Nb}_{0.05}\text{O}_3$ ($x=0\sim0.15$) 的 XRD 谱。合成样品的衍射峰与标准谱(JCPDS 81-0562)一致, 为正交结构, 空间群为 $Pnma$ 。如图 1a 所示, 随着掺杂浓度的增加, 样品的主峰整体逐渐向左偏移。由 Bragg 公式可知:

$$n_0\lambda = 2d \sin \theta \quad (1)$$

式中: θ 为入射线(或反射线)与晶面间的夹角, 称为掠射角或 Bragg 角, 单位为 $^\circ$; λ 为入射线的波长, 单位为 $\text{\AA}$; n_0 为任意正整数, 称为反射级数; d 为平行原子平面的间距, 单位为 $\text{\AA}$ 。晶面间距 d 与 θ 角成反比, θ 角向小角度方向偏移表明体系晶面间距增加。这主要是由于 Dy^{3+} 的离子半径($1.03\text{ \AA}$)大于 Ca^{2+} 的离子半径($0.99\text{ \AA}$), Dy^{3+} 的掺入会导致晶格膨胀, 使 XRD 衍射峰位向左发生偏移。图 1b 为正交结构型钛酸钙晶体结构示意图, 每个钛离子与 6 个氧离子呈八面体排列, 钙离子占据间隙位置^[23]。 Dy^{3+} 和 Nb^{5+} 分别随机占据基体中的 Ca^{2+} 位置和 Ti^{4+} 位置, 在引起晶格膨胀的同时, 引入施主杂质能级, 使 CaTiO_3 从绝缘性的宽带隙半导体转变为具有良好导电性的热电半导体材料。

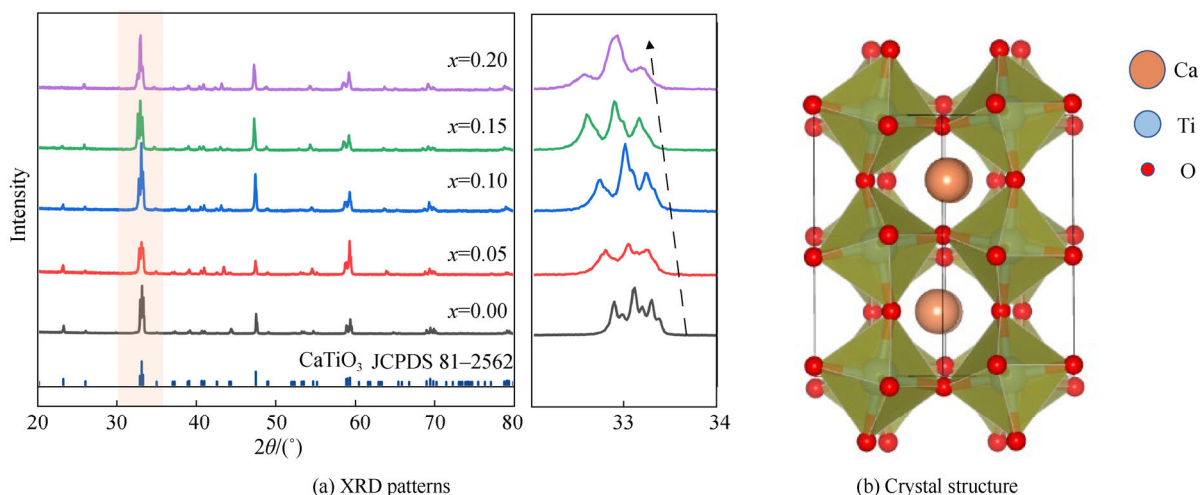


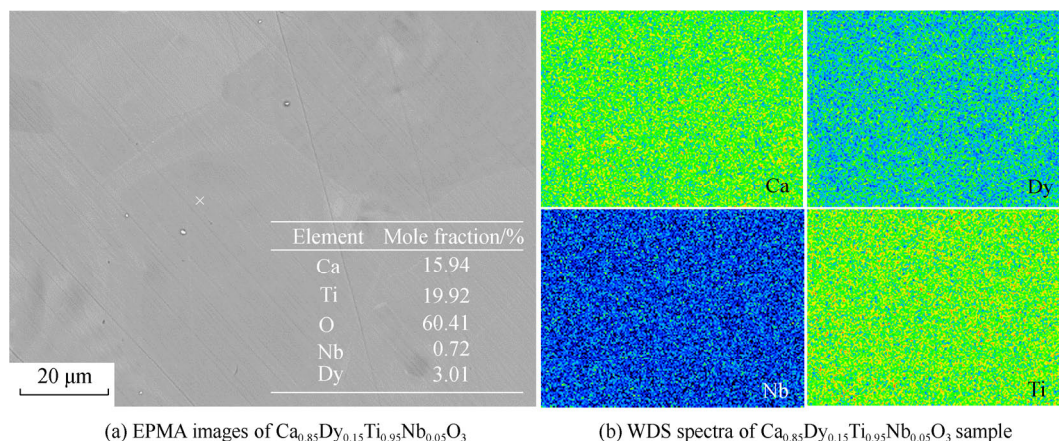
图 1 $\text{Ca}_{1-x}\text{Dy}_x\text{Ti}_{0.95}\text{Nb}_{0.05}\text{O}_3$ ($x=0\sim0.15$) 的 XRD 衍射谱与晶体结构示意图
Fig. 1 XRD patterns and crystal structure of $\text{Ca}_{1-x}\text{Dy}_x\text{Ti}_{0.95}\text{Nb}_{0.05}\text{O}_3$ ($x=0\sim0.15$)

图 2 为使用配备波谱仪(WDS)的 EPMA 设备对真空热压烧结的 $\text{Ca}_{0.85}\text{Dy}_{0.15}\text{Ti}_{0.95}\text{Nb}_{0.05}\text{O}_3$ 块体进行了背散射电子照片与元素面扫描分布图谱分析。由图 2 可见, 所有样品均为单一相, 未检测到第二相分布,

这与 XRD 结果一致。元素含量分析表明, 块体样品中的实际 Dy 和 Nb 元素含量与名义掺杂量基本一致, 这表明, Dy 元素和 Nb 元素成功掺入到 CaTiO_3 基体中, 同时致密度较高, 如表 1 所示。图 3 为

$\text{Ca}_{1-x}\text{Dy}_x\text{Ti}_{0.95}\text{Nb}_{0.05}\text{O}_3$ ($x=0\sim0.15$) 的电导率(σ)和 Seebeck 系数(S)随温度的变化曲线。电导率随温度增加而降低,同时 Seebeck 系数的绝对值随温度增加而增加,说明所合成的样品为简并半导体^[24]。如图 3a 所示,室温电导率从 $5.48\times10^4\text{ S/m}$ ($x=0$)增加到

$26.55\times10^4\text{ S/m}$ ($x=0.15$),这是因为 Dy^{3+} 取代 Ca^{2+} 可以提供大量电子,载流子浓度增加。值得注意的是,对于不同掺杂量的体系,高温下的电导率随温度变化几乎一致。高温时晶格振动显著增强,声学波散射主导了载流子的输运性质^[25]。



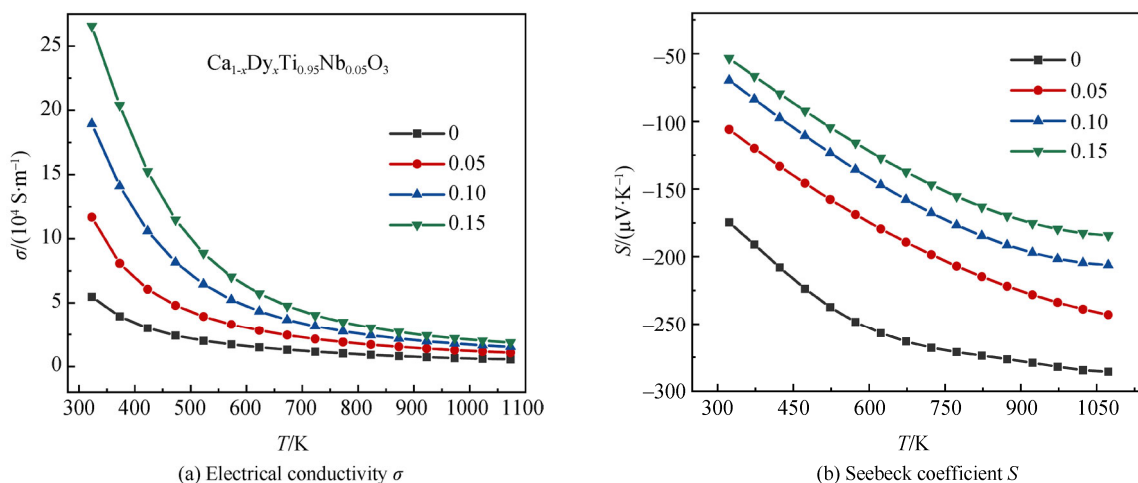
(a) EPMA images of $\text{Ca}_{0.85}\text{Dy}_{0.15}\text{Ti}_{0.95}\text{Nb}_{0.05}\text{O}_3$

(b) WDS spectra of $\text{Ca}_{0.85}\text{Dy}_{0.15}\text{Ti}_{0.95}\text{Nb}_{0.05}\text{O}_3$ sample

WDS is wavelength dispersive X-ray spectroscopy.

图 2 $\text{Ca}_{0.85}\text{Dy}_{0.15}\text{Ti}_{0.95}\text{Nb}_{0.05}\text{O}_3$ 的 EPMA 背散射图与元素面分布图谱

Fig. 2 Electron probe X-ray micro-analyzer (EPMA) analysis of $\text{Ca}_{0.85}\text{Dy}_{0.15}\text{Ti}_{0.95}\text{Nb}_{0.05}\text{O}_3$ and corresponding element distribution maps



(a) Electrical conductivity σ

(b) Seebeck coefficient S

图 3 $\text{Ca}_{1-x}\text{Dy}_x\text{Ti}_{0.95}\text{Nb}_{0.05}\text{O}_3$ ($x=0\sim0.15$) 的电导率(σ)和 Seebeck 系数(S)随温度的变化关系

Fig. 3 Temperature dependences of electrical conductivity (σ) and Seebeck coefficient (S) of $\text{Ca}_{1-x}\text{Dy}_x\text{Ti}_{0.95}\text{Nb}_{0.05}\text{O}_3$ ($x=0\sim0.15$)

表 1 $\text{Ca}_{1-x}\text{Dy}_x\text{Ti}_{0.95}\text{Nb}_{0.05}\text{O}_3$ ($x=0\sim0.15$) 的致密度(ρ)和有效质量(m_e)

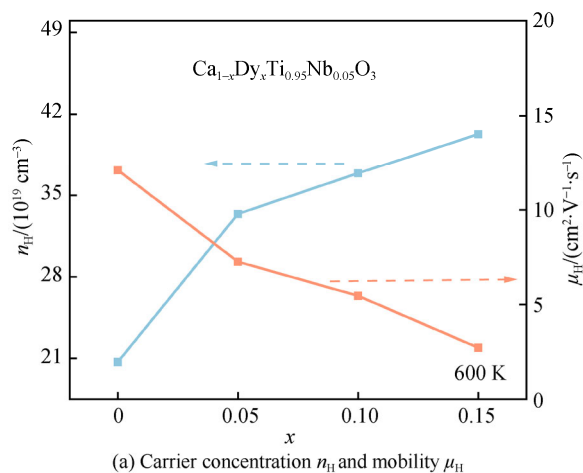
Table 1 Relatively density (ρ) and effective mass (m_e) of $\text{Ca}_{1-x}\text{Dy}_x\text{Ti}_{0.95}\text{Nb}_{0.05}\text{O}_3$ ($x=0\sim0.15$)

Sample	$\rho/\%$	m_e
$\text{CaTi}_{0.95}\text{Nb}_{0.05}\text{O}_3$	97.69	4.04
$\text{Ca}_{0.95}\text{Dy}_{0.05}\text{Ti}_{0.95}\text{Nb}_{0.05}\text{O}_3$	95.40	2.79
$\text{Ca}_{0.90}\text{Dy}_{0.10}\text{Ti}_{0.95}\text{Nb}_{0.05}\text{O}_3$	96.81	2.16
$\text{Ca}_{0.85}\text{Dy}_{0.15}\text{Ti}_{0.95}\text{Nb}_{0.05}\text{O}_3$	98.25	1.86

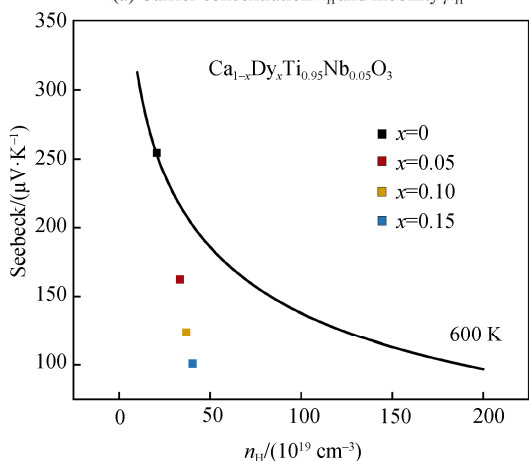
图 3b 为 $\text{Ca}_{1-x}\text{Dy}_x\text{Ti}_{0.95}\text{Nb}_{0.05}\text{O}_3$ ($x=0\sim0.15$) 的 Seebeck 系数随温度的变化关系。Seebeck 系数全部

为负值,表明所合成的体系为 n 型半导体。随着 Dy 含量的增加,载流子浓度增加,因此, Seebeck 系数不断降低。由于氧化物的服役温度通常为高温环境,为了阐明材料的电输运机制,本工作进行了 600 K 温度下的 Hall 效应测试,如图 4a 所示。随着 Dy 含量由 $x=0$ 增加到 $x=0.15$,载流子浓度从 $2.07\times10^{20}\text{ cm}^{-3}$ 增加到 $4.03\times10^{20}\text{ cm}^{-3}$ 。随着 Dy 含量的增加,载流子在输运过程中会遇到更多的电离杂质散射,从而 Hall 迁移率降低,从 $12.10\text{ cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$ ($x=0$) 降低到 $2.72\text{ cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$ ($x=0.15$)。通过 Pisarenko 曲线发现,

Dy 掺杂显著降低了有效质量(表 1), 这与 Jiang 等^[23]报道的 Dy 掺杂 CaTiO_3 会引起基体的能带锐化结果相似。如图 4b 所示, 随着 Dy 含量的增加, 态密度有效质量减小, 有助于获得高的电输运性能^[26]。



(a) Carrier concentration n_H and mobility μ_H



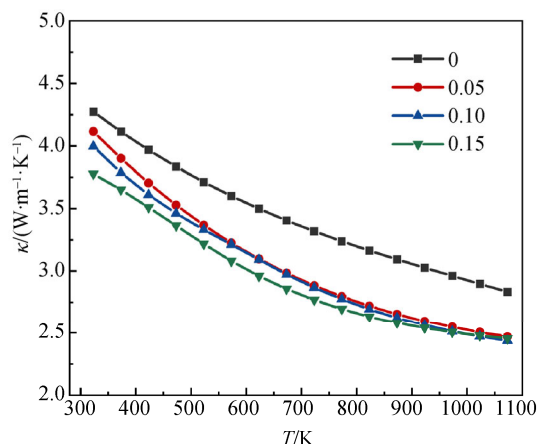
(b) Pisarenko plot

图 4 $\text{Ca}_{1-x}\text{Dy}_x\text{Ti}_{0.95}\text{Nb}_{0.05}\text{O}_3$ 的载流子浓度和迁移率随成分变化曲线、Pisarenko 曲线

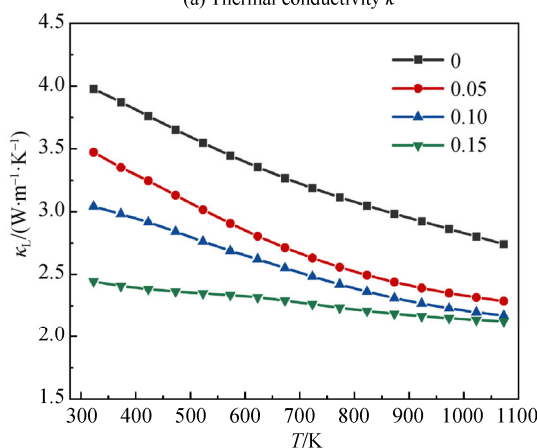
Fig. 4 Carrier concentration and mobility curves of $\text{Ca}_{1-x}\text{Dy}_x\text{Ti}_{0.95}\text{Nb}_{0.05}\text{O}_3$ and the Pisarenko curves

图 5 为 $\text{Ca}_{1-x}\text{Dy}_x\text{Ti}_{0.95}\text{Nb}_{0.05}\text{O}_3$ ($x=0\sim0.15$) 的热导率和晶格热导率随温度的变化关系。由图 5a 可见, 总热导率 κ 随温度的升高而下降。Dy 掺杂使总热导率在 323 K 从 $4.27 \text{ W}/(\text{m}\cdot\text{K}^{-1})$ ($x=0$) 降至 $3.77 \text{ W}/(\text{m}\cdot\text{K}^{-1})$ ($x=0.15$)。总热导率的大幅度降低主要是由晶格热导率贡献的。如图 5b 所示, 323 K 下, $x=0.15$ 的晶格热导率比 $x=0$ 试样下降了 38.53%, 这主要是由于 Dy 的高浓度掺杂在 Ca 晶格位点引入了大的质量场与应力场波动所导致的^[27]。图 6 为 $\text{Ca}_{1-x}\text{Dy}_x\text{Ti}_{0.95}\text{Nb}_{0.05}\text{O}_3$ ($x=0\sim0.15$) 的热电优值随温度的变化关系。在 $x=0.05\sim0.15$ 样品中, zT 随温度的增加而增加。同时, 随着 Dy 含量的增加, 最大 zT 值增加。当 $x=0.15$ 时, 在 1073 K 时, 最大 zT 值可

以达到 0.29。对比文献中不同成分不同制备工艺获得的 CaTiO_3 基热电性能, 本工作中采用的 Dy 与 Nb 双掺结合固相烧结与热压烧结工艺制备出的样品具有优异的热电性能^[22, 28-29]。



(a) Thermal conductivity κ



(b) Lattice thermal conductivity κ_L

图 5 $\text{Ca}_{1-x}\text{Dy}_x\text{Ti}_{0.95}\text{Nb}_{0.05}\text{O}_3$ ($x=0\sim0.15$) 的总热导率和晶格热导率随温度变化曲线

Fig. 5 Temperature dependences of the total thermal conductivity and lattice thermal conductivity of $\text{Ca}_{1-x}\text{Dy}_x\text{Ti}_{0.95}\text{Nb}_{0.05}\text{O}_3$ ($x=0\sim0.15$)

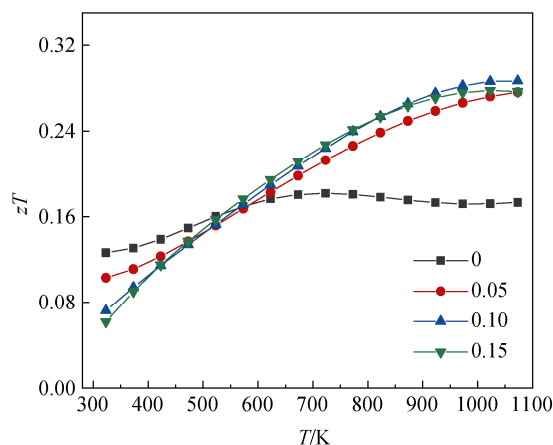


图 6 $\text{Ca}_{1-x}\text{Dy}_x\text{Ti}_{0.95}\text{Nb}_{0.05}\text{O}_3$ 的 zT 值随温度变化曲线

Fig. 6 Temperature dependences of the figure of merit (zT) of $\text{Ca}_{1-x}\text{Dy}_x\text{Ti}_{0.95}\text{Nb}_{0.05}\text{O}_3$ ($x=0\sim0.15$)

3 结论

通过对 $\text{Ca}_{1-x}\text{Dy}_x\text{Ti}_{0.95}\text{Nb}_{0.05}\text{O}_3$ ($x=0\sim 0.15$) 材料的实验研究发现, 在 CaTiO_3 基体中, Dy 掺杂可以显著增加载流子浓度, 有效提高电子输运性能。同时, 由于 Dy^{3+} 和 Ca^{2+} 之间有大的质量差异和共价半径差异, 显著散射高频声子, 使体系的晶格热导率大幅度降低。由于电性能和热性能的同步优化, 在 1073 K 时, $\text{Ca}_{0.85}\text{Dy}_{0.15}\text{Ti}_{0.95}\text{Nb}_{0.05}\text{O}_3$ 获得最大 zT 值约为 0.29, 表明 CaTiO_3 氧化物热电材料具有很大的应用潜力。

参考文献:

- [1] ZEBARJADI M, ESFARJANI K, DRESSELHAUS M S, et al. Perspectives on thermoelectrics: From fundamentals to device applications[J]. *Energy Environ Sci*, 2012, 5(1): 5147–5162.
- [2] 何傲天, 李柏桥, 刘青青, 等. Te/Cr 共掺提高 PbSe 的热电性能[J]. *化学通报*, 2024, 87(7): 845–849.
HE Aotian, LI Baiqiao, LIU Qingqing, et al. *Chemistry*, 2024, 87(7): 845–849.
- [3] TIAN Z, WANG J, YAER X B, et al. Pencil painting like preparation for flexible thermoelectric material of high-performance p-type $\text{Na}_{1.4}\text{Co}_2\text{O}_4$ and novel n-type $\text{Na}_x\text{Co}_2\text{O}_4$ [J]. *J Materiomics*, 2021, 7(5): 1153–1160.
- [4] SARKAR D, GHOSH T, BANIK A, et al. Highly converged valence bands and ultralow lattice thermal conductivity for high-performance SnTe thermoelectrics[J]. *Angew Chem Int Ed Engl*, 2020, 59(27): 11115–11122.
- [5] 傅铁铮, 沈家骏, 忻佳展, 等. 通过 In/Sb 双掺杂优化 SnTe 基材料热电性能[J]. *硅酸盐学报*, 2019, 47(10): 1467–1472.
FU Tiezheng, SHEN Jiajun, XIN Jiazhan, et al. *J Chin Ceram Soc*, 2019, 47(10): 1467–1472.
- [6] 李泉, 邢通, 李小亚, 等. 热挤压工艺对 $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ 材料热电性能和力学性能的影响[J]. *硅酸盐学报*, 2024, 52(10): 3243–3251.
LI Quan, XING Tong, LI Xiaoya, et al. *J Chin Ceram Soc*, 2024, 52(10): 3243–3251.
- [7] XIAO Y, WANG D Y, ZHANG Y, et al. Band sharpening and band alignment enable high quality factor to enhance thermoelectric performance in n-type PbS[J]. *J Am Chem Soc*, 2020, 142(8): 4051–4060.
- [8] BANIK A, SHENOY U S, SAHA S, et al. High power factor and enhanced thermoelectric performance of SnTe-AgInTe₂: Synergistic effect of resonance level and valence band convergence[J]. *J Am Chem Soc*, 2016, 138(39): 13068–13075.
- [9] ZHENG L L, LI W, LIN S Q, et al. Interstitial defects improving thermoelectric SnTe in addition to band convergence[J]. *ACS Energy Lett*, 2017, 2(3): 563–568.
- [10] ZHANG Q, LIAO B L, LAN Y C, et al. High thermoelectric performance by resonant dopant indium in nanostructured SnTe[J]. *Proc Natl Acad Sci USA*, 2013, 110(33): 13261–13266.
- [11] BANIK A, VISHAL B, PERUMAL S, et al. The origin of low thermal conductivity in $\text{Sn}_{1-x}\text{Sb}_x\text{Te}$: Phonon scattering via layered intergrowth nanostructures[J]. *Energy Environ Sci*, 2016, 9(6): 2011–2019.
- [12] MOSHWAN R, SHI X L, LIU W D, et al. Enhancing thermoelectric properties of InTe nanoprecipitate-embedded $\text{Sn}_{1-x}\text{In}_x\text{Te}$ microcrystals through anharmonicity and strain engineering[J]. *ACS Appl Energy Mater*, 2019, 2(4): 2965–2971.
- [13] LI J B, WANG Y X, JIANG X, et al. Emerging homogeneous superlattices in CaTiO_3 bulk thermoelectric materials[J]. *Mater Horiz*, 2023, 10(2): 454–465.
- [14] 巴倩, 刘志愿, 李周, 等. Bi_2Te_3 基材料热电性能优化策略[J]. *材料导报*, 2024, 39: <http://kns.cnki.net/kcms/detail/50.1078.tb.20240910.1344.018.html>.
BA Qian, LIU Zhiyuan, LI Zhou, et al. *Mater Rep*, 2024, <http://kns.cnki.net/kcms/detail/50.1078.tb.20240910.1344.018.html>.
- [15] XIAO Y, WU H J, LI W, et al. Remarkable roles of Cu to synergistically optimize phonon and carrier transport in n-type PbTe-Cu₂Te[J]. *J Am Chem Soc*, 2017, 139(51): 18732–18738.
- [16] ZHOU Y M, WU H J, PEI Y L, et al. Strategy to optimize the overall thermoelectric properties of SnTe via compositing with its property-counter CuInTe₂[J]. *Acta Mater*, 2017, 125: 542–549.
- [17] LI F, LIU X, LI S R, et al. Rare three-valence-band convergence leading to ultrahigh thermoelectric performance in all-scale hierarchical cubic SnTe[J]. *Energy Environ Sci*, 2024, 17(1): 158–172.
- [18] LI J, ZHANG X Y, CHEN Z W, et al. Low-symmetry rhombohedral GeTe thermoelectrics[J]. *Joule*, 2018, 2(5): 976–987.
- [19] LI J, ZHANG X Y, WANG X, et al. High-performance GeTe thermoelectrics in both rhombohedral and cubic phases[J]. *J Am Chem Soc*, 2018, 140(47): 16190–16197.
- [20] BOUDALI A, ABADA A, DRISS KHODJA M, et al. Calculation of structural, elastic, electronic, and thermal properties of orthorhombic CaTiO_3 [J]. *Phys B Condens Matter*, 2010, 405(18): 3879–3884.
- [21] LI J B, WANG Y X, YANG X, et al. Processing bulk insulating CaTiO_3 into a high-performance thermoelectric material[J]. *Chem Eng J*, 2022, 428: 131121.
- [22] LI J B, JIANG Q W, TIAN Z, et al. Controlling precipitation and dopant effects to achieve promising thermoelectric performance in CaTiO_3 [J]. *ACS Appl Energy Mater*, 2023, 6(15): 8053–8062.
- [23] JIANG Q W, LI G S, WANG X H, et al. Enhanced thermoelectric properties for eco-friendly CaTiO_3 by band sharpening and atomic-scale defect phonon scattering[J]. *Mater Today Energy*, 2024, 44: 101655.
- [24] TAN G J, ZHAO L D, SHI F Y, et al. High thermoelectric performance of p-type SnTe via a synergistic band engineering and nanostructuring approach[J]. *J Am Chem Soc*, 2014, 136(19): 7006–7017.
- [25] MAO J, LIU Z H, ZHOU J W, et al. Advances in thermoelectrics[J]. *Adv Phys*, 2018, 67(2): 69–147.
- [26] QIAN X, ZHANG X X, GUO H R, et al. Enhancing thermoelectric performance of n-type AgBi_3S_5 through synergistically optimizing the effective mass and carrier mobility[J]. *J Materiomics*, 2023, 9(5): 874–881.
- [27] WANG X Y, YAO H H, YIN L, et al. Band modulation and strain fluctuation for realizing high average zT in GeTe[J]. *Adv Energy Mater*, 2022, 12(26): 2201043.
- [28] XIAO X X, WIDENMEYER M, XIE W J, et al. Influence of Nb substitution and sintering atmosphere on thermoelectric properties of CaTiO_3 -based ceramics[J]. *Solid State Sci*, 2024, 149: 107467.
- [29] XIAO X X, ARIF S, DING J X, et al. Molten salt synthesized La-substituted CaTiO_3 thermoelectric ceramics[J]. *Open Ceram*, 2024, 17: 100522.

Optimization of Thermoelectric Performance of CaTiO₃-Based Materials by Dy/Nb Co-Doping

JIANG Quanwei, TIAN Zhen, LI Jianbo, SHI Xiaowei, KANG Huijun, WANG Tongmin

(Key Laboratory of Solidification Control and Digital Preparation Technology, School of Materials Science and Engineering, Dalian University of Technology, Dalian 116024, Liaoning, China)

Extended Abstract

Introduction CaTiO₃-based compounds emerge as a promising thermoelectric material due to their environmentally benign, thermally stable, and cost-efficient merits. Nonetheless, pristine CaTiO₃ manifests inherently inferior electronic transport properties. In this paper, Ca_{1-x}Dy_xTi_{0.95}Nb_{0.05}O₃ ($x=0-0.15$) bulk ceramics were prepared via solid-phase sintering combined with hot-pressing sintering, and the composition, microstructure, and thermoelectric properties were analyzed. The results show that Dy and Nb doping can significantly increase the carrier concentration and effectively improve the electronic transport properties. Also, the lattice thermal conductivity is drastically reduced due to the introduction of large mass-field strain and stress-field strain, thus scattering high-frequency phonons. Ca_{0.85}Dy_{0.15}Ti_{0.95}Nb_{0.05}O₃ bulk ceramic has a zT maximum of 0.29 at 1073 K, showing that the CaTiO₃-based materials have a promising prospect for thermoelectric applications.

Methods Ca_{1-x}Dy_xTi_{0.95}Nb_{0.05}O₃ ($x=0-0.15$) bulk ceramics were synthesized by solid-phase sintering and hot pressing. First, powders of CaCO₃, Nb₂O₅, Dy₂O₃, and TiO₂ were mixed and ground in a planetary ball mill for 12 h, then dried and cold-pressed. The pre-burned samples were ground for 6 h and the dried powders were cold-pressed again. The pressed samples were then placed in a graphite mold with a diameter of 13 mm for hot pressing at 1573 K for 1.5 h to obtain dense disks with a thickness of 2 mm.

The phase composition of the bulk samples was performed by a model EMPYREAN X-ray diffractometer (XRD, PANalytical Co., the Netherlands). The elemental distribution of the samples was measured by a model JXA-8530F electron probe X-ray micro-analyzer (EPMA, JEOL Co., Japan). The Seebeck coefficient and resistivity of the samples were measured simultaneously by a model LSR-3 device (Linseis Co., Germany). The samples used for the test were long strips with the sizes of approximately 11.0 mm × 2.0 mm × 2.5 mm. The carrier concentration and Hall mobility of the system were measured by a model 8400 Hall measurement system (Lake Shore Co., Ltd., USA). The thermal conductivity of the system was measured by a model LFA-457 laser flash thermal conductivity meter (Netzsch Co., Germany), and the specific heat capacity of the bulk samples was calculated according to the Debye-Dulong law.

Results and discussion The polycrystalline Ca_{1-x}Dy_xTi_{0.95}Nb_{0.05}O₃ ($x=0-0.15$) samples with a single phase were prepared. The main phase of the synthesized samples is an orthorhombic structure, with a space group of Pnma. Dy³⁺ and Nb⁵⁺ occupy Ca²⁺ and Ti⁴⁺ sites in the matrix, respectively, causing the lattice expansion and introducing the donor impurity levels, transforming CaTiO₃ from an insulating wide-bandgap semiconductor to a good electrical conductivity thermoelectric material. The actual amounts of elements Dy and Nb in the bulk samples are basically consistent with the nominal doping concentrations, indicating that elements Dy and Nb are incorporated into the CaTiO₃ matrix effectively. The electrical conductivity decreases with increasing temperature, while the absolute value of the Seebeck coefficient increases with increasing temperature, showing typical characteristics of degenerate semiconductor electron transport. At high temperatures, the lattice vibrations are violent, and the acoustic wave scattering dominates the carrier transport, with other scattering mechanisms having little effect on the electronic transport properties. As Dy concentration increases, the effective mass of the density of states decreases. When $x=0.15$, the maximum zT value can reach 0.29 at 1073 K, which is comparable to the others reported CaTiO₃ based thermoelectric performances in the literature.

Conclusions Polycrystalline Ca_{1-x}Dy_xTi_{0.95}Nb_{0.05}O₃ ($x=0-0.15$) samples with a single phase were prepared by solid-phase reaction combined with HP sintering. Dy and Nb doping could significantly increase the carrier concentration and effectively improve the electronic transport performance. Meanwhile, the high-frequency phonons were scattered due to the large mass difference and covalent radius difference between Dy³⁺ and Ca²⁺, resulting in a substantial reduction in the lattice thermal conductivity of the system. Ca_{0.85}Dy_{0.15}Ti_{0.95}Nb_{0.05}O₃ achieved the maximum zT value of 0.29 at 1073 K due to the simultaneous optimization of electrical and thermal properties, indicating that CaTiO₃ oxide thermoelectric materials could have a promising prospect for thermoelectric applications.

Keywords calcium titanate thermoelectric material; electrical conductivity; lattice thermal conductivity; figure of merit