

CuO/Li₂CO₃ 对钛酸钡基铁电陶瓷电卡效应的影响

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摘 要: 基于电卡效应(ECE)的固态制冷技术具有高效比、电场直接驱动、易于集成化等优势, 在微制冷技术领域应用前景广阔。钛酸钡基(BaTiO₃)铁电陶瓷因其较高的极化强度和丰富的相结构成为最具潜力的电卡材料之一, 然而, 目前其进一步发展受限于低击穿电场、高烧结温度、高电卡性能以及宽工作温区难以同时实现等难点。本工作采用传统固相反应法制备了一种无铅 Ba_{0.97}Ca_{0.03}Sn_{0.1}Ti_{0.9}O₃-xCuO-yLi₂CO₃ (BCST, x=0, y=0; BCST-C, x=0.2% (质量分数), y=0; BCST-L, x=0, y=1.5%; BCST-CL, x=0.2%, y=1.5%)陶瓷材料, 研究了烧结助剂 CuO/Li₂CO₃ 对 BCST 陶瓷材料物相结构、微观形貌和电学性能的影响。结果表明, 烧结助剂的引入促进了陶瓷晶粒的致密化生长, 优化了击穿电场, 并且在保持 BCST 陶瓷材料宽温域连续相变特性的同时提高了其介电常数。最终, 样品 BCST-CL 陶瓷在宽工作温区获得了提升的电卡性能, 其中: $\Delta T_{\max}=3.37\text{ K}$ (55 °C, 160 kV·cm⁻¹), 该工作为电卡陶瓷材料性能的进一步提升提供了一种可行策略。

关键词: 钛酸钡基陶瓷; 电卡效应; 烧结助剂; 介电常数

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制冷技术广泛应用于军事、商业、工业和民用等领域^[1]。然而, 目前占据市场主导地位的机械压缩制冷技术因其体积庞大、耗电量大、制冷效率低^[2]以及环境不友好等因素无法满足日益发展的新兴科技领域需求^[3], 新一代制冷技术, 如: 热电制冷^[4]、磁卡制冷^[5]、电卡制冷^[6]、压卡制冷^[7]和弹卡制冷^[8]应运而生, 其中, 基于电卡效应的新型的固态电卡制冷器由电能直接驱动, 即可实现热搬运和制冷, 具有能效比高, 易于小型化、集成化和环境友好等优点, 被认为是一种极具发展潜力的高效制冷技术^[9]。

电卡效应(ECE), 是指极性材料中的偶极子在电场的诱导下进行取向, 从而引起熵值变化(ΔS)和温度变化(ΔT)。电卡材料常被分为无机、有机和无机/有机复合 3 类, 其中, 最具代表性的为钙钛矿型铁

电陶瓷类材料, 其具有制备简单、成本低、电卡强度高和易于后期设计等优点, 是制备电卡制冷的最具实用前景的材料之一^[10-11]。钛酸钡基陶瓷因其具有良好的极化强度和丰富的相结构, 在电卡领域受到了广泛研究^[11-13]; 但目前钛酸钡基陶瓷仍存在击穿电场低、烧结温度高、工作温区和极化强度无法同时提高等难点^[14-16], 限制了其迈向实用化和产业化的进程^[17-18]。因此, 如何在降低钛酸钡基材料烧结温度的同时, 提高其击穿电场和电卡强度是其进一步发展亟待解决的问题。

基于此, 本工作采用传统固相反应法制备了一种新型的无铅 Ba_{0.97}Ca_{0.03}Sn_{0.1}Ti_{0.9}O₃-xCuO-yLi₂CO₃ (BCST, x=0, y=0; BCST-C, x=0.2% (质量分数), y=0; BCST-L, x=0, y=1.5%; BCST-CL, x=0.2%, y=1.5%)陶瓷材料。通过对各组陶瓷样品的物相结

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构、微观形貌、电学性能及电卡性能进行系统研究表明,引入 2 种不同的烧结助剂 CuO/Li₂CO₃,不仅降低了烧结温度,提高了 BCST 材料的致密度,优化了击穿性能,还提高了材料的介电常数和极化强度,最终在 BCST-CL 陶瓷材料中获得大幅提升的电卡温变值 $\Delta T_{\max}=3.37\text{ K}(55\text{ }^{\circ}\text{C}, 190\text{ kV}\cdot\text{cm}^{-1})$,为开发新型电卡制冷料提供了一种新的可行策略。

1 实验

1.1 样品制备

采用传统固相反应烧结法制备 Ba_{0.97}Ca_{0.03}Sn_{0.1}Ti_{0.9}O_{3-x}CuO-yLi₂CO₃(BCST, x=0, y=0; BCST-C, x=0.2%, y=0; BCST-L, x=0, y=1.5%; BCST-CL, x=0.2%, y=1.5%)陶瓷样品。以 BaCO₃ (99.8%, 质量分数)、CaCO₃ (99.7%)、SnO₂ (99.5%)、TiO₂ (99.9%)为原料,按照化学计量比称量各配料质量。配料后以无水乙醇和锆球为球磨介质进行湿法球磨,球磨 12 h 后在 60 °C 烘箱中进行烘干,取出干燥后的粉末放入马弗炉中在 1200 °C 预烧 3 h 后,按照相应质量比加入烧结助剂 CuO (99.5%), Li₂CO₃ (99.5%)。将配比后的粉体再次球磨 12 h 并烘干后,使用质量分数为 5% 的聚乙烯醇(PVA)黏结剂进行造粒,将造粒后的陶瓷粉末在 2 MPa 单轴压力冲压下制成直径为 12 mm、厚度为 1.5 mm 的圆片,随后在 120 MPa 的压力下进行冷等静压后得到陶瓷生胚。将陶瓷生胚在空气氛围中烧结,在 600 °C 保温 2 h 以排除生坯中的 PVA 胶体,随后升温到 1350~1500 °C 保温 3 h,随炉冷却至室温后得到样品 BCST、样品 BCST-C、样品 BCST-L 和样品 BCST-CL 共 4 组陶瓷样品。

1.2 样品表征

采用日本岛津公司 7000S/L 型 X 射线衍射仪(XRD)测试陶瓷的物相结构。采用德国 Gemini SEM300 型场发射扫描电子显微镜(SEM)观察陶瓷的微观形貌,并使用 Nano Measure 软件对晶粒尺寸进行测量。采用英国牛津仪器 X-MaxNSN78861 型 X 射线能谱仪(EDS)对陶瓷的微区元素分布进行分析。采用中国武汉研禾科技有限公司的介电性能测试系统(DPTS-RT-600)测试陶瓷的介电常数和介电损耗。采用武汉研禾科技有限公司 FETS-2000 型铁电测试仪测试陶瓷的电滞回线,频率为 10 Hz。采用武汉研禾科技有限公司的电卡测试仪(ECTS-2000)测试样品的电卡性能。

2 结果与讨论

2.1 物相组成分析

图 1 为 BCST-xCuO-yLi₂CO₃ 陶瓷在 10°~90°范围内的 XRD 谱。由图 1a 可见,所有陶瓷样品均具有钙钛矿结构^[19-21],在 XRD 可检测范围内均没有表现出任何杂相的存在迹象,表明 Cu²⁺和 Li⁺已扩散到 BCST 晶格中形成固溶体。所有样品均具有与原始 BCST 陶瓷相似的 XRD 谱,在室温条件下具有相似的对称性。此外,局部放大的 44°~46°范围内的衍射峰随着助烧剂的加入,向低角度移动,如图 1b 所示。根据布拉格方程($2d\sin\theta=\lambda$, 式中: d 为晶面间距; θ 为入射 X 射线与晶面的夹角; λ 为 X 射线的波长),衍射峰向低衍射角的移动表明晶格的扩张行为。由于 Li⁺(0.73 Å)和 Cu²⁺(0.71 Å)的半径大于 B 位 Ti⁴⁺(0.61 Å)和 Sn⁴⁺(0.71 Å)的半径,但小于 A 位 Ba²⁺(1.34 Å)和 Ca²⁺(0.99 Å)的半径。当加入少量的 CuO 和 Li₂CO₃,引入的 Li⁺和 Cu²⁺更倾向于进入晶格中的 B 位^[22-23],从而导致晶格的扩张。此外, Li⁺的半径比 Cu²⁺更大, Li₂CO₃ 的加入量(约 0.075 mol)也大于 CuO 的加入量(约 0.01 mol),导致了样品 BCST-L 的晶格扩张程度大于样品 BCST-C,使得其衍射峰向低角度移动的程度更大。

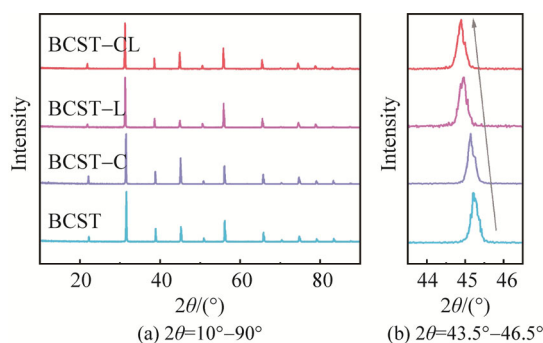


图 1 BCST-xCuO-yLi₂CO₃ 陶瓷的 XRD 谱
Fig. 1 XRD patterns of BCST-xCuO-yLi₂CO₃ ceramics

2.2 微观形貌分析

图 2 为 BCST-xCuO-yLi₂CO₃ 陶瓷热腐蚀表面的 SEM 照片,其中,样品 BCST 陶瓷烧结温度为 1500 °C,添加烧结助剂后,样品 BCST-C,样品 BCST-L 以及样品 BCST-CL 的烧结温度分别降低至 1350、1300 °C 和 1300 °C。由图 2a 可见,BCST 陶瓷具有较多的孔洞,证实在 1500 °C 也难以获得致密的 BCST 陶瓷,这与报道的 BCST 陶瓷致密化温度相符^[24]。加入 CuO/Li₂CO₃ 烧结助剂后,促进

了各组陶瓷样品的晶粒长大, 使其发育完整, 形成了高度致密的微观结构。样品 BCST-C、样品 BCST-L 以及样品 BCST-CL 的晶界清晰、晶粒分布紧密、孔隙率低, 具有良好的致密度。

图 3 为 BCST- x CuO- y Li₂CO₃ 陶瓷的晶粒尺寸分布直方图(采用 Nano Measure 软件对图 2 中的 SEM 照片统计得到)。由图 3 可见, 随着烧结助剂的加入, 样品 BCST-C、样品 BCST-L 以及样品

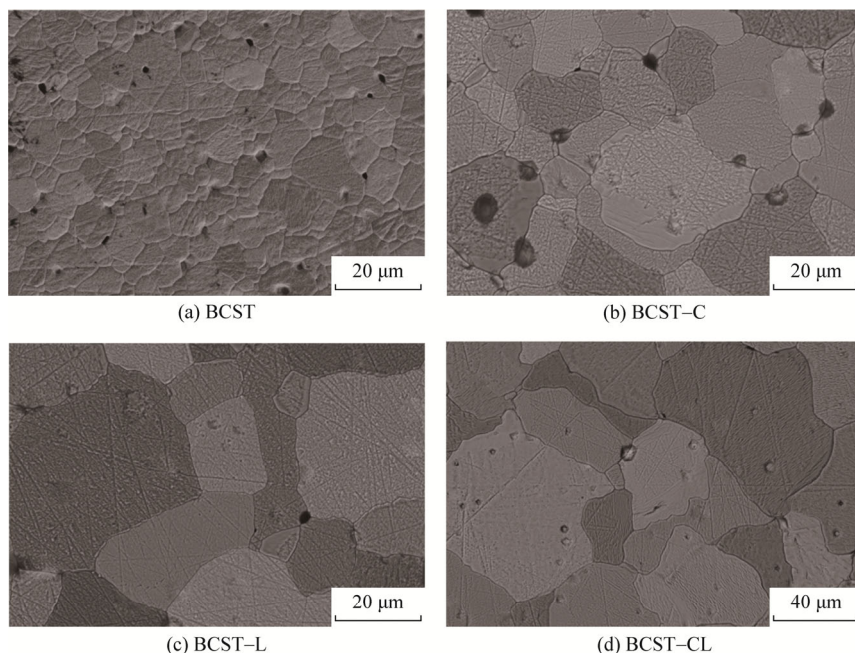


图 2 BCST- x CuO- y Li₂CO₃ 陶瓷热腐蚀表面的 SEM 的照片
Fig. 2 SEM images of the hot corrosive surface of BCST- x CuO- y Li₂CO₃ ceramics

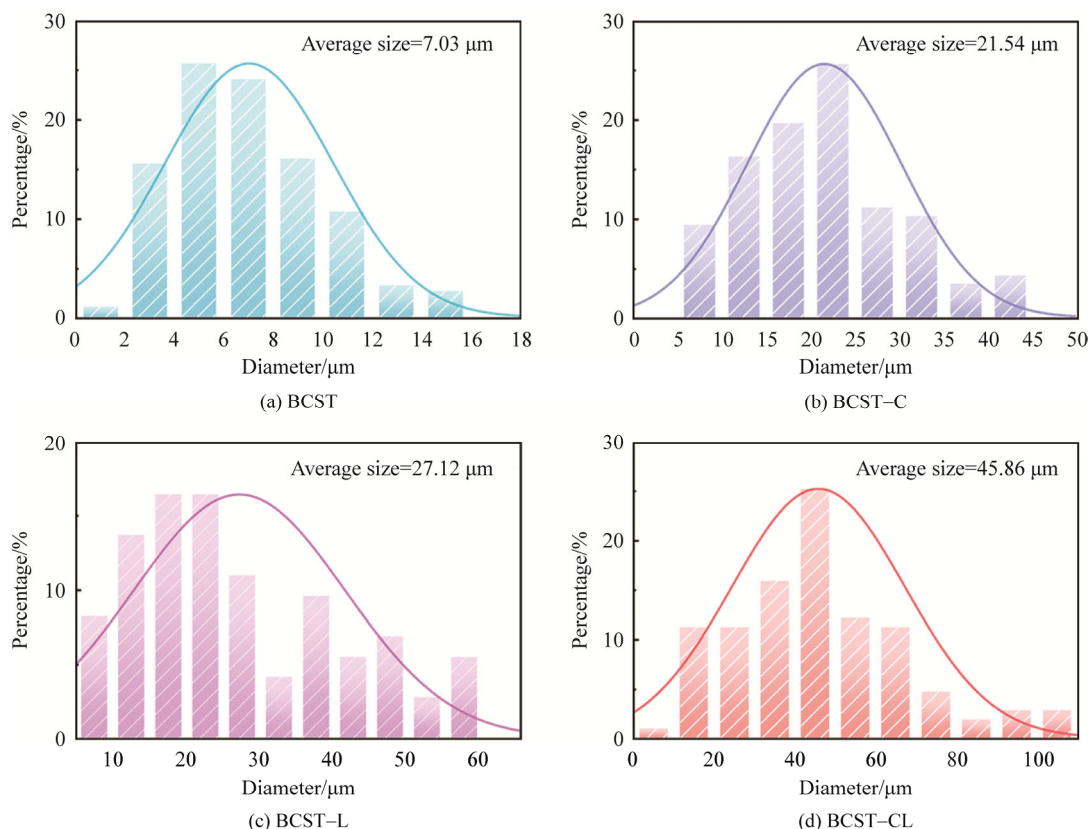


图 3 BCST- x CuO- y Li₂CO₃ 陶瓷的晶粒尺寸分布图
Fig. 3 Grain size (diameter) distributions of BCST- x CuO- y Li₂CO₃ ceramics

BCST-CL 的晶粒尺寸由 BCST 陶瓷的约 $7\ \mu\text{m}$ 分别增大到了约 $22\ \mu\text{m}$ 、约 $27\ \mu\text{m}$ 和约 $46\ \mu\text{m}$, 这种陶瓷晶粒增长情况可归因于所加入的低熔点 $\text{CuO}/\text{Li}_2\text{CO}_3$ 烧结助剂, 在烧结过程的早期阶段会产生液相烧结效应, 促进传质, 使得晶粒长大和陶瓷致密化^[25-26]; 而在烧结后期阶段, Li^+ 和 Cu^{2+} 进入晶格中的 B 位取代 Ti^{4+} 和 Sn^{4+} , 由于离子电荷补偿作用, 这一取代

过程会产生氧空位, 单离子缺陷 $\text{V}_\text{O}^\bullet$ 在烧结过程中的扩散可促进固相传质进而促进晶粒的生长^[27], 从而促进了陶瓷致密化。

图 4 为样品 BCST-CL 的背散射衍射图像和相应的元素分布。由图 4 可见, Li^+ 和 Cu^{2+} 分布均匀, 没有出现富集现象, 进一步表明 Li^+ 和 Cu^{2+} 完全进入了晶格中。

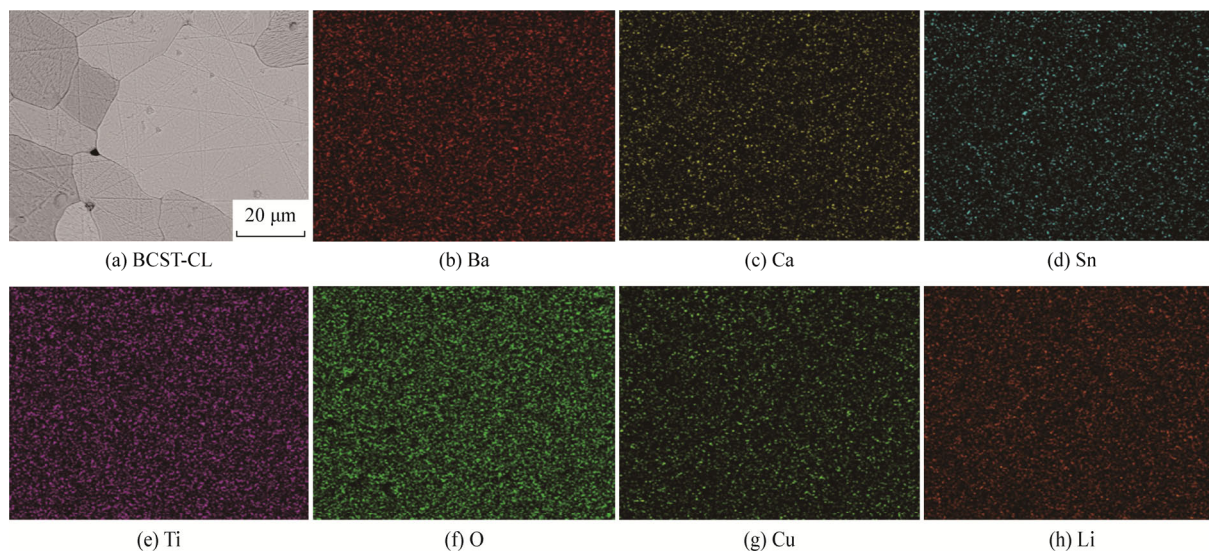


图 4 样品 BCST-CL 热腐蚀表面的背散射衍射图像和相应的元素分布

Fig. 4 Backscattering diffraction images and corresponding elemental distribution of hot corrosive surface of sample BCST-CL

2.3 电学性能分析

图 5 为 $\text{BCST-xCuO-yLi}_2\text{CO}_3$ 陶瓷在 $100\ \text{Hz} \sim 1\ \text{MHz}$ 频率下的介电常数(ϵ_r)和介电损耗($\tan\delta$)在 $25 \sim 150\ ^\circ\text{C}$ 温度范围内的变化曲线。由图 5 可以看出, 各组陶瓷样品的介电常数随着频率的增加而逐渐降低, 介电损耗也随之降低。同时, 除了存在于约 $60\ ^\circ\text{C}$ (T_C) 处的铁电-顺电相变峰, 在约 $50\ ^\circ\text{C}$ ($T_{\text{O-T}}$) 处还能观察到一个平缓的铁电-铁电(正交-四方)相变峰, 这与报道的 BCST 陶瓷介电图谱相一致^[28]。BCST 陶瓷具有一个宽温度范围的亚稳态连续相变区, 包括在室温 $45\ ^\circ\text{C}$ 附近的铁电-铁电相变(三方-正交、正交-四方), 以及 $60\ ^\circ\text{C}$ 附近的铁电-顺电相变, 具有正常铁电相的强极化和由不稳定相结构产生的大极化变化^[28-29], 从而能在宽的温度范围内产生大的电卡温变(ΔT)。由图 5a~图 5d 可以发现, 引入烧结助剂后的样品 BCST-C、样品 BCST-L 以及样品 BCST-CL 依旧保持着连续相变区。由图 5e 可见, 随着 $\text{CuO}/\text{Li}_2\text{CO}_3$ 的加入, 材料的介电常数大幅增加的同时介电损耗下降: 一方面是由于晶粒尺寸的增大导致样品 BCST-C、样品 BCST-L 以及样

品 BCST-CL 的介电常数显著提高^[30]; 另一方面, Cu^{2+} 和 Li^+ 作为异价受主掺杂取代 Ti^{4+} 和 Sn^{4+} , 会产生 $\text{Cu}_{\text{Ti/Sn}}''$ 和 $\text{Li}_{\text{Ti/Sn}}''$ 的晶格缺陷以及氧空位 $\text{V}_\text{O}^\bullet$, 这些缺陷会形成缺陷偶极子, 这些偶极子又在局域聚集耦合形成缺陷偶极子团簇, 这些偶极子团簇不仅贡献了介电常数, 还可以束缚自由载流子, 限制其在晶格间的跳跃, 从而降低介电损耗, 这一现象也被称为电子-钉扎缺陷-偶极子(EPDD)效应^[31]。

与此同时, 随着 $\text{CuO}/\text{Li}_2\text{CO}_3$ 的加入, 材料的相变峰向低温方向移动。对于钙钛矿铁电体, 其介电性能由成分、B 位离子有序度和晶体对称性决定^[32]。 $\text{Cu}^{2+}/\text{Li}^+$ 离子的半径大于 B 位 $\text{Ti}^{4+}/\text{Sn}^{4+}$ 离子, 会使材料晶格膨胀出现随机应场, 打破了铁电长程有序, 使相变温度降低^[33]; 另一方面, $\text{Cu}/\text{Li}-\text{O}$ 键的键能低于 $\text{Ti}-\text{O}$ 键^[34], 削弱钙钛矿结构中 B 位离子与氧离子之间的结合力, 导致 BO_6 八面体扭曲程度减弱和 B—O 键协同振动的“断裂”, 共同导致了相变温度的降低^[35]。同时, T_C 也会随着掺杂浓度的增加而线性减小^[36], 导致本工作中 Li_2CO_3 (约 7.5%, 摩尔分数) 的加入造成的移峰效应比 CuO (约 1%) 更明显。

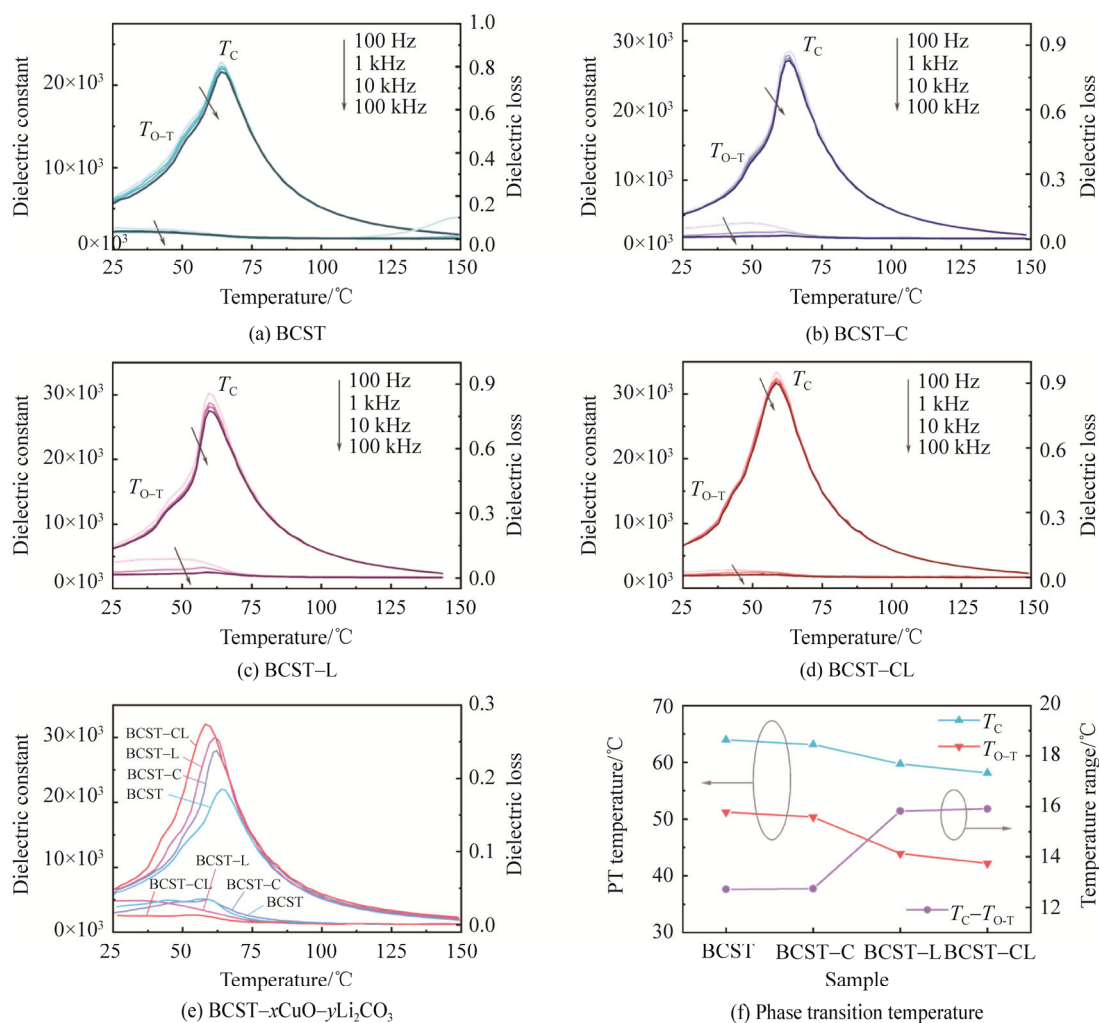
图5 BCST- x CuO- y Li $_2$ CO $_3$ 陶瓷的介电温谱Fig. 5 Dielectric temperature spectra of BCST- x CuO- y Li $_2$ CO $_3$ ceramics

图 6 为室温下 BCST- x CuO- y Li $_2$ CO $_3$ 陶瓷在 $100\text{ kV}\cdot\text{cm}^{-1}$ 电场下的电滞回线。由图 6 可见, 随着烧结助剂的介绍, 样品 BCST-C、样品 BCST-L 以及样品 BCST-CL 的极化强度得到明显提升: 一方面烧结助剂促进了晶粒长大, 弱铁电性的晶界含量降低, 陶瓷整体的极化强度得到提升; 另一方面, 根据电中和定律, 受主掺杂产生的 $V_{\text{O}}^{\bullet}$ 会与 $\text{Cu}_{\text{Ti/Sn}}^{''}$ 和 $\text{Li}_{\text{Ti/Sn}}^{''}$ 形成缺陷偶极子, 缺陷偶极子的极化率比晶胞中电子位移和离子位移的极化率高出约 3 个数量级^[37], 因此, 可以提高材料的极化值, 此外, $V_{\text{O}}^{\bullet}$ 与 $\text{Li}_{\text{Ti/Sn}}^{''}$ 的电价不平衡, 二者形成的缺陷偶极子还需要吸引周围第 3 个电荷(这里是空穴)来达到稳定^[38], 当对材料施加电场时, 载流子会发生移动并聚集在界面(晶界、陶瓷-电极)产生界面极化, 提高材料极化值^[39]。最终, 样品 BCST-C、样品 BCST-L 以及样品 BCST-CL 的极化强度由 BCST 陶瓷的 $24.1\text{ }\mu\text{C}\cdot\text{cm}^{-2}$ 分别增大到了 $28.3\text{ }\mu\text{C}\cdot\text{cm}^{-2}$,

$29.9\text{ }\mu\text{C}\cdot\text{cm}^{-2}$ 和 $31.0\text{ }\mu\text{C}\cdot\text{cm}^{-2}$ 。

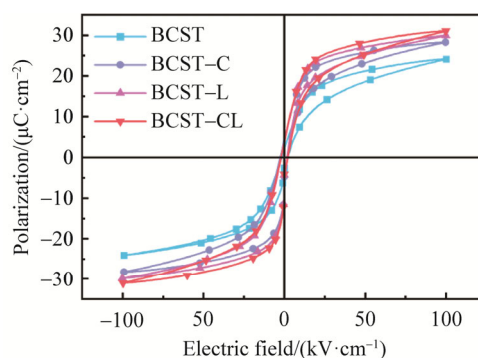
图6 室温下 BCST- x CuO- y Li $_2$ CO $_3$ 陶瓷的电滞回线Fig. 6 P - E hysteresis loops of BCST- x CuO- y Li $_2$ CO $_3$ ceramics at room temperature

图 7 为室温下 BCST- x CuO- y Li $_2$ CO $_3$ 陶瓷的击穿特性。由图 7 可见, 相比于纯 BCST 陶瓷, 烧结助剂 CuO/Li $_2$ CO $_3$ 的加入使得样品 BCST-C、样品 BCST-L 以及样品 BCST-CL 的耐击穿电场由

108.6 kV·cm⁻¹ 分别提高至 185.0 kV·cm⁻¹, 151.1 kV·cm⁻¹ 和 178.8 kV·cm⁻¹, 该耐击穿电场的提升可归因于样品 BCST-C、样品 BCST-L 以及样品 BCST-CL 晶粒的致密化生长。综上, 烧结助剂 CuO/Li₂CO₃ 的加入, 使得 BCST 陶瓷的极化强度和耐击穿场强都得到了很大的提升。

2.4 电卡性能分析

本工作采用热流法(直接法)对电卡材料性能进行测试, 热流传感器通过检测施加/撤去电场时陶瓷材料放热/吸热产生的热量 $Q^{[40]}$, 再由式(1)和式(2)计算可得到:

$$\Delta S = \frac{Q}{(\rho \times V) \times T} \quad (1)$$

$$\Delta T = \frac{Q}{(\rho \times V) \times C_p} = \frac{\Delta S \times T}{C_p} \quad (2)$$

其中: ρ 为陶瓷样品的密度; V 为有效工作体积; T 为测试时的环境温度; C_p 为陶瓷样品的比热容。

图 8 为采用热流法测得的 BCST-xCuO-yLi₂CO₃ 陶瓷的电卡性能。由图 8a 和图 8d 可见, BCST-xCuO-yLi₂CO₃ 陶瓷在约 55 °C 时电卡温变达到最大值, 这是因为在该温度下陶瓷内部处于多相共存状态, 使得陶瓷内部存在更多的极化态, 明显增大了初始熵, 使得施加电场后材料的熵变增大, 从而提高了电卡温变^[41]。在 100 kV·cm⁻¹ 的工作电场条件下, 样品 BCST-CL 的电卡温变值由 BCST 陶瓷的 1.04 K 提高到了 2.32 K, 并且展现出了良好

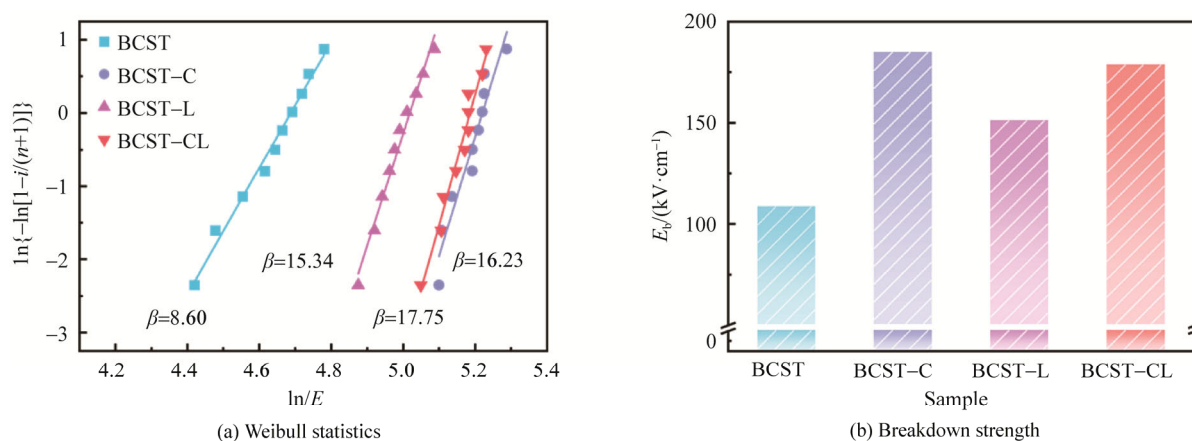


图 7 室温下 BCST-xCuO-yLi₂CO₃ 陶瓷的击穿特性

Fig. 7 Breakdown strength of BCST-xCuO-yLi₂CO₃ ceramics at room temperature

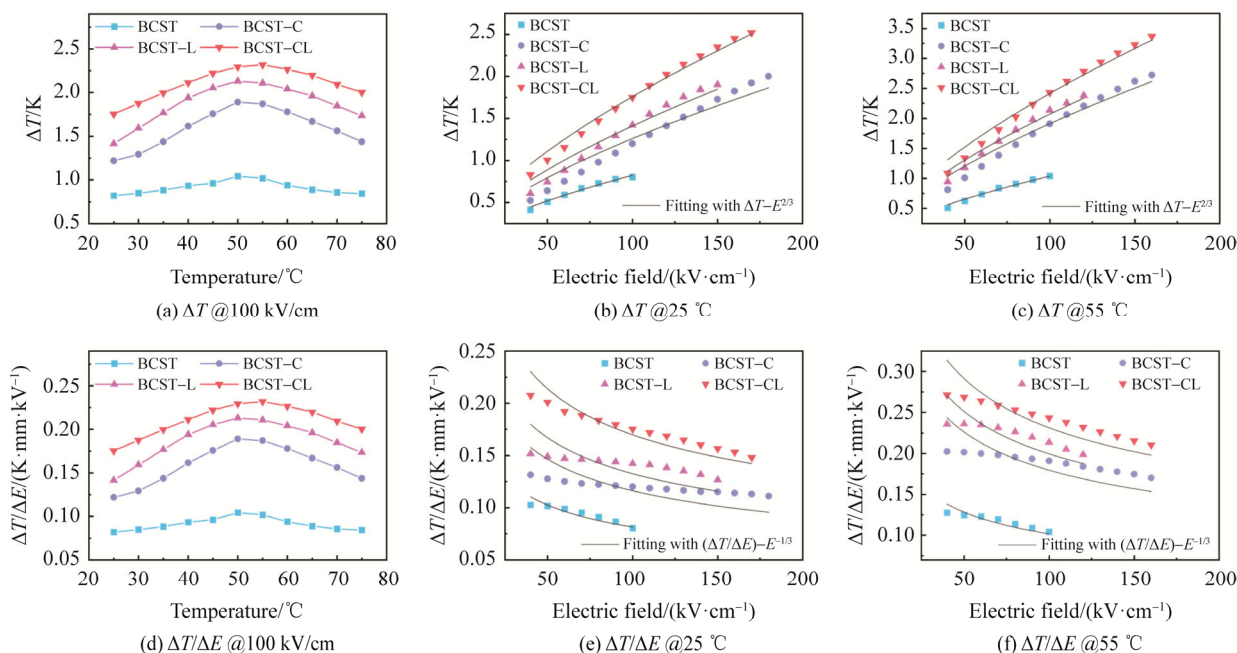


图 8 BCST-xCuO-yLi₂CO₃ 陶瓷的电卡性能

Fig. 8 Electrocaloric effect (ECE) of BCST-xCuO-yLi₂CO₃ ceramics

的温度稳定性, 在 25~75 °C 的宽温区范围内温变值均大于 1.7 K。由图 8b 和图 8e 可见, 随着烧结助剂的引入, 材料电卡性能得到了极大的提升。室温下, 样品 BCST-C、样品 BCST-L 以及样品 BCST-CL 的最大电卡温变值由 BCST 陶瓷的 0.81 K 分别提高到 2.00、1.90 K 和 2.52 K, 提升幅度最大为 3.1 倍。由 2.3 节可知, 烧结助剂的引入能提高陶瓷的致密度, 使得其工作电场得到提升, 同时, Cu^{2+} 和 Li^{+} 进入晶格发生受主取代, 扩张晶格, 铁电位移增大, 产生缺陷偶极子团簇提供额外极化, 从而使得材料的电卡强度也得到提升。击穿场强和极化强度的共同提升, 使得材料的电卡性能得到了极大的增强。

根据 Landau–Devonshire 理论, 弛豫铁电体的 ΔT 在低电场下与 E^2 成正比, 在高电场下与 $E^{2/3}$ 成正比, 随场强变化会显示出不同的电场依赖性^[42], 由图 8b 和图 8c 可知, BCST- $x\text{CuO}-y\text{Li}_2\text{CO}_3$ 陶瓷 ΔT 与 $E^{2/3}$ 表现出良好的依赖性, 而 ΔT 与 E^2 的依赖性

在低电场下并未表现出来, 这是因为多相共存状态下陶瓷内部极化旋转的能垒更低并且畴尺寸小型化, 使得极化旋转变得更容易, 场致畸变更容易发生^[43], 在低电场下 BCST- $x\text{CuO}-y\text{Li}_2\text{CO}_3$ 陶瓷就表现出了弛豫铁电体高电场下的 $\Delta T-E^{2/3}$ 关系, 使其展现出较高的电卡强度。

为了探究材料的最佳电卡性能, 测量了 BCST- $x\text{CuO}-y\text{Li}_2\text{CO}_3$ 陶瓷在约 55 °C 温度条件下临近击穿电场时的电卡温变和电卡强度值(见图 8c 和图 8f)。由图 8c 和图 8f 可见, 材料在铁电–顺电相变温度下仍能保持良好的击穿性能。其中: 样品 BCST-CL 的温变值在 160 $\text{kV}\cdot\text{cm}^{-1}$ 条件下能达到 3.37 K。

表 1 为最近报道的 BaTiO_3 基材料的电卡性能对比图(直接法)。由表 1 可知, 样品 BCST-CL 的电卡性能优异, 展现出 $\text{CuO}/\text{Li}_2\text{CO}_3$ 烧结助剂对于提高材料电卡性能的卓越贡献。

表 1 BaTiO_3 基陶瓷电卡性能对比
Table 1 Comparison of the electrocaloric effect of BaTiO_3 -based ceramics

Material	$T/^\circ\text{C}$	$\Delta E/(\text{kV}\cdot\text{cm}^{-1})$	$\Delta T/^\circ\text{C}$	$\Delta T/\Delta E/(\text{K}\cdot\text{mm}\cdot\text{kV}^{-1})$
BCST-C (This work)	55	160	2.72	0.17
BCST-L (This work)	55	120	2.38	0.20
BCST-CL (This work)	55	160	3.37	0.20
$(\text{Ba}_{0.85}\text{Sr}_{0.15})(\text{Sn}_{0.05}\text{Ti}_{0.95})\text{O}_3$ ^[41]	47	30	1.44	0.48
$0.7\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3-0.3\text{Ba}_{0.7}\text{Ca}_{0.3}\text{TiO}_3$ ^[44]	60	20	0.30	0.15
$(\text{Ba}_{0.98}\text{Ca}_{0.02})(\text{Zr}_{0.085}\text{Ti}_{0.915})\text{O}_3$ ^[45]	85	40	0.60	0.15
$(\text{Ba}_{0.95}\text{Ca}_{0.05})(\text{Ti}_{0.94}\text{Sn}_{0.06})\text{O}_3$ (tape casting) ^[46]	72	180	2.00	0.11
$0.65\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-0.35(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ ^[47]	65	20	0.33	0.17
$(\text{Ba}_{0.9}\text{Sr}_{0.1})[(\text{Ti}_{0.9}\text{Zr}_{0.1})_{0.95}\text{Sn}_{0.05}]\text{O}_3$ ^[48]	30	15	0.38	0.25
$(\text{Ba}_{0.87}\text{Ca}_{0.13})(\text{Ti}_{0.87}\text{Hf}_{0.13})\text{O}_3$ ^[49]	65	10	0.30	0.30
$(\text{Ba}_{0.85}\text{Sr}_{0.15})(\text{Zr}_{0.15}\text{Ti}_{0.85})\text{O}_3$ ^[50]	41.7	50	2.43	0.49

3 结论

加入不同含量 $\text{CuO}/\text{Li}_2\text{CO}_3$ 烧结助剂的 $\text{Ba}_{0.97}\text{Ca}_{0.03}\text{Sn}_{0.1}\text{Ti}_{0.9}\text{O}_3$ 陶瓷样品具有单一的钙钛矿结构, 晶粒大而完整, 结构致密。 $\text{CuO}/\text{Li}_2\text{CO}_3$ 烧结助剂的加入, 可以提高材料的介电常数, 同时保持 BCST 材料的宽连续相变温区。在烧结过程中 Cu^{2+} 和 Li^{+} 会进入晶粒, 扩张晶格, 增大材料的铁电位移; 并且作为受主掺杂, 与氧空位形成缺陷偶极子团簇, 提高了材料的极化强度。直接法测试表明, 陶瓷样品的电卡温变值得到极大提升同时保持着良好的工作稳定性。最终, 在样品 BCST-CL 中获得了最大

值 $\Delta T=3.37\text{ K}$ (55 °C, 160 $\text{kV}\cdot\text{cm}^{-1}$), 为电卡陶瓷材料性能的进一步提升提供了一种新的可行策略。

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Effect of CuO/Li₂CO₃ on Electrocaloric Effect of Barium Titanate-Based Ferroelectric Ceramics

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Extended Abstract

Introduction Refrigeration technology is widely used in military, commercial, industrial, and civilian fields. However, the existing mechanical compression refrigeration technology faces limitations such as large volume, high energy consumption, low cooling efficiency, and environmental unfriendliness, making it unable to meet the growing demands of emerging technological fields. The electrocaloric effect (ECE), which refers to the alignment of dipoles in polar materials under an electric field, leading to changes in entropy (ΔS) and temperature (ΔT), offers a promising alternative. Solid-state electrocaloric coolers based on the ECE are directly driven by electrical energy, which can achieve heat transfer and cooling. They exhibit some advantages such as high energy efficiency, ease of miniaturization and integration, and environmental friendliness, making them a highly potential and efficient refrigeration technology. Barium titanate (BaTiO₃)-based ceramics have attracted extensive research attention in the electrocaloric field due to their excellent polarization strength and rich phase structures. However, some challenges such as low breakdown electric fields, high sintering temperatures, and the inability to simultaneously optimize working temperature ranges and polarization strength hinder their practical applications. To address these issues, this work was to incorporate sintering additives CuO/Li₂CO₃ into lead-free Ba_{0.97}Ca_{0.03}Sn_{0.1}Ti_{0.9}O₃ ceramics to promote dense grain growth and optimize the breakdown electric field. The dielectric constant was improved, while maintaining the broad temperature range and continuous phase transition characteristics of BCST ceramics, ultimately achieving a large electrocaloric temperature change of 3.37 K (@55 °C, 160 kV·cm⁻¹).

Methods Ba_{0.97}Ca_{0.03}Sn_{0.1}Ti_{0.9}O₃ powder was synthesized by a conventional solid-state reaction sintering method at 1200 °C with BaCO₃, CaCO₃, SnO₂, and TiO₂ as raw materials in a stoichiometric ratio. The ceramic powder was then pressed into disks with the dimensions of $\phi 13$ mm×1 mm and sintered at 1350–1500 °C for 3 h to obtain dense ceramic samples. After sintering, the ceramic samples were polished, and gold electrodes were sputtered onto their surfaces. The polarization-electric field hysteresis loops (P - E loop) at room temperature were recorded by a model FETS-2000 ferroelectric tester (Wuhan Yanhe Technology Co., Ltd., China) under a frequency of 10 Hz. The values of ΔT were tested through a model RdF P/N 27134-3 heat flux sensor. The dielectric properties were obtained by a model PK-CPT1705 test system (PolyK Technologies Co., USA) with a testing temperature range from 25 to 150 °C and a frequency range from 100 Hz to 100 kHz. The microstructure of the grain was determined by a model GeminiSEM 300 scanning electron microscope (SEM) (Zeiss Co., Germany) and a model 7000 S/L X-ray diffractometer (XRD) (Shimadzu Corp., Japan).

Results and discussion The XRD patterns reveal that all ceramic samples exhibit a pure perovskite structure, indicating that Cu²⁺ and Li⁺ ions diffuse into the BCST lattice to form a solid solution. The addition of CuO/Li₂CO₃ causes the XRD diffraction peaks shifting to lower angles, indicating that Li⁺ (the radius of 0.73 Å) and Cu²⁺ (0.71 Å) substitute the B-site Ti⁴⁺ (0.61 Å) and Sn⁴⁺ (0.71 Å), leading to a lattice expansion. The SEM images demonstrate that the incorporation of CuO/Li₂CO₃ results in significant grain growth and well-developed, highly dense microstructures in the ceramic samples. The grain size increases from 7 μm to 46 μm due to the low melting points of CuO/Li₂CO₃, which induces liquid-phase sintering effects during the early stages of the sintering process, thus promoting mass transfer and facilitating grain growth and ceramic densification. Dielectric temperature spectra indicate that the addition of CuO/Li₂CO₃ significantly enhances the dielectric constant of BCST ceramics. This improvement can be attributed to two factors, i.e., the increase in grain size; second, the aliovalent acceptor doping of Cu²⁺ and Li⁺ substituting Ti⁴⁺ and Sn⁴⁺, which generates lattice defects and oxygen vacancies V_O^{••}. These defects coupled to form dipole clusters, thereby enhancing the dielectric constant. Also, the local random electric fields caused by the charge mismatch between Cu²⁺/Li⁺ and Ti⁴⁺/Sn⁴⁺, as well as the average ionic size effect, due to the reduction in the phase transition temperature. Polarization–electric field (*P–E*) loops show a significant increase in the polarization strength of the ceramic samples with the addition of CuO/Li₂CO₃, which can also be attributed to the role of dipole clusters. The electrocaloric performance of the material is greatly enhanced, with the BCST-CL ceramic achieving a giant electrocaloric temperature change of $\Delta T = 3.37$ K (i.e., at 55 °C, *E* = 160 kV·cm⁻¹).

Conclusions The Ba_{0.97}Ca_{0.03}Sn_{0.1}Ti_{0.9}O₃ (BCST) ceramic samples with varying amounts of CuO/Li₂CO₃ sintering additives exhibited a single perovskite structure, characterized by large, well-developed grains and a dense microstructure. The addition of CuO/Li₂CO₃ sintering agents enhanced the dielectric constant of the material, while preserving the broad continuous phase transition temperature range of BCST. During the sintering process, Cu²⁺ and Li⁺ ions entered the grains, leading to lattice expansion and increased ferroelectric displacement. Also, as acceptor dopants, they formed defect dipole clusters with oxygen vacancies, thereby improving the material's polarization strength. The direct measurement tests demonstrated a significant enhancement in the electrocaloric temperature change (ΔT) of the ceramic samples, while maintaining excellent operational stability. The BCST-CL composition achieved a maximum ΔT of 3.37 K (at 55 °C, 160 kV·cm⁻¹), providing a feasible strategy for further improving the performance of electrocaloric ceramic materials.

Keywords barium titanate-based ceramics; electrocaloric effect; sintering additives; dielectric constant