

$\text{K}_{0.5}\text{Bi}_{0.5}\text{TiO}_3\text{--SrTiO}_3$ 陶瓷的制备及储能性能

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摘 要: 为应对铅基电介质陶瓷带来的环境问题并满足高性能、高功率储能电容器的需求, 开发高效无铅储能材料至关重要。本工作采用传统固相反应法成功制备了 $(1-x)\text{K}_{0.5}\text{Bi}_{0.5}\text{TiO}_3\text{--}x\text{SrTiO}_3$ (KBT-ST) 无铅介电陶瓷体系。系统研究了 SrTiO_3 引入对材料微观结构、相演变及电学性能的影响。结果表明, 所有组分均形成单一钙钛矿相, 且显微结构致密; 随着 SrTiO_3 含量的增加, 陶瓷的介电常数温度稳定性显著提升, 介电峰向低温移动; 电滞回线逐渐变细证明材料从典型铁电体转变为弛豫铁电体。其中, 最优组分 0.6KBT-0.4ST 在 210 kV/cm 电场下获得了高达 3.64 J/cm^3 的可回收储能密度及 70 % 的能量效率, 表明 KBT-ST 陶瓷极具应用前景的高性能无铅储能电介质体系。

关键词: 无铅介电陶瓷; 弛豫铁电体; 储能密度; 钛酸铋钾陶瓷

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介电电容器是一种利用静电感应原理储存电能的电子元器件, 具有高功率密度、长寿命、低成本等特点, 在电磁弹射、脉冲高功率系统、精密电子、微波通信、电动汽车等领域得到大量应用^[1-3]; 然而, 与锂离子电池、燃料电池等储能器件相比, 介电电容器的能量密度较低^[4]。电介质材料通过极化效应能够显著提高电容器的电容值, 是电容器的核心部件。铅基钙钛矿铁电陶瓷 (如 PZT 基材料) 因具有优异的介电、压电及储能性能, 长期主导电子元器件市场^[5], 但铅元素的高毒性会对生态环境和人体健康造成严重危害。随着全球环保法规日趋严格及“无铅化”技术趋势的推进, 开发高性能铅基陶瓷替代材料成为材料科学与电子工程交叉领域的研究热点。

铅基钙钛矿铁电材料的优异性能很大程度上来源于 Pb 6s 轨道与 O 2p 轨道的杂化^[6], 这种孤对电子效应使铅基氧化物铁电材料具有高极化强度。而无铅铁电材料 (如 BaTiO_3 、 $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ 等) 由于不存在这种轨道杂化, 其极化强度低于铅基铁电材料。因为与 Pb^{2+} 具有类似的电子构型, 含有 Bi^{3+} 的铁电

材料被认为具有能与铅基铁电材料相媲美的铁电性质, 因此铋基钙钛矿铁电材料 (如 BiFeO_3 、 $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ 、 $\text{K}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ 等) 受到广泛关注。

然而, 铁电和线性电介质材料在储能应用中存在固有短板: 铁电体 (如 BiFeO_3 、 BaTiO_3 、 $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ 等) 核心特征是其存在长程有序的铁电畴, 在无外电场时, 内部电偶极子会自发沿某个特定晶向平行排列, 这使其具备高自发极化 (P_s), 但也导致高剩余极化 (P_r) 和低击穿强度 (BDS)。线性电介质 (如 TiO_2 、 CaTiO_3 、 SrZrO_3 等^[7-10]) 因禁带宽度较大, 故能承受更高的外加电场而不被击穿。但是其介电常数低, 极化能力较弱。这些缺点导致铁电和线性电介质材料难以同时满足高储能密度、高能量效率、高稳定性的需求。在介电储能材料中, W 是储存的总能量 [如式 (1) 所示], 可回收能量密度 (W_{rec}) [如式 (2) 所示] 与储能效率 (η) [如式 (3) 所示] 是评价其性能的关键指标, 可通过电滞回线 ($P\text{--}E$) 积分计算得出^[3,11]:

$$W = \int_0^{P_{\max}} E dP \quad (1)$$

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$$W_{\text{rec}} = \int_{P_r}^{P_{\text{max}}} EdP \quad (2)$$

$$\eta = \frac{W_{\text{rec}}}{W} \times 100\% \quad (3)$$

其中： P_{max} 为最大极化强度； P_r 为剩余极化强度。理想的介电储能材料应同时具备高的 W_{rec} 与 η 。

为克服这些缺点，许多学者通过将不同类型的介电材料进行固溶以结合各类材料的优势。目前已经有许多二元/三元固溶体系被提出，展现出良好的储能性能和温度特性。其中将铁电电介质和顺电电介质进行固溶可实现材料的极化特性与击穿性能的协同优化的方法受到了学界的广泛关注^[12–15]。将铁电性的 BiFeO_3 与顺电性的 SrTiO_3 进行固溶，打破铁电体的固有结构局限，得到兼具高极化强度和高击穿场强的薄膜材料^[9]。

钛酸铋钾(KBT)作为新兴的无铅钙钛矿型铁电材料，凭借其优异的铁电特性及环境友好性，成为最具潜力的铅基替代材料之一。在室温下 KBT 具有四方晶格，四方晶格畸变(c/a 比)约为 1.02，空间群是 $P4mm$ ^[16]；由于 Bi^{3+} 的孤对电子效应，KBT 的理论自发极化很高($P_s = 50 \mu\text{C}/\text{cm}^2$)^[17]；同时，KBT 的带隙较高($\sim 3.31 \text{ eV}$)，高于 $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ ($\sim 3.23 \text{ eV}$) 和 BiFeO_3 ($\sim 2.67 \text{ eV}$)^[18]。大自发极化和大带隙均有利于其实现高储能密度^[11]。然而室温下 KBT 呈铁电相，具有较高的剩余极化强度，导致陶瓷的储能性能不佳。将顺电材料固溶进铁电材料形成弛豫铁电体，是提高铁电材料储能性能的常用策略之一，如在 $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3\text{--SrTiO}_3$ ^[19]、 $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3\text{--BaTiO}_3\text{--SrTiO}_3$ ^[20]、 $\text{BaTiO}_3\text{--Bi}(\text{Mg}_{0.5}\text{Hf}_{0.5})\text{O}_3\text{--SrTiO}_3$ ^[12] 中，由于顺电组元 SrTiO_3 的加入，铁电体的长程有序结构被打破，材料的剩余极化强度显著降低，储能性能得到了提高。

为了增强 KBT 的弛豫特性，并提升其介电性能的温度稳定性，本工作选择 SrTiO_3 (ST)与 KBT 形成固溶体。ST 是具有量子顺电特性的钙钛矿材料，即便在极低温下，也不会转变为铁电态^[21,22]。除此之外，ST 在室温下为立方相，还具有高介电常数、低介电损耗和良好的化学稳定性等优点。因此，本工作聚焦 $\text{K}_{0.5}\text{Bi}_{0.5}\text{TiO}_3\text{--SrTiO}_3$ (KBT–ST)体系，将 ST 顺电体引入 KBT 铁电体中，能抑制 KBT 长程铁电有序，有效减小铁电畴的尺寸，形成极性纳米区域(PNRs)，因为 PNRs 尺寸小、彼此耦合弱，在外电场下可快速、灵活地定向翻转，无须克服大范围畴壁移动的阻力，宏观上表现为 P_r 降低和电滞回线变

细，从而改善 KBT 的储能性能。随着 ST 含量的增加，KBT–ST 陶瓷始终具有纯钙钛矿结构，且晶粒尺寸逐渐增大，介电峰向低温移动且介电温度稳定性提升，电滞回线逐渐变细，极化强度降低。储能性能最优的组分是 0.6KBT–0.4ST，在 $210 \text{ kV}/\text{cm}$ 电场下，实现了 $3.64 \text{ J}/\text{cm}^3$ 的可回收能量密度，储能效率为 70%，并拥有良好的介电常数温度稳定性和频率稳定性。

1 实验

1.1 样品制备

采用传统固相烧结法制备了 $(1-x)\text{KBT}\text{--}x\text{ST}$ (其中 $x = 0, 0.2, 0.4, 0.6, 0.8, 1.0$) 陶瓷样品，所采用的原料为 Bi_2O_3 ($\geq 99\%$)、 K_2CO_3 ($\geq 99\%$)、 TiO_2 ($\geq 99\%$)、 SrCO_3 ($\geq 99\%$)，均为 Aladdin 厂家生产。称量前，将 K_2CO_3 粉末放置在马弗炉中以 200°C 烘干 2 h 以去除其所吸收的水分，随后按照化学计量比称取一定质量的原料放入装有氧化锆磨球的尼龙球磨罐中，加入异丙醇为湿磨介质进行球磨，第 1 次球磨时间为 12 h。球磨结束后，将球磨罐中的浆料倒出烘干，在 850°C 煅烧 2 h，然后将煅烧后的粉末与异丙醇混合进行 22 h 的 2 次球磨，向浆料中加入 0.2% (质量分数) 的黏结剂并继续球磨 2 h。将 2 次球磨后的浆料烘干过筛后，将陶瓷粉压成直径为 10 mm、厚度 1~2 mm 的陶瓷生片。将生片放置在马弗炉中以 $2^\circ\text{C}/\text{min}$ 的速率升温至 600°C 并保温 6 h，使黏结剂分解排除。将排胶结束后的陶瓷生片放于氧化铝坩埚中并使用相同成分的煅烧后未加黏结剂的粉末进行包埋，再升温至 $1050\sim 1400^\circ\text{C}$ (ST 含量越高，烧结温度越高) 保温 2 h 进行烧结。将烧结后的陶瓷研磨至 $500\sim 650 \mu\text{m}$ 厚度后进行抛光，在陶瓷两面涂上银浆并在 850°C 热处理 20 min 形成银电极；或通过离子溅射仪在陶瓷两面沉积金膜形成金电极。用于储能性能测试的陶瓷样品，在研磨抛光后的最终厚度为 $130\sim 160 \mu\text{m}$ 。

1.2 样品表征

本文用 Rigaku 公司的 Smartlab 型号 X 射线衍射仪分析陶瓷粉末的物相组成；使用拉曼光谱仪 (Alpha 300R, WITec) 在精细抛光后的陶瓷样品上收集拉曼数据；采用 Hitachi 公司的高分辨冷场发射扫描电子显微镜 (Regulus 8230 SEM) 进行材料微观形貌表征；通过配有加热台 (INSTEC HCP421V-MP) 的 LCR 表 (HIOKI IM3536) 测试陶瓷样品的介电温谱；使用 Radiant Mutiferroic II 铁电分析仪测试陶瓷

的电滞回线。

2 结果与讨论

2.1 相结构与微观形貌分析

图 1 为室温下不同比例的 KBT- x ST 陶瓷的 X 射线衍射(XRD)谱。由图 1 可见, 纯 KBT 陶瓷在室温下表现出明显的(200)衍射峰劈裂特征, 证明其具有四方相结构^[23]; 随着 ST 含量的增加, 样品的四方畸变减弱, 晶体结构逐渐转变为立方相。(111)

衍射峰向高角度偏移, 说明晶胞体积随着 ST 含量的增加而逐渐减小。这是因为在钙钛矿 A 位十二配位环境下, Sr^{2+} 的半径(1.44 Å)小于原有的 $(\text{K}_{0.5}\text{Bi}_{0.5})^{2+}$ 离子半径(1.49 Å)^[24], 当更小半径的 Sr^{2+} 取代 A 位的更大半径的 K^+ 和 Bi^{3+} 后会引起晶格体积的缩小。所有比例的样品均可标定为钙钛矿结构, 未观察到第二相的出现。其中, KBT 和 0.8KBT-0.2ST 样品具有四方相结构, 0.6KBT-0.4ST、0.4KBT-0.6ST、0.2KBT-0.8ST 和 ST 可标定为立方相。

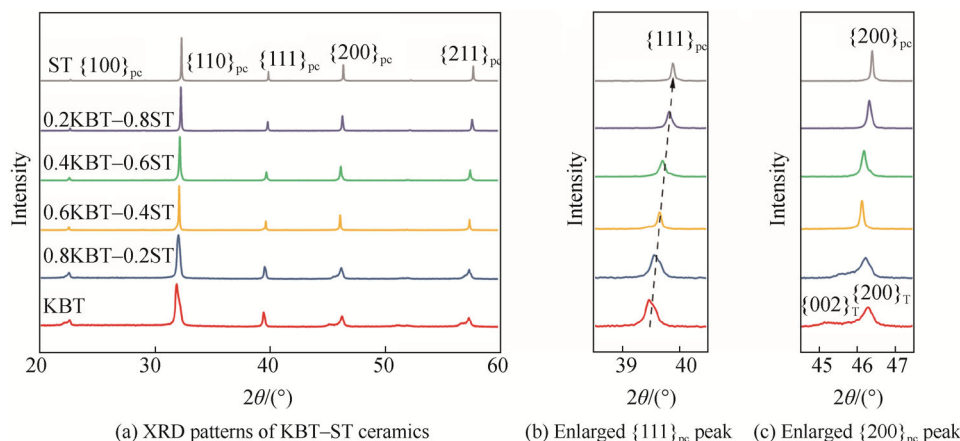


图 1 KBT- x ST 陶瓷的 XRD 谱
Fig. 1 XRD patterns of KBT- x ST ceramics

拉曼光谱能反映材料微观结构的细微变化, 可以与 XRD 结果互补^[18]。图 2 为室温下 KBT- x ST 陶瓷的拉曼光谱。由图 2 可见, 钙钛矿结构的拉曼光谱主要有 4 个区域: 180 cm^{-1} 以下的拉曼位移代表的是 A 位离子 (K^+ 、 Bi^{3+} 和 Sr^{2+})的振动模式; 在 180~400 cm^{-1} 范围内的拉曼位移对应 B—O 键(Ti—O)的振动模式; 高频区域(400~800 cm^{-1})的振动模式与 TiO_6 氧八面体的振动相关; 波数大于 800 cm^{-1} 的振动与纵向光学 A_1 和 E 有关^[11,25,26]。如图 2 所示, KBT 和 ST 在室温下的拉曼光谱与此前文献报道的光谱结果一致^[18,22]。随着 ST 含量的增加, 450~750 cm^{-1} 波数区间对应 $[\text{BO}_6]$ 八面体的拉曼峰逐渐宽化, B 位离子在八面体的不对称性增强^[27]。此外, KBT-ST 的大多数拉曼峰出现宽化和重叠现象, 证明了随着 Sr^{2+} 对 A 位的取代, 陶瓷的弛豫特性增强^[28]。这主要由 3 方面因素导致: 1)多晶陶瓷晶格排列存在无序性; 2)KBT 的 A 位存在 K^+ 、 Bi^{3+} 、 Sr^{2+} 的随机占位, 引发成分无序; 3)在较宽的组分范围内, KBT 和 ST 不同对称性的物相(四方相、立方相)共存, 不同相的拉曼信号相互叠加^[29,30]。增强的弛豫特性有利于电滞回线的滞回降低, 提升储能

性能。

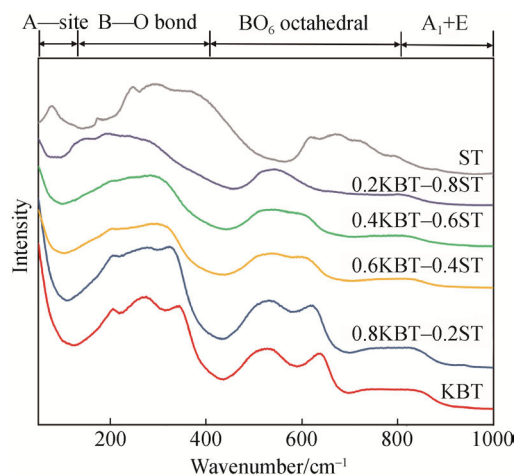


图 2 室温下 KBT- x ST 陶瓷的拉曼光谱($x = 0, 0.2, 0.4, 0.6, 0.8, 1.0$)
Fig. 2 Raman spectra of KBT- x ST ceramics at room temperature ($x = 0, 0.2, 0.4, 0.6, 0.8, 1.0$)

材料的宏观性能是微观结构的外在展现, 对材料内部微结构的解析可以更好地解释优异储能性能的来源。图 3 为 KBT-ST 陶瓷的断面显微形貌 SEM 照片, 并且标注了平均晶粒尺寸(G_a)。晶粒是陶瓷

的重要特征,改善晶粒尺寸对陶瓷的介电、储能性能等有着重要的影响^[31–35]。由图 3 可见,KBT–ST 陶瓷均呈现致密且均匀的微观结构,陶瓷的致密度高,气孔率低。随着 ST 掺杂含量的提升,陶瓷的平均晶粒尺寸增大。低 ST 含量组分晶粒较小的主

要原因是其烧结温度相对较低,抑制了晶粒的长大过程,导致最终晶粒尺寸较小;而纯 ST 陶瓷因烧结温度较高,晶粒生长更充分。致密的微观结构、较小的晶粒尺寸是实现大击穿强度、高可回收能量密度的关键^[11]。

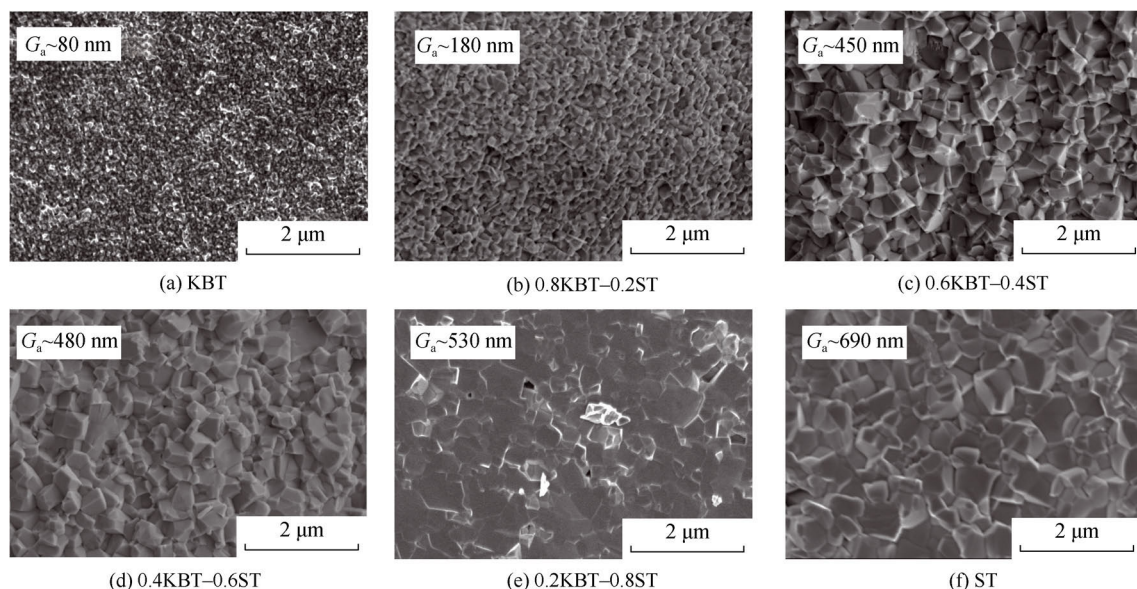


图 3 KBT–ST 陶瓷断面的 SEM 照片

Fig. 3 SEM images of fracture surfaces of KBT–ST ceramics

2.2 电学性能测试

图 4 为陶瓷介电常数和介电损耗随温度和频率变化曲线。由图 4a~图 4f 可见,随着 ST 含量的增加,介电峰(最大介电常数对应的温度)逐渐向低温方向移动,同时出现明显的色散现象,即介电峰对应的温度随测试频率的提高而增大,这是弛豫铁电体的典型特征^[36]。弛豫铁电体的频率色散程度可以用弛豫参数 γ 表征,可通过式(4)计算^[37,38]:

$$\frac{1}{\varepsilon} - \frac{1}{\varepsilon_m} = \frac{(T - T_m)^\gamma}{C} \quad (4)$$

式中: ε 和 ε_m 分别表示温度为 T 时的介电常数以及介电峰值温度(T_m)处对应的最大介电常数; C 为居里-外斯常数。 $\gamma=1$ 对应于正常铁电体, $\gamma=2$ 则对应理想弛豫铁电体。

由图 4i 可见, 0.6KBT–0.4ST 的 γ 值最大,说明其频率色散行为更明显。图 4g 对比了在 1 kHz 的测试频率下, KBT– x ST 陶瓷的介电常数随温度的变化曲线。由图 4g 可以看出,室温下的介电常数先增大后减小, 0.6KBT–0.4ST 组分达到了最大值(~ 3000),具备实现大储能密度的潜力^[11]。所有组分

在高温下都出现了介电损耗剧增的现象,是由于氧空位引起的电导损耗提高^[39]。

图 5 为 KBT–ST 陶瓷的 P – E 曲线。KBT 陶瓷的 P – E 曲线呈圆形,说明陶瓷存在较大的漏电流^[40],掩盖了 KBT 的铁电性质,与文献结果类似^[41]。随着 ST 含量的增加,陶瓷的 P – E 曲线逐渐变细,与介电温谱显示的弛豫特性增强相一致。 Sr^{2+} 掺杂破坏了 KBT 中的铁电长程有序结构,使大尺寸的铁电畴转变为尺寸较小的 PNRs。PNRs 能够随外加电场快速翻转,这就会使得 P – E 回线变细,能量效率提升。同时,由于低极化 ST 的加入,陶瓷的极化强度下降。

图 6 为 0.6KBT–0.4ST 陶瓷的电滞回线、储能特性、Weibull 分布、循环稳定性测试、温度稳定性测试,插图是对应的循环次数和不同温度下的电滞回线。由图 6 可见,凭借其高 $P_{\max}$ 和弛豫特性, 0.6KBT–0.4ST 陶瓷在 210 kV/cm 下获得了本工作研究的陶瓷中最高的可回收能量密度($W_{\text{rec}} = 3.64 \text{ J/cm}^3$)和能量效率($\eta = 70\%$)。在 210 kV/cm 电场下, 0.6KBT–0.4ST 的极化强度高达 $51.8 \mu\text{C/cm}^2$,这来源于 KBT 基材料本身的 Bi 6s 与 O 2p 之间的轨道杂

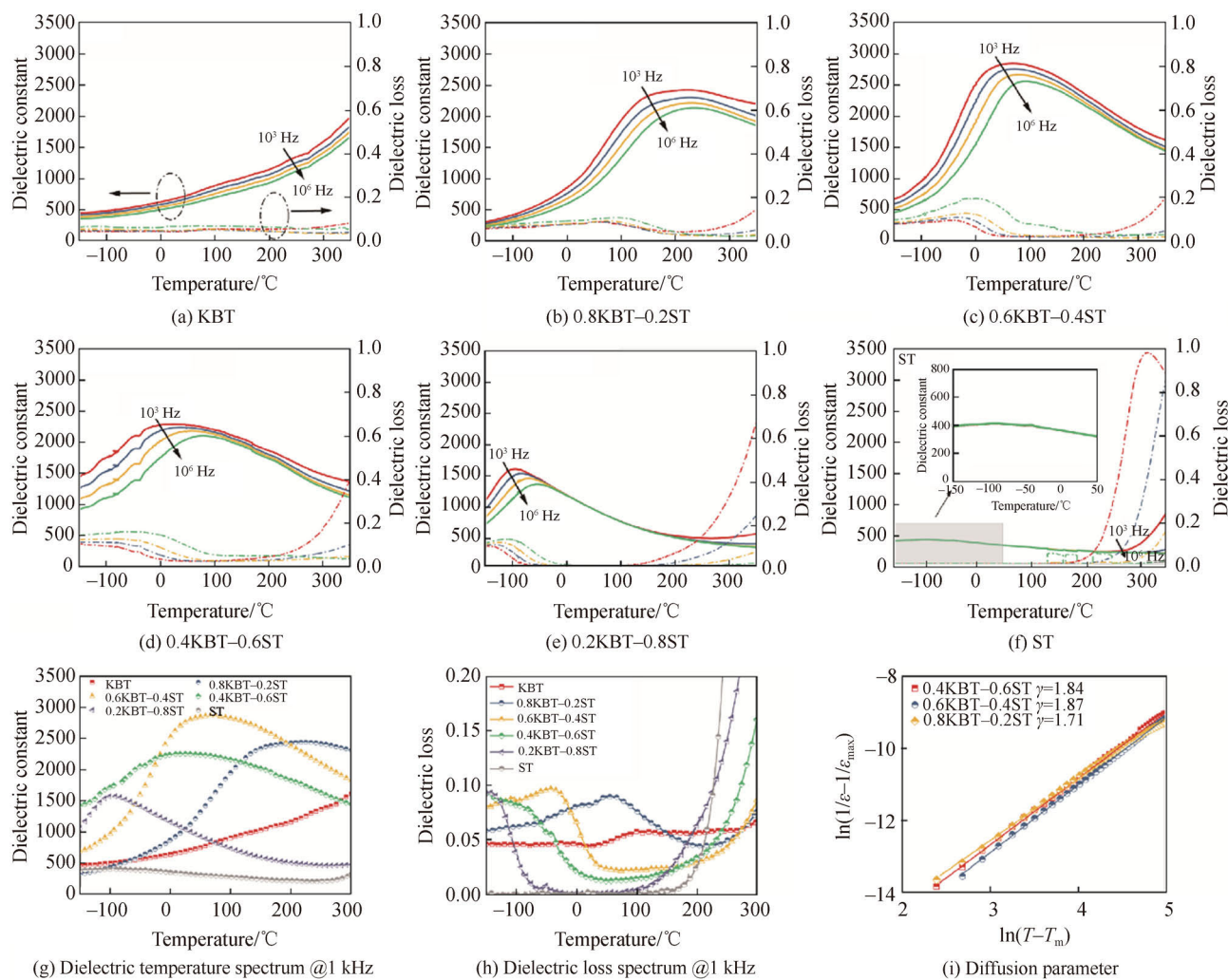


图 4 KBT-xST 陶瓷在不同频率下的介温曲线和弛豫系数

Fig. 4 Temperature dependence of dielectric spectrum of KBT-xST ceramics measured at different frequencies and diffusion parameter

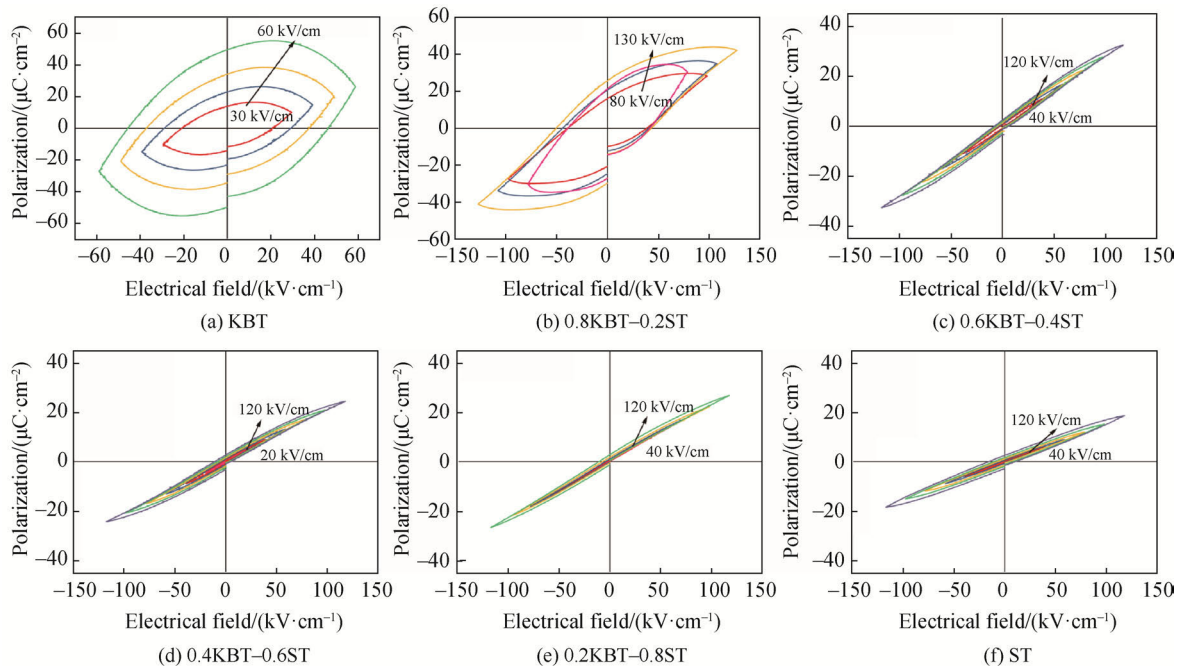


图 5 KBT-xST 陶瓷在不同电场下的电滞回线

Fig. 5 P - E loops under various electric fields of KBT-xST ceramics

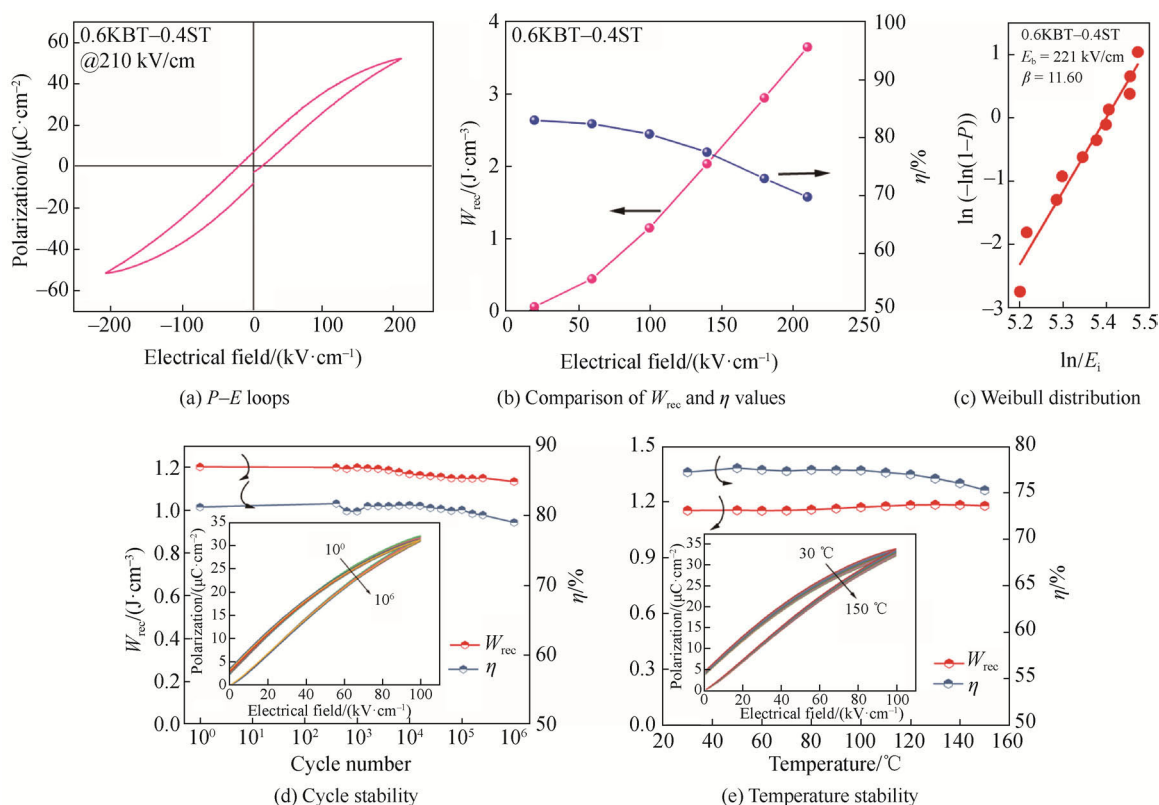


图6 0.6KBT-0.4ST陶瓷的电滞回线、储能特性、Weibull分布、循环稳定性测试、温度稳定性测试

Fig. 6 P - E loop of 0.6KBT-0.4ST, comparison of the recoverable energy storage density and efficiency of 0.6KBT-0.4ST, Weibull distribution of 0.6KBT-0.4ST, the cycling reliability and temperature stability

化^[42]；然而，随着电场的增大，0.6KBT-0.4ST陶瓷的剩余极化强度 P_r 从40 kV/cm下的 $0.5 \mu\text{C}/\text{cm}^2$ 增加到210 kV/cm下的 $6.0 \mu\text{C}/\text{cm}^2$ ，导致陶瓷的能量效率降低。由图6c可见，陶瓷 E_b 为211 kV/cm，威布尔模数 β 为11.60，证明其可靠性较高。由图6d可见，对0.6KBT-0.4ST陶瓷在100 kV/cm的电场下进行循环稳定性测试发现，在经历 10^6 次充放电循环后，材料性能变化极小(小于2.9%)，证实其具备优异的耐久性；由图6e可见，对0.6KBT-0.4ST陶瓷在100 kV/cm的电场下进行温度稳定性测试发现，陶瓷的储能密度在30~150℃温度范围变化小于1.4%，证明其具有良好的温度稳定性。

3 结论

本工作通过固相烧结法制备了 $(1-x)(\text{K}_{0.5}\text{Bi}_{0.5})\text{TiO}_3-x\text{SrTiO}_3$ ($x=0, 0.2, 0.4, 0.6, 0.8, 1.0$)无铅陶瓷，系统研究了其结构和性能变化，以及在介电储能应用中的潜力。主要结论如下：成功合成了单一钙钛矿结构的KBT-ST固溶体，随着ST含量的增加，晶格发生收缩，且 Sr^{2+} 的掺入有效引入了A位的无序度。ST的引入有效抑制了长程铁电有序，诱导材料从铁电体转变为弛豫铁电体，表现为介电峰的频

率色散增强、电滞回线变细、介电常数温度稳定性提高。在组分 $x=0.4$ (0.6KBT-0.4ST)中获得最优异的综合储能性能。ST的引入有效抑制了长程铁电有序，诱导材料从铁电体转变为弛豫铁电体，表现为介电峰的频率色散增强、电滞回线变细、介电常数温度稳定性提高。0.6KBT-0.4ST的高击穿场强与Bi 6s和O 2p轨道杂化贡献的高极化强度相结合，共同实现了 $3.64 \text{ J}/\text{cm}^3$ 的高可回收能量密度和70%的高能量效率。同时该组分的储能性能还展示出了优异的循环稳定性和温度稳定性。

综上所述，通过 SrTiO_3 固溶对KBT陶瓷进行A位改性，是优化其储能性能的有效途径。本工作不仅获得了一种具有应用前景的无铅储能陶瓷体系，也为通过调控局域结构无序性设计高性能弛豫铁电材料提供了参考。

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Energy Storage Properties of $\text{K}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ – SrTiO_3 Ceramics

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Extended Abstract

Introduction Dielectric capacitors are widely used in pulsed power and electronic systems due to their high power density, long lifespan, and low cost. However, their energy density is considerably lower than that of batteries. Dielectric materials are the core components for enhancing capacitor performance. Although conventional lead-based ceramics (*e.g.*, PZT) exhibit the superior properties, their toxicity drives the development of environmentally friendly lead-free alternatives as a major research focus. Bismuth-based perovskite materials, due to the similar electronic configurations of Bi^{3+} and Pb^{2+} , demonstrate ferroelectric properties comparable to those of lead-based materials. Among them, bismuth potassium titanate (*i.e.*, $\text{K}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$, KBT) stands out as a highly promising lead-free energy storage candidate due to its combination of high theoretical polarization and a wide bandgap. However, a pure KBT is a typical ferroelectric with a high remnant polarization, which limits its energy storage performance. In general, introducing a paraelectric material into a ferroelectric to form a relaxor ferroelectric can disrupt a long-range order and refine ferroelectric domains, thereby improving energy storage characteristics. This study selected quantum paraelectric SrTiO_3 (ST) to form a solid solution with KBT. The effect of ST content on the crystal structure, microstructure, dielectric, and ferroelectric properties was investigated. The ceramics maintained a pure perovskite phase with increasing ST content, showing a shift of the dielectric peak to lower temperatures with an enhanced frequency dispersion and gradually slimmer polarization–electric field hysteresis loops. The optimal composition (*i.e.*, 0.6KBT–0.4ST) achieved a recoverable energy storage density of 3.64 J/cm^3 and an energy efficiency of 70% in an electric field of 210 kV/cm , along with good temperature and frequency stability. The results indicated that KBT-ST is a promising class of high-performance lead-free dielectric materials for energy storage applications.

Methods In this study, $(1-x)\text{KBT}-x\text{ST}$ ceramics (where $x = 0, 0.2, 0.4, 0.6, 0.8$, and 1.0) were prepared by a conventional solid-state sintering method. The starting raw materials were Bi_2O_3 ($\geq 99\%$), K_2CO_3 ($\geq 99\%$), TiO_2 ($\geq 99\%$), and SrCO_3 ($\geq 99\%$), from Aladdin Co., China. Prior to weighing, K_2CO_3 powder was dried in a muffle furnace at 200°C for 2 h to remove absorbed moisture. The raw materials were then weighed according to the stoichiometric ratio and placed in a nylon milling jar with zirconia grinding balls. Isopropanol was added as a medium in grinding, and the raw materials were wet ground for 12 h. After grinding, the slurry was poured out, dried, and calcined at 850°C for 2 h. The calcined powder with isopropanol was further ground for 22 h. Afterwards, the slurry with 0.2% of binder was ground for additional 2 h. The slurry obtained after further grinding was dried, sieved, and pressed into green ceramic pellets with a diameter of 10 mm and a thickness of 1–2 mm. The green pellets were placed in a muffle furnace, heated at a rate of 2°C/min to 600°C , and held for 6 h to allow binder burnout. After debinding, the pellets were embedded in an alumina crucible with calcined powder of the same composition (without binder) and sintered at 1050 – 1400°C (with higher sintering temperatures corresponding to higher ST content) for 2 h. The sintered ceramics were then ground and polished. Silver paste was applied on the both sides of the ceramics and heat-treated at 850°C for 20 min to form silver electrodes. Alternatively, gold electrodes were deposited on the both sides by an ion sputtering coater. The phase composition of the ceramic powders was analyzed by a model Smartlab X-ray diffractometer (XRD) (Rigaku Co., Japan). The Raman spectra were determined on well-polished ceramic samples by a model Alpha 300R Raman imaging microscope (WITec Co., Germany). The microstructure of the materials was characterized by a model Regulus 8230 high-resolution cold-field emission scanning electron microscope (Hitachi Co., Japan). The temperature-dependent dielectric properties were measured by a model IM3536 LCR meter (HIOKI Co., Japan) equipped with a model HCP421V-MP heating stage (INTEC Co., USA). The polarization–electric field (P – E) hysteresis loops of the ceramics were tested by a model Multiferroic II ferroelectric analyzer (Radiant Co., USA).

Results and discussion The results show that the $(1-x)\text{K}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ – $x\text{SrTiO}_3$ (KBT–ST) lead-free dielectric ceramic system is synthesized by a conventional solid-state reaction method. The effect of SrTiO_3 incorporation on the microstructure, phase evolution, and electrical properties of the materials is systematically investigated.

The XRD patterns and SEM images confirm the formation of a single perovskite phase and a dense microstructure for all the compositions. The temperature stability of the dielectric constant is significantly enhanced, accompanied by a shift of the dielectric

peak towards lower temperatures, as SrTiO_3 content increases. The gradual slimming of polarization-electric field hysteresis loops indicates a transformation from a typical ferroelectric to a relaxor ferroelectric state. The optimal composition (*i.e.*, 0.6KBT-0.4ST) exhibits a high recoverable energy storage density of 3.64 J/cm^3 and an energy efficiency of 70 % in an electric field of 210 kV/cm . This work demonstrates that KBT-ST ceramics constitute a highly promising lead-free dielectric system for high-performance energy storage applications.

Conclusions In this work, KBT-ST lead-free ceramics were prepared by a solid-state sintering method. Their structural evolution, properties, and potential for dielectric energy storage applications were systematically investigated. Single-phase perovskite-structured KBT-ST solid solutions were successfully synthesized. The lattice contraction occurred, and the incorporation of Sr^{2+} effectively introduced A-site compositional disorder as the ST content increased. The addition of ST effectively suppressed a long-range ferroelectric order, thus inducing a transition from a ferroelectric to a relaxor ferroelectric state. This transition was evidenced by enhanced frequency dispersion of the dielectric peak, slimmer polarization-electric field hysteresis loops, and improved temperature stability of the dielectric constant. The optimal energy storage performance was achieved in the composition with x of 0.4, which exhibited the optimal overall energy storage properties. The introduction of Sr^{2+} produced a synergistic effect. It enhanced a local polarization, and suppressed a long-range ferroelectric order, promoting the formation of an ergodic relaxor state. The effects both contributed to a reduction in $(P_{\text{max}}-P_{\text{r}})$. The high breakdown strength of 0.6KBT-0.4ST, combined with the high polarization contributed by the hybridization between Bi $6s$ and O $2p$ orbitals, collectively yielding a high recoverable energy density of 3.64 J/cm^3 and a high energy efficiency of 70 %. Furthermore, this composition demonstrated superior cycling stability and temperature stability in its energy storage performance. In summary, A-site modification of KBT ceramics through SrTiO_3 solid solution was an effective strategy for optimizing their energy storage properties. This study could present a promising lead-free energy storage ceramic system and provide a valuable reference for designing high-performance relaxor ferroelectrics *via* tuning local structural disorder.

Keywords lead-free dielectric ceramics; relaxor ferroelectrics; energy storage density; potassium bismuth titanate ceramics