

铌酸钠基无铅陶瓷的弛豫反铁电相构筑与储能特性优化

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摘 要: 开发具有优异综合储能特性的无铅陶瓷电容器是脉冲功率技术领域的迫切需求。相较于其他无铅储能陶瓷体系, NaNbO_3 (NN)陶瓷具有结构相变丰富、理论密度低、电学可调性强、轻量化发展潜力大等显著优点, 因而备受关注, 成为当前的研究热点。基于降低容忍因子稳定反铁电相和增强陶瓷弛豫性的策略, 开展了 NN 基弛豫反铁电陶瓷的制备与储能特性研究。通过引入 BiFeO_3 和 $\text{Sr}(\text{Ti}_{0.85}\text{Zr}_{0.15})\text{O}_3$ 成功制备了 $0.9[0.9\text{NaNbO}_3-0.1\text{BiFeO}_3]-0.1\text{Sr}(\text{Ti}_{0.85}\text{Zr}_{0.15})\text{O}_3$ 陶瓷, 相较于纯 NN 陶瓷(0.14 J/cm^3 、6.39%)和 $0.9\text{NaNbO}_3-0.1\text{BiFeO}_3$ 陶瓷(3.55 J/cm^3 和 70.61%), 其储能特性显著提升, 储能密度(W_{rec})与储能效率(η)分别达到了 5.22 J/cm^3 、83.92%。其优异的储能特性源于 BiFeO_3 和 $\text{Sr}(\text{Ti}_{0.85}\text{Zr}_{0.15})\text{O}_3$ 掺杂对陶瓷的晶粒细化、反铁电相稳定性和弛豫特性的双增强机制。同时, $0.9[0.9\text{NaNbO}_3-0.1\text{BiFeO}_3]-0.1\text{Sr}(\text{Ti}_{0.85}\text{Zr}_{0.15})\text{O}_3$ 陶瓷表现出良好的温度及频率稳定性, 是一种极具应用前景的电介质储能材料。

关键词: 铌酸钠; 无铅陶瓷; 反铁电; 储能特性; 充放电特性

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以高电压、大电流、高功率为特征的脉冲功率技术在国防工业领域具有极其广泛与重要的应用。电介质电容器是脉冲功率装置的关键储能元器件之一, 其储能特性的优化是推动脉冲功率技术深度应用的关键。陶瓷电介质电容器具有充放电速率快、机电性能好、抗老化、耐极端条件等优点, 是当前电介质储能领域的重点关注材料之一^[1-5]。然而, 目前 BaTiO_3 基电介质陶瓷在高场下的储能特性普遍偏低, 而铅基陶瓷电容器因含有剧毒元素铅而受到限制。因此, 开发具有优异综合储能特性的无铅陶瓷电容器, 是当前脉冲功率技术领域的迫切需求, 更是电子元器件向小型化、集成化、轻量化发展的必然要求^[6-17]。

纯 NaNbO_3 陶瓷在室温时为亚稳态反铁电 P 相 (P_{bcm}), 当受到外电场作用时, 它将不可逆地转变为铁电 Q 相(P_{21ma})^[18]。这是因为反铁电 P 相和诱

导铁电正交 Q 相的自由能非常接近。因此, 纯 NaNbO_3 陶瓷的电滞回线是方形的 $P-E$ 回线, 而非双电滞回线, 具有非常低的击穿电场(E_b)和高的剩余极化强度(P_r), 因此可释放能量密度(W_{rec})和储能效率(η)都非常低^[19]。为了改善 NaNbO_3 陶瓷的储能特性, 研究人员通过掺杂改性、优化制备工艺等手段对弛豫铁电、反铁电和弛豫反铁电型 NaNbO_3 基陶瓷做了大量的研究^[20-32]。相对于典型的无铅反铁电体 AgNbO_3 来说, NN 作为另一类重要的无铅反铁电体, 具有理论密度低(4.55 g/cm^3)、极化强度大($40\text{ }\mu\text{C/cm}^2$)、制备工艺简单(无需在氧气氛下烧结)、且原材料价格相对低的优点, 因而更有利于未来商业化和储能装置的轻量化、集成化发展。目前, NN 基弛豫反铁电储能陶瓷的研究仍然处于起步阶段。虽然已有报道显示该材料具有高的储能密度, 但要开发具有优异综合储能特性的 NN 基弛豫反铁电陶

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瓷仍然面临挑战。因此, 进一步探索 NN 基弛豫反铁电陶瓷的结构与储能特性之间的关联仍然是 NN 基储能陶瓷研究工作的重点。

ABO₃ 钙钛矿结构的稳定性可由经典的容忍因子 t 来描述, 如式(1)所示:

$$t = \frac{R_A + R_O}{\sqrt{2}(R_B + R_O)} \quad (1)$$

其中: R_A , R_B , R_O 分别为 A 位, B 位阳离子和 O²⁻ 的半径。当掺杂后, A/B 位离子不唯一时, 需要使用平均离子半径来计算结构的容忍因子。当 t 处于 0.85 到 1.05 的范围之间时, 钙钛矿结构是稳定的; 当 t 大于 1 时, B 位阳离子尺寸较小, 可发生偏心位移, 结构趋于铁电稳定状态; 当 t 小于 1 时, A 位阳离子相对较小, 氧八面体发生倾斜, 结构趋于反铁电稳定状态。因此, 通过元素掺杂来降低 NN 的容忍因子是稳定其反铁电相的有效手段^[33-36]。

本工作采用降低容忍因子的策略, 在纯 NN 中掺入 10%(摩尔分数)具有低容忍因子的 BiFeO₃(BF, 容忍因子: 0.954 3)作为第 2 组元, 将 NN 陶瓷的反铁电 R 相(*Pbnm*)稳定到室温, 在此基础上, 引入第 3 组元 Sr(Ti_{0.85}Zr_{0.15})O₃(STZ)来进一步提高陶瓷的弛豫性, 进而在 NN 基陶瓷中实现了弛豫反铁电体的构筑。基于此, 对陶瓷的相结构、显微结构、储能特性与稳定性以及脉冲充放电性能进行系统分析, 进一步揭示了 NN 基弛豫反铁电陶瓷的性能改善机制和调控方法, 为 NN 基陶瓷电介质的创新发展和深度应用提供了启示。

1 实验

1.1 样品制备

本工作中陶瓷化学组成为 NaNbO₃, 0.9NaNbO₃-0.1BiFeO₃, 以及 (1- x)[0.9NaNbO₃-0.1BiFeO₃]- x Sr(Ti_{0.85}Zr_{0.15})O₃, 其中 $x=0.05, 0.10, 0.15$, 为了方便说明, 将其简记为: NN, NN-BF 以及 NN-BF- x STZ, $x=5, 10, 15$, 所有陶瓷均采用传统固相法制备。首先, 将化学原料按照化学计量比进行精确称量, 将称取的原料和一定比例的球磨介质(无水乙醇和氧化锆球, 料、球、无水乙醇的质量比为 1:2:1)置于行星式球磨机上, 球磨 24 h, 转速为 300 r/min。球磨结束后, 将浆料置于鼓风干燥箱中烘干, 再将粉体装入氧化铝坩埚中, 并置于高温箱式电阻炉内进行预烧, 预烧温度为 850 °C, 保温时间为 5 h。在预合成的陶瓷粉体中加入质量浓度为 8%(质量分数)的聚乙烯醇(PVA)水溶液进行造粒, 对

造粒好的陶瓷粉体过 80 目筛, 并静置陈化 24 h, 单次称取 0.27 g 造粒后的陶瓷粉体, 均匀置于直径为 12 mm 的不锈钢模具内, 在 200 MPa 的压力下保压约 30 s, 脱模后即可得厚度约为 0.8 mm 的陶瓷生坯。最后, 将陶瓷生坯放置于排胶炉内进行排胶, 加温程序为以 1 °C/min 的升温速率加热到 600 °C, 保温 10 小时。最后, 将陶瓷生坯放置于马弗炉内进行烧结, 升温速率为 3 °C/min, 烧结温度为 1 230~1 260 °C, 保温时间为 2 h。

1.2 样品表征

采用 DX-2700BH(Haoyuan Instrument)型 X 射线衍射仪分析陶瓷的晶体结构, 扫描范围为 20°~80°, 扫描速率为 2 (°)/min。本工作使用的拉曼光谱仪是由法国 HORIBA 公司生产的 Lab-Ram HR800 型光谱仪, 激光波长为 532 nm。拉曼光谱的原位变温测试是在 Linkam THMS600 控温台上进行的。用于原位电场下拉曼光谱测试的样品, 采用离子溅射法镀电极, 设置溅射电流为 6 mA, 溅射时间为 2 min, 以保证样品同时具有导电性和拉曼光谱测试激光的穿透性。使用台式扫描电子显微镜(Phenom Scientific)对样品自然表面形貌进行观测, 并使用 Nano Measurer 软件对陶瓷晶粒尺寸进行统计。将样品减薄后, 采样日本电子株式会社的 JEM-2100F 型场发射透射电子显微镜观察陶瓷样品的电畴结构。将样品打磨到 0.5 mm, 清洗干净, 在样品上下表面镀银电极后, 采用美国 Agilent 公司生产的 E4980A 精密 LCR 电桥, 在 -120~450 °C 温度范围内测试陶瓷样品的介电性能。本工作采用美国 Radiant 公司生产的 Precision Premier II 型铁电测试仪测试陶瓷样品的电滞回线, 测试样品厚度为 150 μm。

2 结果与讨论

2.1 相结构分析

图 1a 和图 1b 为 NN, NN-BF 和 NN-BF- x STZ 陶瓷的 XRD 谱及其局布放大图。由图 1a~图 1b 可见, 所有组分陶瓷均为纯的钙钛矿结构, 未发现第 2 相的衍射峰, 表明所有掺杂元素均能进入 NN 晶格形成固溶体。通过与标准卡片比对发现, NN 陶瓷室温下为反铁电正交 *P*(*Pbcm*)相, 表现为劈裂的 (110)和(200)衍射峰。然而由于 X 射线衍射精度的限制, 反铁电 *P* 相的超晶格衍射峰无法明显看到。随着 BF 和 STZ 的掺入, 正交相特征消失, 表现为(110)和(200)衍射峰从劈裂状态变为单峰, 说明 BF 和 STZ 的掺入使陶瓷的对称性提高, 转变为立方相。

为了进一步说明陶瓷的相结构演变,对陶瓷进行了介电温谱和拉曼光谱测试,如图 1c 和图 1d 所示。从介电温谱中可以看到,NN 陶瓷在 400 °C 附近存在一个明显的介电异常峰,代表其反铁电 P 相到反铁电 R 相的转变。BF 的掺入引起了结构相变, P-R 相变峰消失,在 -100 °C 附近出现一个弥散的介电异常峰,且和 NN 陶瓷相比, NN-BF 陶瓷的室温介电常数明显增大,从先前的研究可以判断,这主要是由于陶瓷中出现了反铁电 R 相引起的。进一步地,随着 STZ 的掺杂,该峰变得更加扁平化,说明多种、异质离子的引入增大了随机无规场,破坏了陶瓷的反铁电长程有序,使陶瓷的弛豫性得到增强,同时,当 STZ 掺杂含量从 0 增大到 0.15,陶瓷的介

电常数从 850 降低到了 585,该特点有助于储能特性和温度稳定性的改善。

图 1d 为陶瓷的拉曼光谱,可以发现,NN 在 $100\sim300\text{ cm}^{-1}$ 的范围内能够观察到多个峰,这些峰来源于 Nb—O 键长的差异和复杂的氧八面体倾斜,和 XRD 及介电温谱的结果相互印证,表明 NN 在室温下是具有低对称性的反铁电 P 相。在 NN-BF 陶瓷中,由于 Nb—O 键的键长差异减小,这些峰合并消失,陶瓷对称性增强,反铁电畸变减弱,表明 NN-BF 陶瓷室温下为反铁电 R 相。随着 STZ 的进一步掺杂,分别与 B—O 键和 BO_6 八面体振动相关的 ν_5 和 ν_1 振动模有宽化和峰强降低的趋势,说明陶瓷的极性降低、无序性增强,与介电温谱的结果相一致^[26,37]。

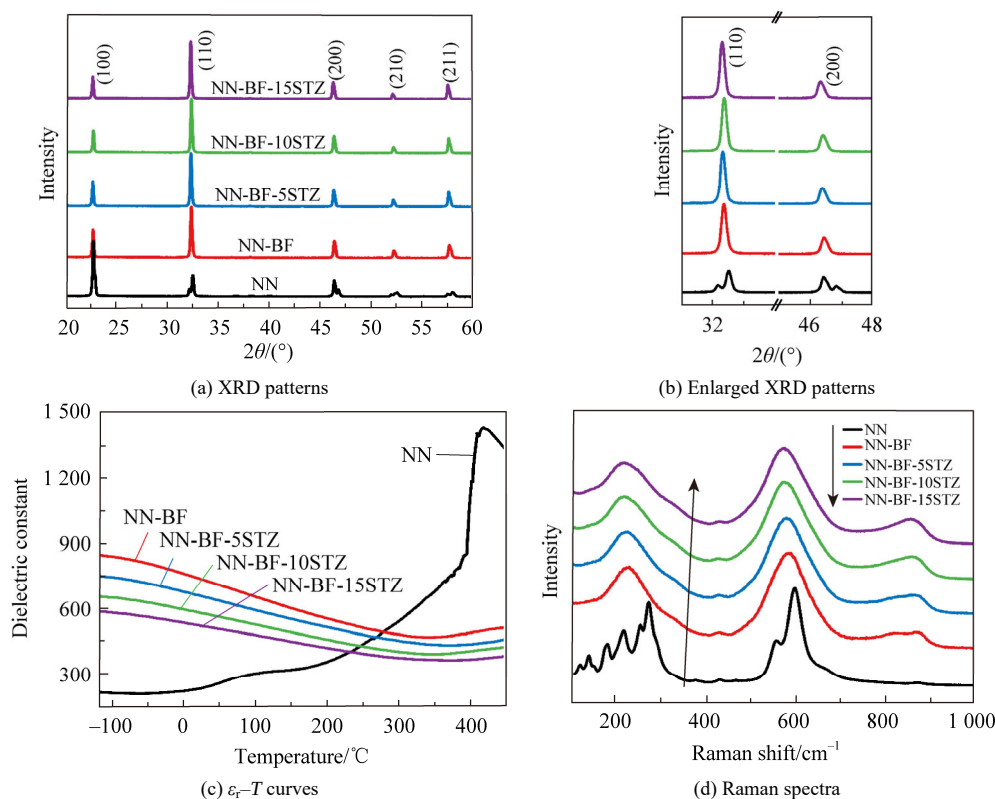


图 1 NN、NN-BF 和 NN-BF-xSTZ 陶瓷的 XRD 图谱、介电温谱及拉曼光谱

Fig. 1 XRD patterns, temperature-dependent dielectric constant and Raman spectra of NN, NN-BF and NN-BF-xSTZ ceramics

为了探究 NN-BF-10STZ 陶瓷相结构随温度和电场的变化,对 NN-BF-10STZ 陶瓷在 30~300 °C 温度范围内进行 XRD 测试,如图 2 所示,从图中可以观察到,NN-BF-10STZ 陶瓷在测试温度范围内均为纯的钙钛矿结构,(110)和(200)衍射峰没有明显的劈裂,表明该陶瓷在相对较宽的温度范围内具有稳定的赝立方相。此外,XRD 衍射峰随温度升高逐渐向低角度移动,这主要是高温引起的晶格膨胀引起的。图 3a 为 NN-BF-10STZ 陶瓷不同温度下的拉曼光谱,可以发现,拉曼振动模数在 -120~250 °C

温度区间内没有明显改变,表明 NN-BF-10STZ 陶瓷的局域结构的对称性具有良好的温度稳定性,这与介电温谱和变温 XRD 的结果相一致。图 3b 为 NN-BF-10STZ 陶瓷在不同电场下的拉曼光谱,在 0~300 kV/cm 的电场强度下,拉曼光谱始终维持稳定的曲线形状而没有发生明显的改变。

2.2 显微结构分析

图 4a、图 4c 和图 4e 为 NN、NN-BF 和 NN-BF-10STZ 陶瓷的表面形貌照片,从图中可见,各陶瓷样品气孔较少,且均具有非常致密的结

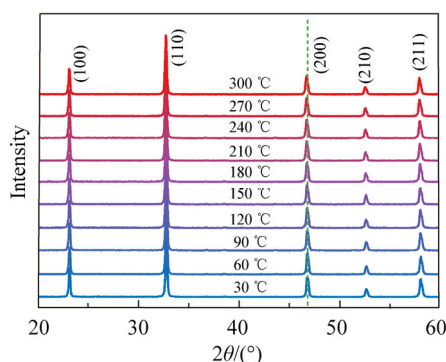
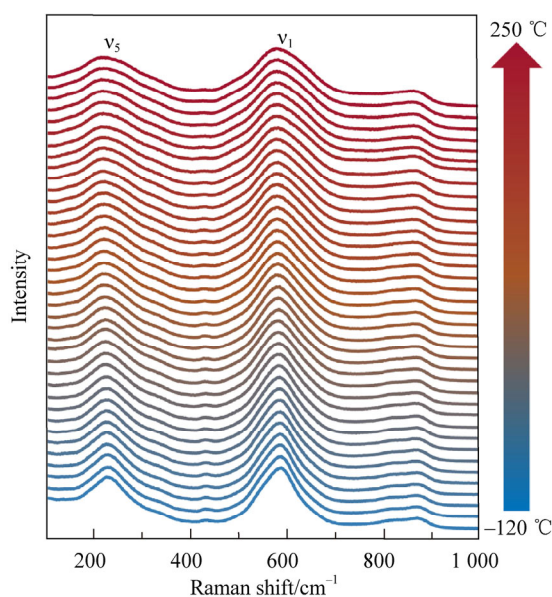
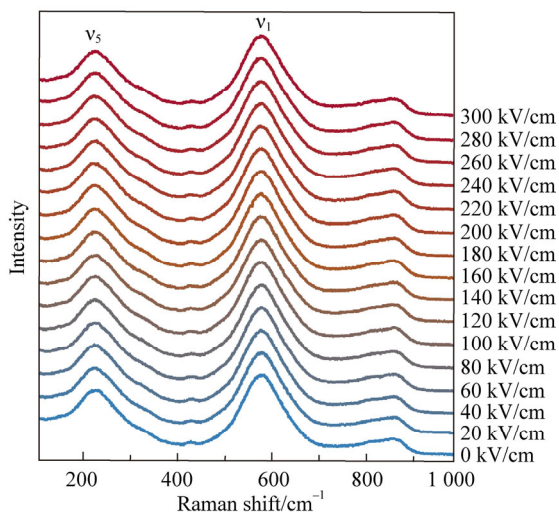


图 2 NN-BF-10STZ 陶瓷的变温 XRD 谱

Fig. 2 XRD patterns of the NN-BF-xSTZ ceramics under different temperatures



(a) Raman spectra under different temperatures



(b) Raman spectra under different electric fields

图 3 NN-BF-10STZ 陶瓷的拉曼光谱随温度和电场的变化

Fig. 3 Raman spectra of the NN-BF-10STZ ceramics under different temperatures and electric fields

构。图 4a 显示, NN 陶瓷的微观结构由大小晶粒紧密结合而成, 大尺寸晶粒周围散落着小尺寸晶粒, 晶粒尺寸分布不均匀。BF 的加入, 显著抑制了晶粒长大, 相比于图 4a, 陶瓷中大尺寸晶粒的数目明显减少, 晶粒分布的均匀性得到提高。随着 STZ 的加入, 陶瓷的晶粒尺寸进一步降低。

图 4b、图 4d、图 4f 为陶瓷的晶粒尺寸统计分布。由图中可知, BF 掺杂将陶瓷的晶粒尺寸从 $5.73 \mu\text{m}$ 降低到了 $3.74 \mu\text{m}$, STZ 掺杂进一步将晶粒尺寸降低到了 $3.56 \mu\text{m}$ 。对晶粒尺寸分布作高斯拟合, 结果为图 4b、图 4d、图 4f 中的紫色实线。NN-BF 和 NN-BF-10STZ 陶瓷的晶粒分布符合正态分布, 而 NN 陶瓷的晶粒分布为偏态分布, 说明 BF 和 STZ 掺杂以后陶瓷的晶粒分布均匀性显著提高, 而均匀的晶粒分布有利于陶瓷内部电场分布的均匀性。在晶粒尺寸降低和分布均匀性提高的共同作用下, 陶瓷的耐击穿场强有望得到增强^[38-40]。

BF 及 STZ 掺杂使陶瓷的长程有序结构被破坏, 弛豫性增强, 促进纳米反电畴形成。为了直观地观察陶瓷的电畴结构, 采用 TEM 对 NN-BF 及 NN-BF-10STZ 陶瓷的电畴结构进行了表征, 如图 5 所示。从图中可以明显观察到 STZ 掺杂明显降低了反铁电畴的尺寸, 增加了畴密度, 由于纳米电畴的高活性和低能量壁垒, 在电场作用下更容易发生翻转从而产生大的极化强度, 而当电场撤去以后纳米电畴能够很快恢复到初始的状态因此可以降低剩余极化强度和极化滞后, 有利于储能特性, 特别是储能效率的优化。

2.3 极化和储能特性分析

图 6 为样品 NN、NN-BF 以及 NN-BF-10STZ 陶瓷的双极电滞回线。其中, NN 陶瓷由于亚稳态的反铁电 P 相在电场作用下不可逆地转变为铁电 Q 相, 因此其反铁电-铁电相变只出现于第一次加载电场时。当引入 BF 第 2 组元以后, 陶瓷的反铁电 R 相得以稳定, 同时弛豫性增强, $P-E$ 曲线表现出“束腰型”的类双电滞回线特征。此后, 随着 STZ 第 3 组元的引入, 陶瓷的弛豫特性得以进一步增强, NN-BF-10STZ 陶瓷的 $P-E$ 曲线变得更加细长, 极化滞后得到显著抑制。

为了计算陶瓷的储能密度和储能效率, 对 NN、NN-BF 和 NN-BF-xSTZ 陶瓷进行了单极 $P-E$ 曲线测试, 如图 7 所示。其中 NN 陶瓷由于电场诱导的铁电 Q 相, 因而导致其 P_{max} 超过 $40 \mu\text{C}/\text{cm}^2$, 但过高的 P_r 和低的击穿场强, 使其 W_{rec} 仅为 $0.14 \text{ J}/\text{cm}^3$, η

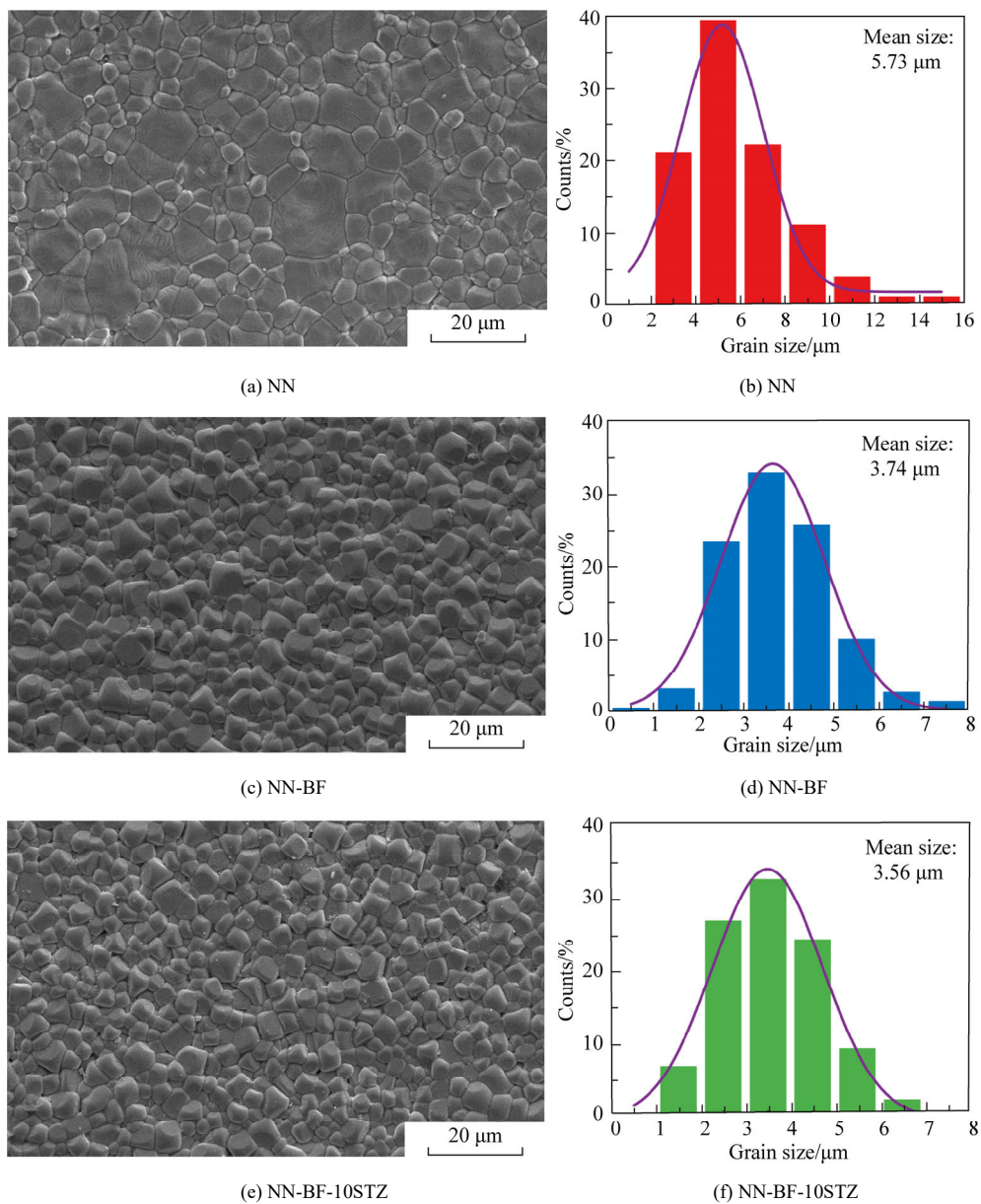


图4 NN、NN-BF 和 NN-BF-10STZ 陶瓷的 SEM 照片及其晶粒尺寸统计分布

Fig. 4 SEM images and grain size distribution of the NN, NN-BF, and NN-BF-10STZ ceramics

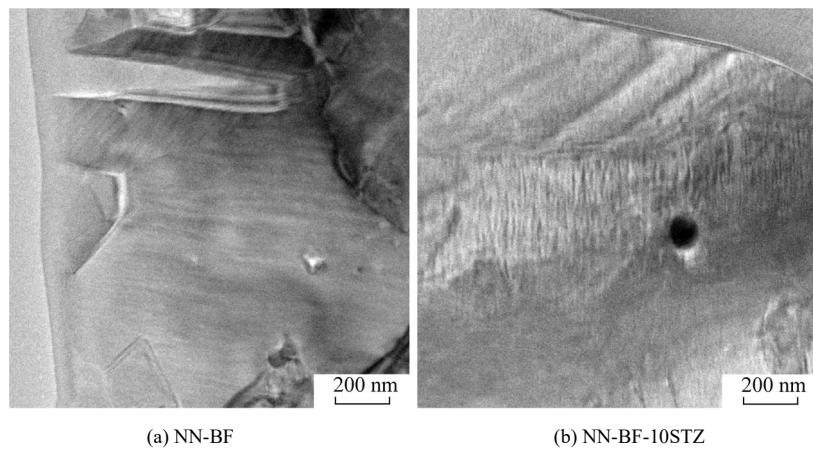


图5 NN-BF 和 NN-BF-10STZ 陶瓷的 TEM 照片

Fig. 5 TEM images of NN-BF and NN-BF-10STZ ceramics

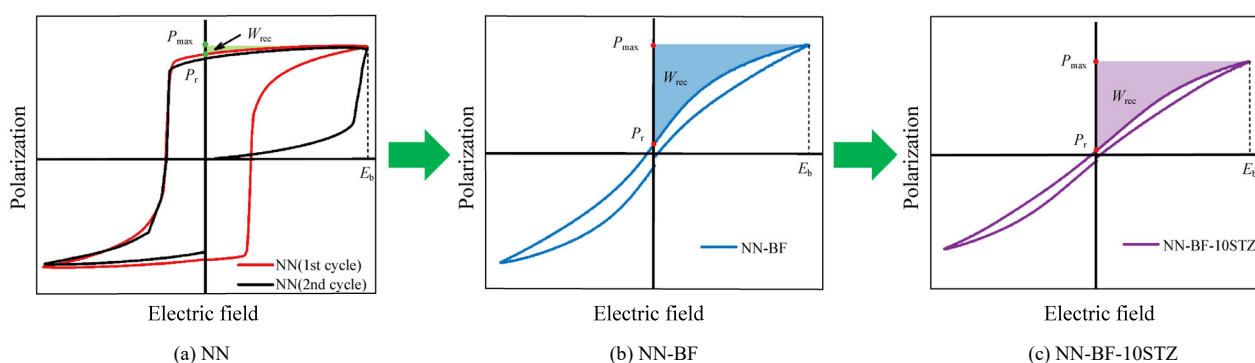


图 6 NN、NN-BF 和 NN-BF-10STZ 陶瓷的双极 P - E 曲线
Fig. 6 Bipolar P - E loops of NN, NN-BF and NN-BF-10STZ ceramics

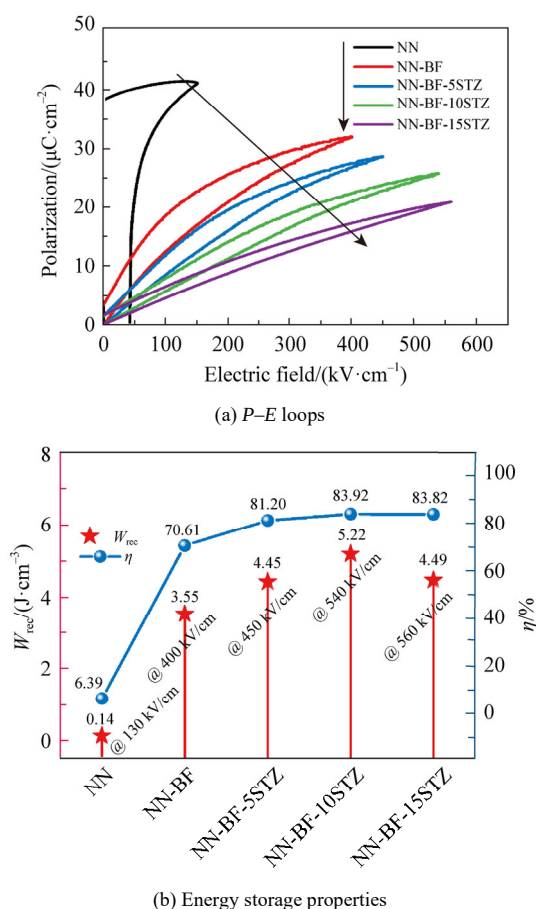


图 7 NN、NN-BF 和 NN-BF- x STZ 陶瓷的单极 P - E 曲线和储能特性
Fig. 7 Unipolar P - E loops and energy storage properties of NN, NN-BF, and NN-BF-10STZ ceramics

仅为 6.39%。随着 BF 第 2 组元的引入, 陶瓷表现出一定的反铁电特征, 表现为在 100 kV/cm 电场附近陶瓷极化强度变化率有明显的改变; 随着 STZ 的进一步掺杂, 陶瓷的 P - E 曲线变得更加“细长”, $P_{\max}$ 从 32.05 $\mu\text{C}/\text{cm}^2$ 降至 20.8 $\mu\text{C}/\text{cm}^2$, P_r 从 3.28 $\mu\text{C}/\text{cm}^2$ 降至 1.70 $\mu\text{C}/\text{cm}^2$, E_b 从 400 kV/cm 提升至 560 kV/cm。在极化强度和击穿场强的综合作用下, NN-BF-

10STZ 实现了最优的综合储能特性, W_{rec} 达到了 5.22 J/cm^3 , 同时其 η 保持于 83.92%。

图 8 为 NN-BF-10STZ 陶瓷在不同电场下的 P - E 曲线。可以看出, 在低电场强度下, 陶瓷极化强度随电场强度线性增大。当电场强度达到 400 kV/cm, 回滞明显增大, 这源于陶瓷所发生的反铁电-铁电相变。但是由于其强弛豫特性, 双电滞回线特征并不明显。随着电场强度增加至 500 kV/cm, P - E 曲线出现拐点而“低头”, 意味着陶瓷已经达到了饱和极化强度。当外加电场撤去以后, 电场诱导的铁电相会迅速恢复到反铁电相, P_r 降低从而产生大的 ΔP , 如图 8b 所示。NN-BF-10STZ 陶瓷不同电场下的储能特性如图 8c 所示, W_{tot} 和 W_{rec} 随电场强度增大而增大, η 随电场强度增大不断降低, 但始终能够保持在 80% 以上。

基于此相结构和弛豫性调控, 陶瓷的储能特性得到显著优化, 如图 9 所示。 W_{rec} 和 η 分别从 NN 陶瓷的 0.14 J/cm^3 、6.69% 上升至 NN-BF 陶瓷的 3.55 J/cm^3 、70.61%, 再到 NN-BF-10STZ 陶瓷的 5.22 J/cm^3 、83.92%。可以发现, NN-BF-10STZ 相对与纯 NN 陶瓷来说, 储能特性得到了很大的提升。

2.4 储能特性的稳定性评价

图 10a 为 NN-BF-10STZ 陶瓷在 10 Hz, 300 kV/cm 电场强度和不同测试温度下的 P - E 曲线, 相应的极化强度($P_{\max}$, P_r 和 ΔP)随温度的变化如图 10b 所示。随着温度从 25 $^{\circ}\text{C}$ 升高到 120 $^{\circ}\text{C}$, $P_{\max}$ 虽然趋于降低, 但是在 120 $^{\circ}\text{C}$ 时 $P_{\max}$ 仍可达到 18.54 $\mu\text{C}/\text{cm}^2$, P_r 不超过 1.00 $\mu\text{C}/\text{cm}^2$ 。图 10c 为根据 P - E 曲线计算得到的不同温度下的 W_{tot} , W_{rec} 和 η 。在 25~120 $^{\circ}\text{C}$ 温度区间内, W_{tot} 和 W_{rec} 能够保持在 2.69 J/cm^3 和 2.38 J/cm^3 以上, η 始终保持在 85% 以上。图 10d 为 NN-BF-10STZ 陶瓷室温下, 300 kV/cm 电场强度和不同频率下的 P - E 曲线。从

图中可以看出, P - E 曲线和极化强度在 10~150 Hz 的频率范围内没有显著的变化, $P_{\max}$ 维持在 20.43~19.31 $\mu\text{C}/\text{cm}^2$ 之间, P_r 始终低于 1.20 $\mu\text{C}/\text{cm}^2$, 相应的 ΔP 保持在 19.24~18.70 $\mu\text{C}/\text{cm}^2$ 之间。图 10f 为

W_{tot} , W_{rec} 和 η 随频率的变化。 W_{tot} 和 W_{rec} 分别稳定在 2.87~2.70 J/cm^3 和 2.47~2.39 J/cm^3 之间, 相应的 η 保持在 88% 左右。以上结果表明 NN-BF-10STZ 陶瓷具有优异的温度和频率稳定性。

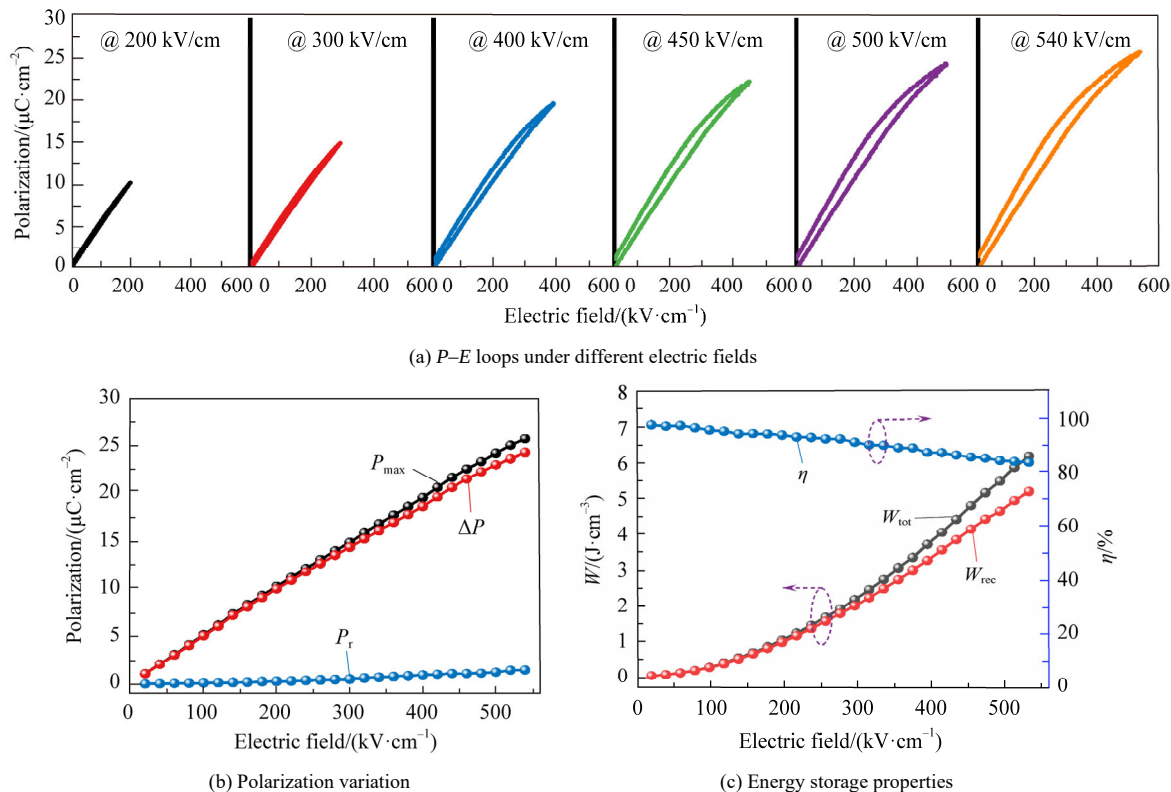


图 8 NN-BF-10STZ 陶瓷不同电场下的单极 P - E 曲线、极化强度和储能特性

Fig. 8 Unipolar P - E loops, polarization variation and energy storage properties of NN-BF-10STZ ceramics under different electric fields

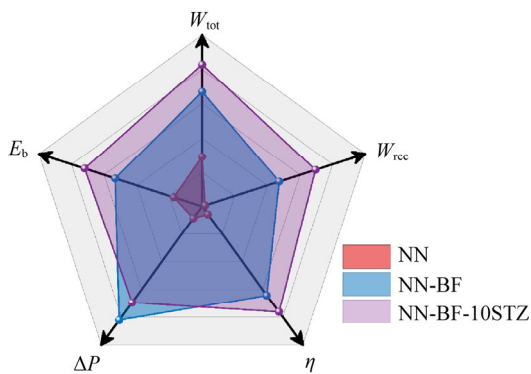


图 9 NN、NN-BF 和 NN-BF-10STZ 陶瓷的储能特性比较

Fig. 9 Comparison of energy storage properties of NN, NN-BF and NN-BF-10STZ ceramics

2.5 脉冲充放电性能分析

图 11 为 NN-BF-10STZ 陶瓷在不同电场强度下的欠阻尼放电电流曲线, 图中显示欠阻尼放电电流可以在非常短的短时间内达到最大值, 然后快速衰减,

反映出该陶瓷具有非常快的放电速率。同时, $I_{\max}$ 随着电场强度的增大从 5.31 A 增至 44.69 A。基于欠阻尼放电曲线计算得到的 C_d 和 P_d 随电场强度的变化曲线如图 11b 所示, C_d 和 P_d 随电场强度的增大均呈现不断增大的趋势。当电场强度从 30 kV/cm 提高至 270 kV/cm 时, C_d 和 P_d 分别从 169.17 A/cm^2 和 2.54 MW/cm^3 增加至 1 423.15 A/cm^2 和 192.13 MW/cm^3 。图 11c 为 NN-BF-10STZ 陶瓷在不同电场强度下测得的过阻尼放电电流曲线, 其测试过程中使用的负载电阻为 380 Ω 。通过公式计算得到的 W_d 随时间的变化曲线如插图 11d 所示。可以看出, W_d 能够在极短的时间内达到最大值。基于过阻尼放电电流曲线得到的 $I_{\max}$ 、 W_d 和 $t_{0.9}$ 随电场强度的变化如图 11e 所示。从图中可以观察到, $I_{\max}$ 和 W_d 随电场强度的提高不断增大, 分别从 0.09 A 和 0.02 J/cm^3 增大到 6.59 A 和 1.17 J/cm^3 , $t_{0.9}$ 在 100 ns 附近有略微的波动。

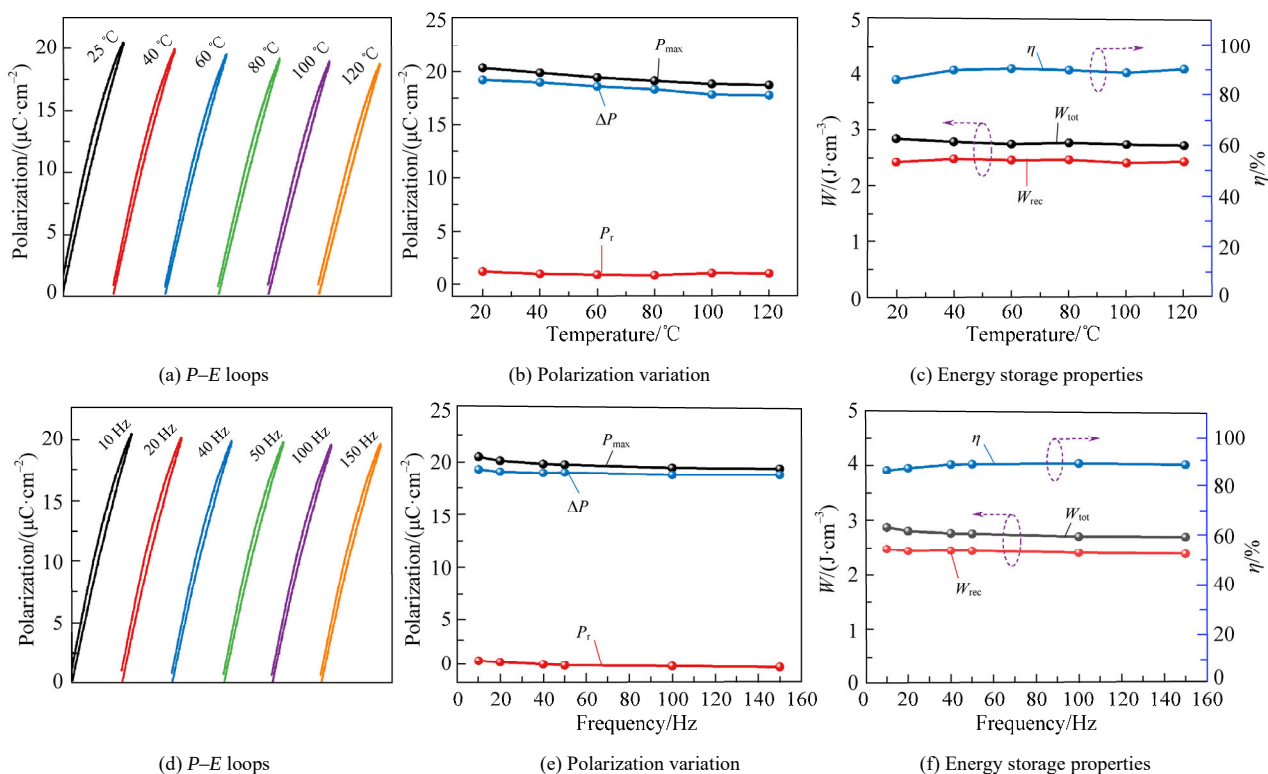
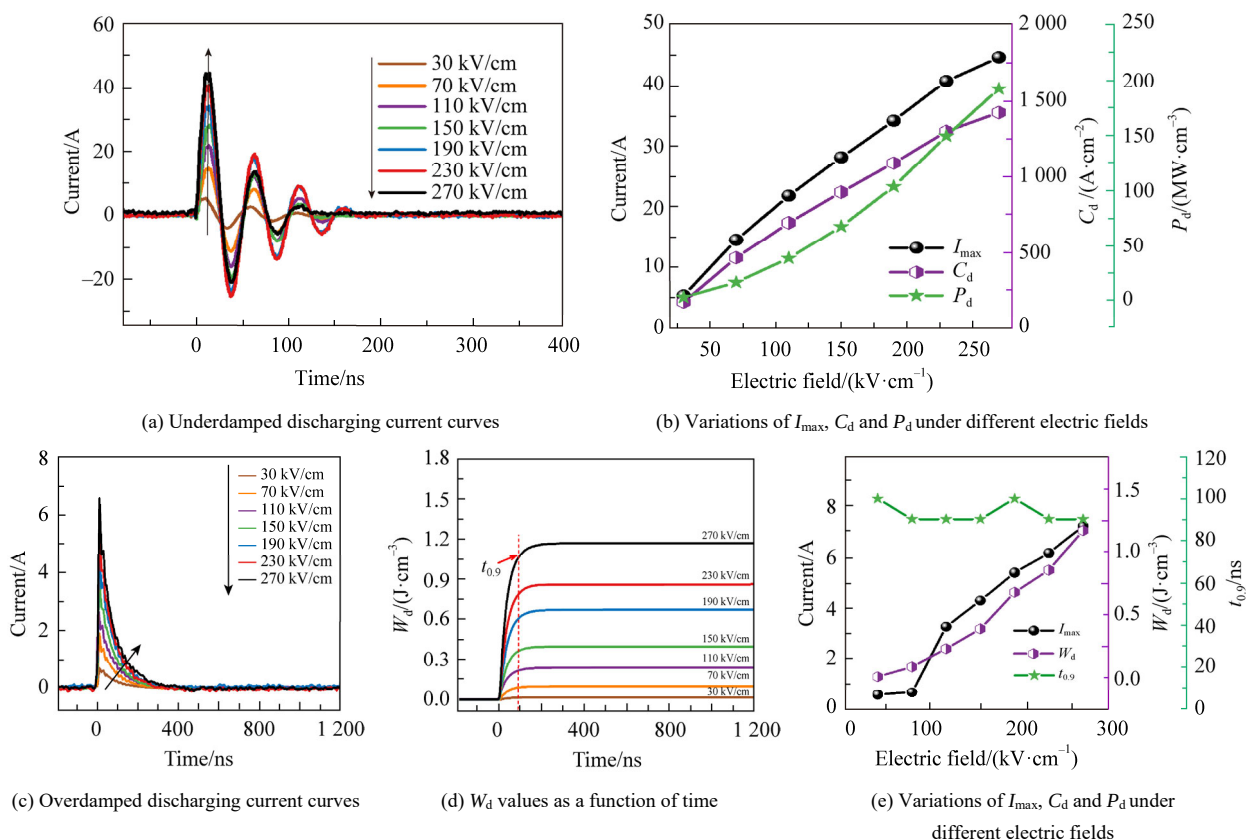
图 10 NN-BF-10STZ 陶瓷不同温度和频率下的单极 $P-E$ 曲线、极化强度和储能特性Fig. 10 Unipolar $P-E$ loops, polarization variation and energy storage properties of NN-BF-10STZ ceramics under different temperatures and electric fields

图 11 NN-BF-10STZ 陶瓷在不同电场下的脉冲充放电性能

Fig. 11 Charging-discharging properties of NN-BF-10STZ ceramics under different electric fields

3 结论

采用降低容忍因子和增强陶瓷弛豫特性的策略,开展了 NaNbO_3 (NN)基弛豫反铁电陶瓷的制备与储能特性研究。在 NN 陶瓷中掺入第 2 组元 BiFeO_3 (BF),将 NN 陶瓷的反铁电 R 相稳定到室温,在此基础上,通过第 3 组元 $\text{Sr}(\text{Ti}_{0.85}\text{Zr}_{0.15})\text{O}_3$ (STZ)的引入进一步提高了陶瓷的弛豫特性,制备了 NN 基弛豫反铁电储能陶瓷。纯 NN 陶瓷表现出典型的方形电滞回线,具有极低的储能密度和储能效率($W_{\text{rec}} \sim 0.14 \text{ J/cm}^3$, $\eta \sim 6.69\%$); BF 第 2 组元引入后,陶瓷表现出类反铁电体的双电滞回线,储能特性得到优化($W_{\text{rec}} \sim 3.55 \text{ J/cm}^3$, $\eta \sim 70.61\%$),进一步地,STZ 的引入使陶瓷弛豫性增强,电滞回线的极化滞后明显降低,储能特性得到显著优化($W_{\text{rec}} \sim 5.22 \text{ J/cm}^3$, $\eta \sim 83.92\%$)。具有最优储能特性的 $0.9[0.9\text{NaNbO}_3-0.1\text{BiFeO}_3]-0.1\text{Sr}(\text{Ti}_{0.85}\text{Zr}_{0.15})\text{O}_3$ 陶瓷同时表现出良好温度、频率稳定性,是一种极具应用前景的电介质储能材料。

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Relaxor Antiferroelectric Phase and Optimized Energy Storage Properties of NaNbO_3 -Based Lead-Free Ceramics

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Abstract

Introduction Pulse power technology has important applications in national defense industry. Dielectric capacitor is one of the energy storage components of pulse power devices. Ceramic dielectric capacitors have some advantages like fast charging-discharging speed, good electromechanical performance, anti-aging, and resistance to extreme conditions, which can be used in dielectric energy storage. The existing energy storage properties of BaTiO_3 -based dielectric ceramics are generally low at a high electric field, and lead-based ceramic capacitors are increasingly limited because of the presence of lead as a highly toxic element. It is thus necessary for pulse power technology to develop lead-free ceramic capacitors with superior comprehensive energy storage properties. NaNbO_3 (NN) ceramics have a rich structural phase transition and a low theoretical density, which makes their electrical properties highly adjustable and is conducive to the development of lightweight capacitors. Recent work on relaxor ferroelectric, anti-ferroelectric and relaxor antiferroelectric NaNbO_3 -based ceramics are performed. Compared with the typical lead-free antiferroelectric AgNbO_3 , NN as one of lead-free antiferroelectric materials has some advantages like low theoretical density (*i.e.*, 4.55 g/cm^3), high polarization intensity (*i.e.*, $40 \text{ } \mu\text{C/cm}^2$), simple preparation process, and relatively low raw material cost. Developing NN-based relaxor antiferroelectric ceramics with superior comprehensive energy storage properties is still a challenge because of the contradiction between polarization and breakdown strength. Therefore, exploring a relationship between the structure and energy storage properties of NN-based relaxor antiferroelectric ceramics is still a research aspect for NN-based ceramics. In this paper, a strategy of reducing tolerance factor was adopted to stabilize the antiferroelectric phase of NN-based ceramics. 10% (in mole fraction) $\text{BiFeO}_3(\text{BF})$ with a low tolerance factor (*i.e.*, 0.954 3) was incorporated into pure NN as a second end member, and the antiferroelectric R phase (*Pbnm*) of NN ceramics was stabilized at room temperature. The third end member $\text{Sr}(\text{Ti}_{0.85}\text{Zr}_{0.15})\text{O}_3(\text{STZ})$

was introduced to further improve the relaxor characteristic of the ceramics, and then the relaxor antiferroelectric phase was constructed in NN-based ceramics. In addition, the phase structure, microstructure, energy storage properties, stability and charging-discharging performance of the ceramics were also analyzed.

Methods The chemical composition of the ceramics was NaNbO_3 , $0.9\text{NaNbO}_3\text{-}0.1\text{BiFeO}_3$, and $(1-x)[0.9\text{NaNbO}_3\text{-}0.1\text{BiFeO}_3]\text{-}x\text{Sr}(\text{Ti}_{0.85}\text{Zr}_{0.15})\text{O}_3$, where $x=0.05, 0.10, 0.15$. All the ceramics were prepared by a conventional solid phase method. The ceramics were prepared via sintering at $1\,230\text{--}1\,260\text{ }^\circ\text{C}$ for 2 h. The crystal structure of ceramics was analyzed by a model DX-2700BH X-ray diffractometer (Haoyuan Instrument Co., China) and a model Lab-Ram HR800 spectrometer (HORIBA Co., France) with a laser wavelength of 532 nm. The in-situ temperature test for Raman spectra was performed on a model Linkam THMS600 temperature control platform. The sample used for in-situ electric field Raman spectroscopy test was plated with an electrode by an ion sputtering method. The sputtering current was set to 6 mA and the sputtering time to 2 min to ensure that the sample had both electrical conductivity and the penetration in Raman spectroscopic laser. The natural surface morphology of the samples was determined by a scanning electron microscope, and the grain size of the ceramics was determined using a software named Nano Measurer. After the sample was thinned, the domain structure of the ceramics was characterized by a model JEM-2100F field emission transmission electron microscope. The sample was polished to 0.5 mm thickness, cleaned, and coated with silver electrodes on the upper and lower surfaces of the sample. The dielectric properties of the ceramics were measured at $-120\text{--}450\text{ }^\circ\text{C}$ by a model E4980A precision LCR bridge (Agilent Co., USA). The hysteresis loops of the ceramics with the thickness of 150 μm were tested by a model Precision Premier II ferroelectric tester (Radiant Co., USA).

Results and discussion Based on the XRD patterns, NN, NN-BF and NN-BF- x STZ ceramics are a pure perovskite structure. NN ceramics show diffraction peaks for phases (110) and (200), manifesting that they are antiferroelectric orthogonal $P(\text{Pbcm})$ phases at room temperature. The orthogonal phase features disappear, and the diffraction peaks of phases (110) and (200) change from split state to single peak with the addition of BF and STZ, indicating that the addition of BF and STZ improves the symmetry of the ceramic and the ceramic transforms into a pseudo-cubic phase. NN ceramics have a dielectric anomaly peak at $400\text{ }^\circ\text{C}$, which represents a transition from the antiferroelectric P phase to the antiferroelectric R phase. For NN-BF and NN-BF- x STZ ceramics, the P-R phase transition peak disappears, and a diffuse dielectric anomaly peak appears at $-100\text{ }^\circ\text{C}$. Compared with NN ceramics, the room temperature dielectric constant of NN-BF ceramics increases, which is mainly due to the presence of anti-ferroelectric R phase in the ceramics. The in-situ XRD and Raman measurements show that the symmetry of the local structure of NN-BF-10STZ ceramics has a good stability. After BF and STZ doping, the grain size of the ceramics is reduced and the grain distribution uniformity is improved. The breakdown strength of ceramics can be enhanced due to the effect of decreasing grain size and improving distribution uniformity. STZ doping reduces the size of antiferroelectric domains. They can respond quickly to an external electric field due to the high activity and low energy barrier of nano-domains, thus reducing the remanent polarization, which is conducive to improving the energy storage properties. The transformation from antiferroelectric phase to ferroelectric phase of NN ceramics only occurs in the presence of the electric field. After the introduction of BF, the antiferroelectric R phase of the ceramics is stabilized, and the P - E curve shows a double hysteresis loop. The relaxation characteristics of the ceramics are further enhanced with the introduction of STZ. The P - E loops of NN-BF-10STZ ceramics become more elongated, and the polarization hysteresis is suppressed. The NN-BF-10STZ achieves the optimal energy storage properties (*i.e.*, W_{rec} of 5.22 J/cm^3 and η of 83.92%). Also, NN-BF-10STZ ceramics have a superior stability at $25\text{--}120\text{ }^\circ\text{C}$ and $10\text{--}150\text{ Hz}$.

Conclusions Pure NN ceramics exhibited a typical square hysteresis loop with low energy storage density and efficiency (*i.e.*, W_{rec} of 0.14 J/cm^3 , and η of 6.69%). After the introduction of the second component of BF, the ceramics had a double hysteresis loop like antiferroelectric, and the energy storage characteristics (*i.e.*, $W_{\text{rec}}\sim 3.55\text{ J/cm}^3$, $\eta\sim 70.61\%$) were optimized. Furthermore, the introduction of STZ enhanced the relaxation of the ceramics, and reduced the polarization hysteresis of the hysteresis loop. The energy storage properties were optimized (*i.e.*, $W_{\text{rec}}\sim 5.22\text{ J/cm}^3$, $\eta\sim 83.92\%$). $0.9[0.9\text{NaNbO}_3\text{-}0.1\text{BiFeO}_3]\text{-}0.1\text{Sr}(\text{Ti}_{0.85}\text{Zr}_{0.15})\text{O}_3$ ceramics with the optimal energy storage performance had a stability at different temperatures and frequencies, which could be used as a promising dielectric energy storage material with application prospects.

Keywords sodium niobate; lead-free ceramics; antiferroelectric; energy storage properties; charging-discharging properties