

SrAl_{0.5}Nb_{0.5}O₃ 调控 BiFeO₃ 基弛豫铁电陶瓷的储能性能

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摘 要: 本工作采用两步烧结法制备了 $(0.7-x)\text{Bi}_{1.02}\text{FeO}_3\text{-BaTiO}_3\text{-}x\text{Sr}(\text{Nb}_{0.5}\text{Al}_{0.5})\text{O}_3$ $((0.7-x)\text{BF-0.3BT-}x\text{SAN})$ 高温弛豫铁电陶瓷。所有的陶瓷展示了伪立方相结构, 且随着 x 增加, 陶瓷的晶格收缩, BO_6 八面体中局部结构无序性增强。0.54BF-0.3BT-0.16SAN 陶瓷中适当介电常数(f 为 1000)有利于提高其击穿场强。两步烧结的 0.54BF-0.3BT-0.16SAN 陶瓷在 100 Hz、370 kV/cm 时同时获得 3.90 J/cm^3 的可恢复储能密度和 85.5% 储能效率的优异能量存储性能。此外, 0.54BF-0.3BT-0.16SAN 陶瓷具有优异的宽温($-20\sim 100^\circ\text{C}$)、频率($1\sim 1000 \text{ Hz}$)和疲劳(10^5 次循环)稳定性。目前的工作为设计高性能介电材料提供了一种有前景的策略。

关键词: 铁酸铋基陶瓷; 弛豫铁电体; 储能性能; 畴演变

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介电电容器因其高的功率密度、快速充放电能力、优异的抗疲劳性及温度稳定性等特性作为储能材料被广泛应用于脉冲功率系统^[1-3], 但关键问题在于其储能性能差。可恢复储能密度(W_r)和储能效率(η)是评估介电电容器储能性能的关键指标^[4], 它们依赖于外加电场(E)、最大极化($P_{\max}$)和剩余极化(P_r), 由下式可知:

$$W_r = \int_{P_r}^{P_{\max}} E dP \quad (1)$$

$$\eta = \frac{W_r}{W_r + W_{\text{loss}}} \times 100\% \quad (2)$$

因此, 高 W_r 、 η 和击穿场强(E_b)是介电电容器具备高储能能力的必要条件。介电电容器材料包括弛豫铁电、铁电、反铁电和线性介电体 4 类材料。弛豫铁电体由于其阳离子有序-无序和伴随的随机电场形成的异质极性纳米微区(PNRs)贡献大极化变化($\Delta P = P_{\max} - P_r$)和低介电损耗而被广泛研究^[5, 6]。环境友好型铁酸铋(BiFeO_3 , BF)材料因其高居里温度

($T_c \approx 830^\circ\text{C}$)和大自发极化($P_s = 100 \mu\text{C/cm}^2$)等备受关注^[7, 8]。纯 BF 陶瓷的典型铁电性导致其大的 P_r , Bi^{3+} 挥发和 Fe^{3+} 变价引起的高漏电流限制击穿场强, 致使其储能性能严重受限^[9-11]。通过固溶组分(如 BF-ST 和 BF-BT 等)不仅可在 BF 铁电体中诱导弛豫特性, 还可调控其结构, 优化其储能性能^[10, 12-15]。Yan 等^[12]结合流延法和两步烧结法制备了 BF-ST 陶瓷。ST 明显减小了 BF 的畴尺寸, 两步烧结进一步降低体系晶粒尺寸。在准同型相界(MPB)的 BF-BT 弛豫铁电陶瓷因其高的 $P_{\max}$ 被认为是最具潜力的基体材料^[16-18]。近年来, 研究者们从调控极化响应和提升击穿场强角度出发, 基于离子掺杂、固溶组分及优化烧结工艺等通过调控陶瓷弛豫行为、畴结构及带隙相结构等进一步优化了 BF-BT 弛豫铁电陶瓷的储能性能^[19]。Montecillo 等^[20]通过增加 Sm^{3+} 在 $0.1\%\text{MnO}_2\text{-}0.5\text{BF-}0.5\text{BT}$ 陶瓷中的含量, 使体系由伪立方相和菱形相共存态转变为正交相, 调控了其微观结构和极化有序性。Zhao 等^[21]发现在

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0.5BF–0.5BT 基体中引入宽带隙的 $\text{CaHfO}_3(\text{CH})$ 后, 0.5BF–0.4BT–0.1CH 陶瓷获得 $W_{\text{rec}}=4.70 \text{ J/cm}^3$ 和 $\eta=79.0\%$ 的优良储能性能。Chen 等^[17]添加具有弛豫铁电特性的 SBT 至 0.67BF–0.33BT 中, 增强了其弛豫特性, 使体系在 180 kV/cm 的小场下获得 $W_{\text{rec}}=2.4 \text{ J/cm}^3$ 和 $\eta=90.4\%$ 的储能性能。由上述可知, 通过在 BF–BT 弛豫铁电陶瓷中添加合适组分和改变烧结工艺等策略, 可诱导更多极性纳米微区, 扰乱基体的长程有序和调控弛豫行为, 从而有效提升其储能性能。

本工作结合组分固溶和两步烧结法制备了一系列 $(0.7-x)\text{Bi}_{1.02}\text{FeO}_3\text{--BaTiO}_3\text{--}x\text{Sr}(\text{Nb}_{0.5}\text{Al}_{0.5})\text{O}_3$ [(0.7– x)BF–0.3BT– x SAN] 高温弛豫铁电陶瓷。选取 MPB 处 0.7BF–0.3BT 为基体材料是由于其铁电宏畴/微畴可贡献高的 P_{max} 和高的 T_{C} 。引入弛豫特性的 SAN, 可扰乱体系的长程有序, 形成更多 PNRs, 调控体系的畴结构和弛豫特性, 从而降低 P_r , 优化极化响应^[22]。此外, 两步烧结法是一种很有效的降低晶粒尺寸的方法, 在较高温度(T_1)短时间停留有利于陶瓷形成连续、致密的晶界网络, 再在较低温度(T_2)长时间保温, 使晶界迁移活性被限制, 晶粒不能继续长大^[23]。并且作者在前期研究中也证实了两步烧结法可有效降低陶瓷的晶粒尺寸从而提高其 E_b ^[24]。因此, 在上述策略的协同作用下, 0.54BF–0.3BT–0.16SAN 弛豫铁电陶瓷在 370 kV/cm 的电场下获得优良的储能性能 ($W_{\text{rec}}=3.90 \text{ J/cm}^3$ 和 $\eta=85.5\%$), 且该陶瓷表现出良好的频率、温度和循环稳定性。

1 实验

1.1 样品制备

采用两步烧结法制备了 $(0.7-x)\text{Bi}_{1.02}\text{FeO}_3\text{--BaTiO}_3\text{--}x\text{Sr}(\text{Al}_{0.5}\text{Nb}_{0.5})\text{O}_3$ [简称 (0.7– x)BF–0.3BT– x SAN, $x=0.00\sim 0.18$] 弛豫铁电陶瓷。原料粉 Bi_2O_3 (99.975%)、 Fe_2O_3 (99.945%)、 BaCO_3 (99.950%)、 TiO_2 (99.800%)、 SrCO_3 (99.000%)、 MnO_2 (99.900%)、 Nb_2O_5 (99.900%) 和 Al_2O_3 (99.500%) 均为分析纯。按比例称量后, 原料粉以 400 r/min 在乙醇中球磨 12 h 后干燥。随后粉末在 850°C 煅烧。为提高陶瓷的电阻率和绝缘性在煅烧后的粉末中加少量 MnO_2 后再次球磨 12 h 后干燥。干燥粉末经 200 MPa 冷等静压 2 min, 压成直径 10 mm 、厚度 1 mm 的圆片。圆片置于带盖的氧化铝坩埚中以防止 Bi 挥发, 于 $1050\sim 1110^\circ\text{C}$ 条件下保温 2 min 后降至 $1020\sim 1050^\circ\text{C}$

烧结。陶瓷片经抛光后用于微结构表征。为测试电学性能, 于 0.7 mm 厚陶瓷片两面涂覆银浆, 700°C 保温 20 min 形成电极。

1.2 样品表征

采用 X 射线衍射(XRD, X'Pert 衍射仪, 德国)研究陶瓷的晶体结构。采用压电力显微镜(PFM, MFP–3D, 美国)观察陶瓷的微观畴结构。通过场发射扫描电子显微镜(FE–SEM, MAIA3 LMH, 美国)观察陶瓷的表面微观形貌, 并结合“纳米测量”软件确定晶粒的分布。通过拉曼散射光谱仪(Horiba–Jobin Yvon HR800, 法国), 采用 532 nm 激光激发, 获得陶瓷在 $90\sim 900 \text{ cm}^{-1}$ 范围内的拉曼光谱。利用 LCR 仪(安捷伦, 4980 A, 美国)测试陶瓷的介电性能(介电常数 ϵ_r 和介电损耗 $\tan\delta$)随频率($1\sim 1000 \text{ kHz}$)和温度($25\sim 500^\circ\text{C}$)的变化情况。采用 Precision Premier II 铁电测量系统测量陶瓷的电滞回线(P – E 曲线), 陶瓷的厚度为 0.08 mm , 直径为 1.5 mm 。

2 结果与讨论

2.1 物相结构分析

图 1 为 $(0.7-x)\text{BF–0.3BT–}x\text{SAN}$ 陶瓷在 $20^\circ\sim 70^\circ$ 范围的 XRD 谱。由图 1a 可见, (110)的主衍射峰表现出不对称的单峰, 表明所有陶瓷的晶体结构均为伪立方(Pseudocubic, P_c)^[25]。纯 0.7BF–0.3BT 陶瓷显示出纯钙钛矿结构。当 $x=0.10$ 时, 陶瓷中出现了少量的第 2 相 $\text{Bi}_{24}\text{Fe}_2\text{O}_{39}$ (PDF 42–0201)^[26]。当 x 继续增加, 第 2 相峰强明显增加, 即其含量逐渐增加。这与 SAN 在 BF–BT 陶瓷中的固溶度限制有关。杂质含量会影响陶瓷在铁电测试中的击穿场强, 这可由后述 x 为 0.18 时陶瓷中击穿场强明显降低得到。此外, 由 XRD 放大图(图 1b)可见, 随着 x 增加, (111)衍射峰向高角度移动, 表明晶格体积发生明显收缩, 这是由于相较于 0.7BF–0.3BT 晶格中 B 位 Ti^{4+} ($r=0.605 \text{ \AA}$) 和 Fe^{3+} ($0.630 \text{ \AA}$) 的平均离子半径($0.623 \text{ \AA}$), Nb^{5+} ($0.640 \text{ \AA}$) 和 Al^{3+} ($0.535 \text{ \AA}$) 的平均离子半径($0.588 \text{ \AA}$) 更小所致。

2.2 微观结构分析

进一步采用拉曼光谱仪研究 $(0.7-x)\text{BF–0.3BT–}x\text{SAN}$ 陶瓷在室温下的局部结构变化(图 2)。波数小于 150 cm^{-1} 、在 $150\sim 400 \text{ cm}^{-1}$ 之间和高于 400 cm^{-1} 的拉曼峰分别为 A 位离子、B–O 键及 BO_6 八面体的振动^[10]。由图 2 可知, 随着 SAN 的增加, $(0.7-x)\text{BF–0.3BT–}x\text{SAN}$ 陶瓷的拉曼峰没有明显位移, 但峰的半峰宽逐渐增大, 这归因于体系中增

加的纳米畴/极性纳米微区(PNRs)引起的结构无序性的增加。为了更细致地研究局部结构的改变,进一步对拉曼峰进行分峰拟合^[14]。470 cm^{-1} 和 680 cm^{-1} 附近的振动模式为 R_{3c} 的 A1-4 和 E-7 振动模式,尤其是 BO_6 八面体的扭曲与 E-7 模式密切相关^[27]。随着 x 的增加,第 3 个峰逐渐向小波数移动,表明 Sr^{2+} 引起 A 位离子偏离中心位置,导致 A—O

键强度减弱和晶格局部对称性的破坏。第 4 个峰亦随着 x 的增加向低波数移动,说明 B—O 键强度和晶胞极性的降低。第 7 和第 9 个峰分别随着 x 的增加向低波数和高波数移动,表明共掺 Sr^{2+} 和 $(\text{Nb}_{0.5}\text{Al}_{0.5})^{4+}$ 后增加了 BO_6 八面体中的局部结构无序性,有利于形成局部随机电场和促进极性纳米微区的形成^[9]。

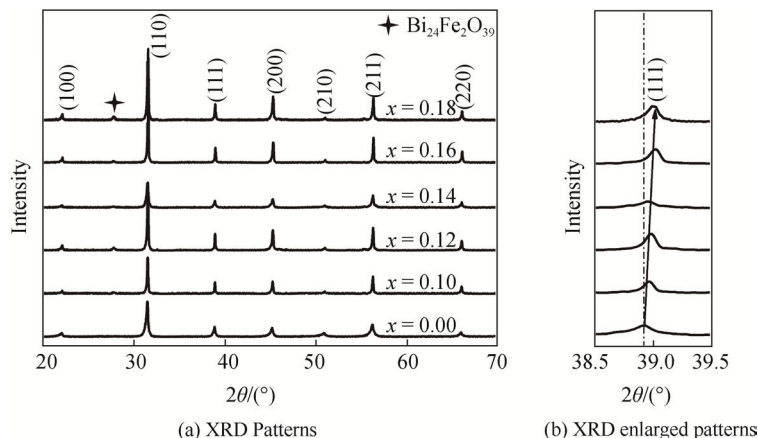


图 1 $(0.7-x)\text{BF}-0.3\text{BT}-x\text{SAN}$ 陶瓷的 XRD 谱
Fig. 1 XRD patterns of $(0.7-x)\text{BF}-0.3\text{BT}-x\text{SAN}$ ceramics

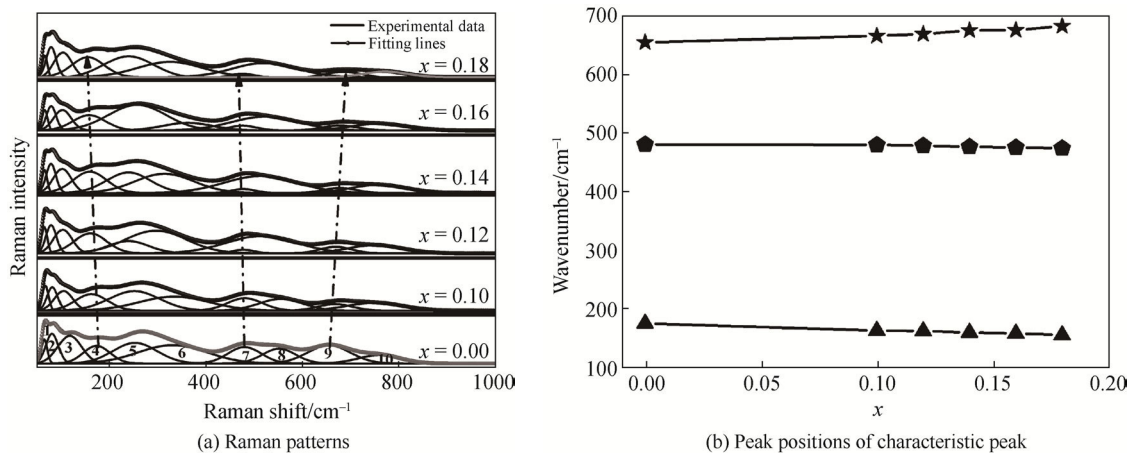


图 2 $(0.7-x)\text{BF}-0.3\text{BT}-x\text{SAN}$ 陶瓷的拉曼光谱
Fig. 2 Raman patterns of $(0.7-x)\text{BF}-0.3\text{BT}-x\text{SAN}$ ceramics

图 3 为 $(0.7-x)\text{BF}-0.3\text{BT}-x\text{SAN}$ 陶瓷的 SEM 照片和对应的晶粒分布图。由图 3 可以看出,所有陶瓷均具有致密的微观结构,且随着 x 含量的增加,陶瓷的晶粒尺寸逐渐减小。纯 $0.7\text{BF}-0.3\text{BT}$ 陶瓷的平均晶粒尺寸约 3.35 μm , 低于采用传统固相法烧结的同成分的陶瓷^[28, 29], 表明采用两步烧结法可有效降低陶瓷的晶粒尺寸。当 x 由 0.10 增加至 0.12 时,陶瓷的晶粒尺寸由约 2.76 μm 减至 2.19 μm 。特别是 x 含量继续增至 0.16 和 0.18 时,晶粒尺寸明显减小,约为 1.61~1.85 μm , 说

明 $(0.7-x)\text{BF}-0.3\text{BT}-x\text{SAN}$ 陶瓷的晶粒尺寸明显减小,这有利于提高陶瓷的 E_b 。因为晶粒尺寸是影响 E_b 的关键因素之一,这从晶粒尺寸(G)和 E_b 之间的关系 $[E_b \propto (G)^a]$ ^[30]可知。

为了进一步研究 $(0.7-x)\text{BF}-0.3\text{BT}-x\text{SAN}$ 陶瓷的微观畴结构,采用 PFM 测试了 $0.7\text{BF}-0.3\text{BT}$ 基体陶瓷和最佳成分 $0.54\text{BF}-0.3\text{BT}-0.16\text{SAN}$ 陶瓷在不同放大倍数下的局部振幅(图 4a~图 4d)和相位图(图 4e~图 4h)。PFM 振幅图反映样品的压电响应强弱,相位图反映样品的极化方向的取向。振幅图中强、

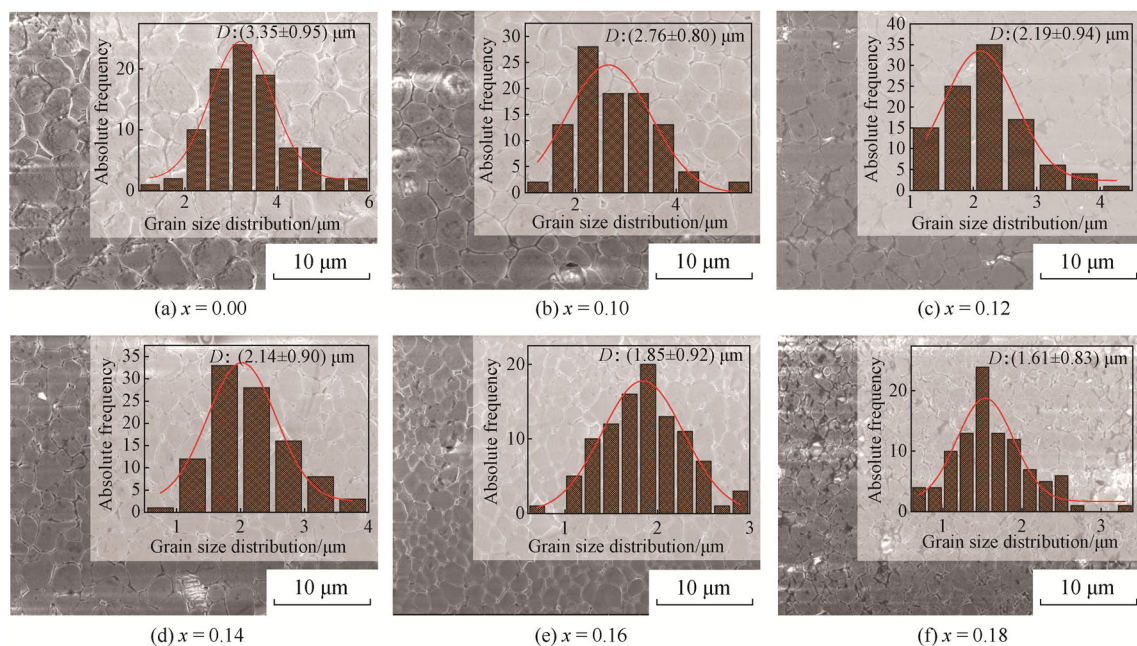


图3 (0.7-x)BF-0.3BT-xSAN 陶瓷的 SEM 照片和晶粒分布图
Fig. 3 SEM and grain size distribution images of (0.7-x)BF-0.3BT-xSAN ceramics

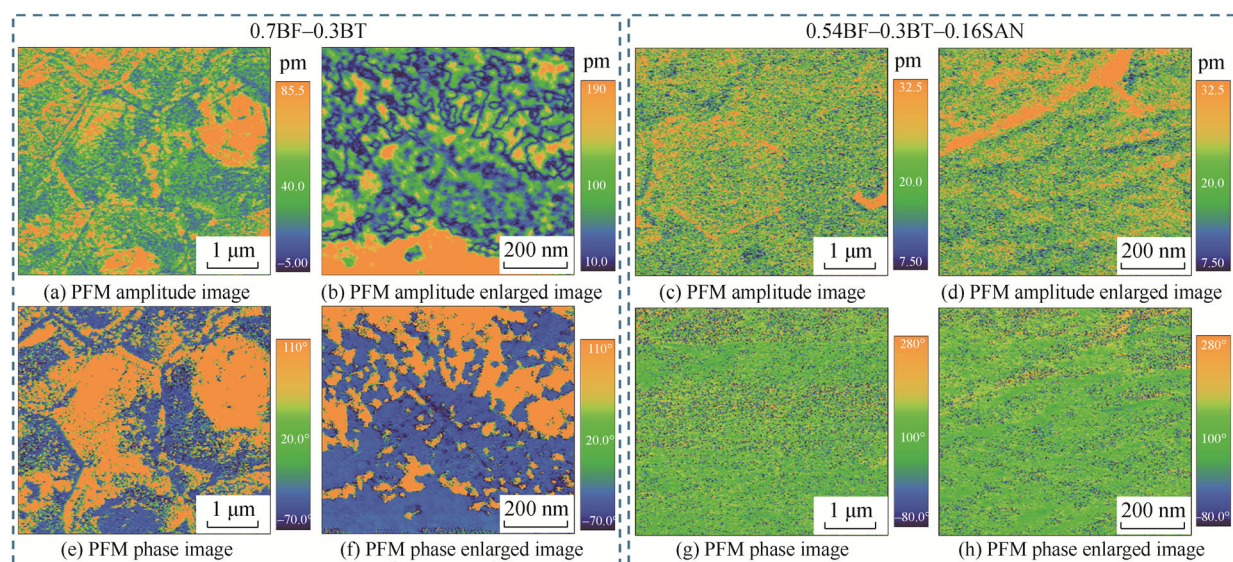


图4 0.7BF-0.3BT 和 0.54BF-0.3BT-0.16SAN 陶瓷的 PFM 振幅和相位图
Fig. 4 PFM amplitude and phase images of 0.7BF-0.3BT and 0.54BF-0.3BT-0.16SAN ceramics

弱压电响应分开的细小区域及相位图中不同极化方向对应体系中不同的畴。由图 4a 和图 4c 可以看出, 2 个陶瓷中均发现强压电响应(振幅中黄色区域)晶粒和弱压电响应(振幅中绿蓝区域)晶粒共存的特殊结构。对应的图 4e 和图 4g 相位图显示了强压电响应和弱压电响应晶粒中不同畴的极化方向。图 4a 中强压电响应区的振幅值比图 4c 中大, 表明 0.7BF-0.3BT 陶瓷的压电响应明显强于 0.54BF-0.3BT-0.16SAN 陶瓷。为了进一步观察陶瓷中的畴结构, 对 0.7BF-0.3BT 和 0.54BF-0.3BT-0.16SAN 陶瓷的局部进一步放大,

结果见振幅(图 4b 和图 4d)和相位(图 4f 和图 4h)放大图。由图 4b 和图 4d 可以看出, 同一晶粒内会有不同压电响应强度的纳米畴存在。且 0.7BF-0.3BT 陶瓷(图 4b)中的畴结构为较强压电响应的“岛状”纳米畴, 0.54BF-0.3BT-0.16SAN 陶瓷(图 4d)则展示了更弱压电响应的更小纳米畴。

2.3 介电性能分析

图 5 为(0.7-x)BF-0.3BT-xSAN 陶瓷的介电温谱和弛豫扩散拟合图。由图 5a~图 5f 可见, 所有陶瓷都具有明显的频率色散和扩散相变, 表面陶

瓷具有强的弛豫行为^[31]。图 5 b~图 5f 中高温下的异常峰值主要是由于高温下热驱动促进了氧空位的移动。由图 5 g 可以看出, ϵ_r 随着 x 的增加而减小, 且介电峰明显变宽, 这表明陶瓷的弛豫程度显著增强, 且介电热稳定性不断提高。此外, 0.54BF-0.3BT-0.16SAN 陶瓷显示了 1000 左右的中等介电常数, 这有利于实现优异的储能性能^[32]。弛豫程度增加是由于在 B 位的 Al/Nb 以不同的化合价和半径替代了 0.7BF-0.3BT 中的 Fe/Ti, 这有利于扰

乱长程铁电有序, 形成纳米畴或极性纳米微区。此外, 弛豫扩散程度可由修正居里-外斯定律 $[1/\epsilon - 1/\epsilon_m = (T - T_m)^\gamma / C]$ 中的扩散系数(γ)来评估。 $\gamma=1$ 表示陶瓷为典型的铁电体; $\gamma=2$ 则说明陶瓷为典型的弛豫铁电体^[25]。由图 5 h 可见, 纯 0.7BF-0.3BT 陶瓷的 γ 为 1.65, 表明其具有一定的弛豫性。当 SAN 含量增加为 0.16 时, γ 值增加至 1.91, 表明 SAN 有效提高了 0.54BF-0.3BT-0.16SAN 陶瓷的弛豫扩散程度。

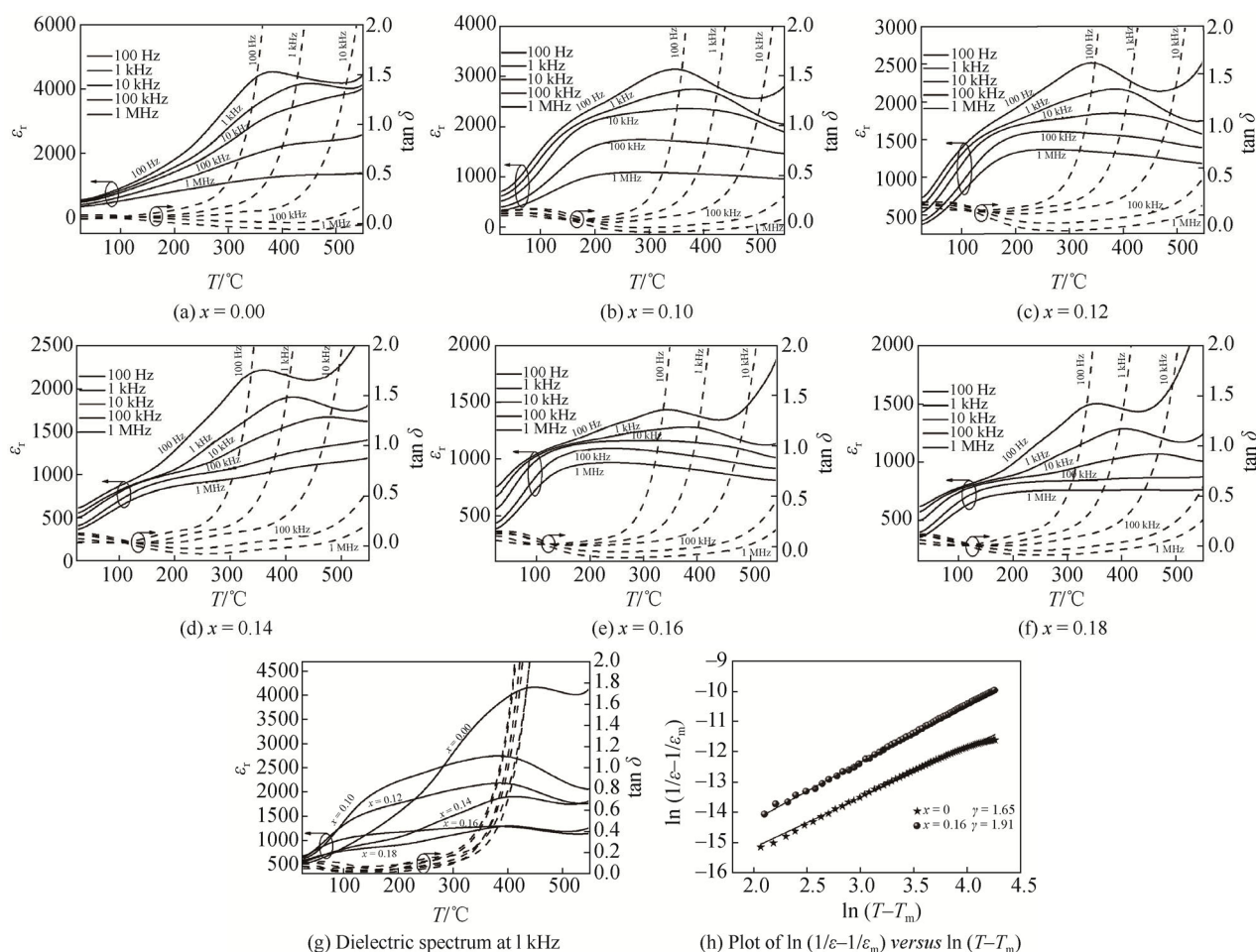


图 5 (0.7-x)BF-0.3BT-xSAN 陶瓷的介电温谱和弛豫扩散拟合图

Fig. 5 Dielectric temperature spectrum and relaxor diffuse fitting images of (0.7-x)BF-0.3BT-xSAN ceramics

2.4 储能性能分析

图 6 为(0.7-x)BF-0.3BT-xSAN 陶瓷的单极 $P-E$ 图、韦布尔分布及储能性能图。由图 6a 可见, 纯 0.7BF-0.3BT 陶瓷具有宽的 $P-E$ 线, 表明其具有较强的铁电性。0.7BF-0.3BT 陶瓷中较低的极化强度可能与其两步烧结得到的小晶粒尺寸有关。随着 x 的增加, $P-E$ 线变窄, 表明(0.7-x)BF-0.3BT-xSAN 的弛豫特性增强, 铁电性降低。 E_b 在改善电介质电容器中能量存储性能中至关重要, 可通过韦布

尔(Weibull)分布公式中的 X_i 和 Y_i 之间的线性拟合来计算 E_b ^[21]:

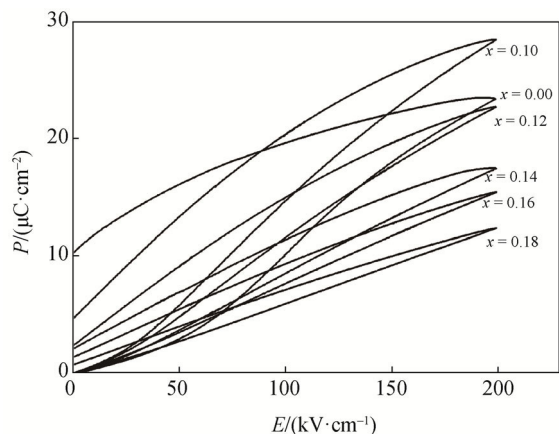
$$X_i = \ln E_i \quad (3)$$

$$Y_i = \ln \{-\ln[1 - i/(n+1)]\} \quad (4)$$

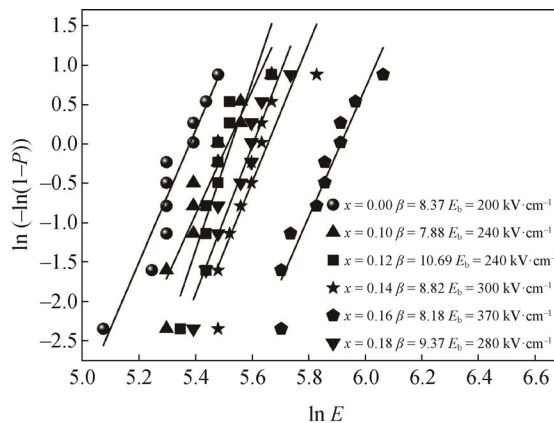
式中: E_i 、 i 和 n 分别为按升序排列的第 i 个样本的 E_b 、序列和样本总数。由图 6b 可见, 所有陶瓷都被拟合, 且 β 高于 7.85, 表明拟合得到的 E_b 可靠性很高。由图 6c 和图 6d 可见, 随着 x 的增加, E_b 先增加后降低, 0.54BF-0.3BT-0.16SAN

陶瓷的 E_b 可达 370 kV/cm, 该陶瓷中小的晶粒尺寸、中等介电常数和高活性纳米畴的协同作用贡献其大 E_b 。当 x 增至 0.18, E_b 明显降低, 可能由于 0.52BF–0.3BT–0.18SAN 陶瓷中的更多杂质。当 x 从 0.10 增至 0.16, 相应的 W_{tot} 、 W_r 和 η 分别从 240 kV/cm 的 4.12 J/cm³、2.85 J/cm³ 和 69.0% 增至 370 kV/cm 的 4.57 J/cm³、3.90 J/cm³ 和 85.5%。当 x 增

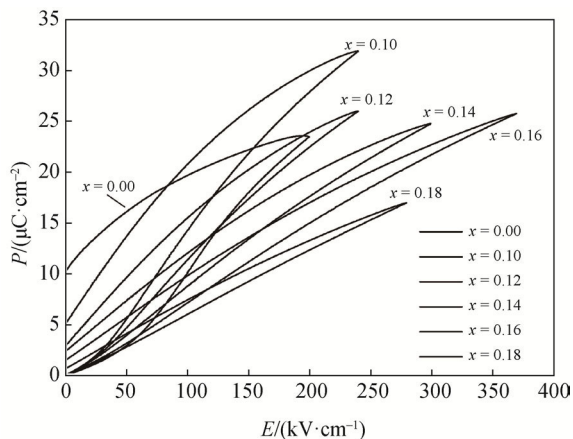
加到 0.18, W_{tot} 和 W_r 分别降至 2.38 J/cm³ 和 2.09 J/cm³, η 增至 88.0%(280 kV/cm)。0.54BF–0.3BT–0.16SAN 陶瓷中大 E_b 和高 ΔP 贡献高的 W_r 和 η 。高 ΔP 可归因于 0.54BF–0.3BT–0.16SAN 中 Bi–O 杂化、弛豫–铁电相转变与纳米畴翻转协同提升 P_{max} , 同时 SAN 引入增强局部随机场, 促使更多纳米畴在卸载电场后恢复至初始态, 从而降低 P_r 。



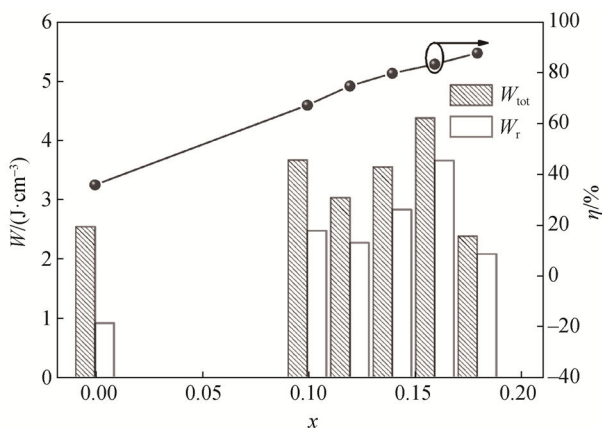
(a) Unipolar P – E loops under 200 kV/cm at RT



(b) Weibull distribution of dielectric breakdown strength



(c) Unipolar P – E loops under E_b



(d) Energy storage properties under E_b

图 6 (0.7– x)BF–0.3BT– x SAN 陶瓷的单极 P – E 图、韦布尔分布及储能性能图

Fig. 6 Unipolar P – E loops, Weibull distributions and changes of W and η for (0.7– x)BF–0.3BT– x SAN

图 7a~图 7c、图 7d~图 7f 和图 7g~图 7i 分别为 0.54BF–0.3BT–0.16SAN 陶瓷随频率、温度和循环次数增加的 P – E 电滞回线、 P 、 W 和 η 对比图。图 7a 和图 7b 为 0.54BF–0.3BT–0.16SAN 陶瓷在 1~1000 Hz 的 P – E 线和 P_{max} 、 P_r 和 ΔP 值 (200 kV/cm)。由图 7a 可知, 随着频率增加, P_{max} 逐渐减小, P_r 小幅增加, 从而使 ΔP 略有减小, P 值的具体变化规律见图 7b。由图 7c 可知, 0.54BF–0.3BT–0.16SAN 陶瓷的 W_r 和 η 分别由 1 Hz 下的 1.36 J/cm³ 和 89.5% 变至 1000 Hz 下的 1.24 J/cm³ 和 82.5%, W_r 和 η 的变化率分别为 9.49% 和 9.2%。

因此, 0.54BF–0.3BT–0.16SAN 陶瓷具有良好的频率稳定性。图 7d 为 0.54BF–0.3BT–0.16SAN 陶瓷在 –40~140 °C 温度范围的单极 P – E 线, 发现在整个温度范围内陶瓷始终展现出细长的 P – E 回线。随着温度的升高, 由图 7e 可见, P_{max} 单调递增, P_r 先降低后增大, 导致 ΔP 和 η 呈现先增后减的规律。 P_{max} 增加主要归因于热驱动引起更多畴翻转, P_r 降低则是因为更多纳米畴恢复至初始态, 但在更高温度下 P_r 的增加则是由于传导损耗的增加。温度由 –40 °C 升至 140 °C, 由图 7f 可见, W_r 从 1.14 J/cm³ 先增至 1.42 J/cm³ 后降至 1.37 J/cm³, η 从 72.3% 增至 88.8%

后降至 77.8%, 该温度范围内 W_r 和 η 随温度的变化率分别为 24.56% 和 22.89%, 变化率相对较大。在 $-20 \sim 100^\circ\text{C}$ 范围, W_r 和 η 随温度的变化率分别为 9.23% 和 7.89%, 表明该陶瓷在 $-20 \sim 100^\circ\text{C}$ 范围内具有良好的温度稳定性。由图 7g 可见, 10^5 次循环后陶瓷保持相似的 $P_{\max}$ 和略增大的 P_r , 表明其

具有良好的抗疲劳特性。由图 7h 和图 7i 可见, 循环 10^5 次后, 0.54BF-0.3BT-0.16SAN 陶瓷的 W_{tot} 、 W_r 和 η 分别保持在 1.55 J/cm^3 、 1.34 J/cm^3 和 85.5%, 且 W_r 和 η 的变化小于 2.6% 和 3.5%, 说明陶瓷具有优异的疲劳稳定性。综上所述, 陶瓷具有良好的频率、循环和温度稳定性。

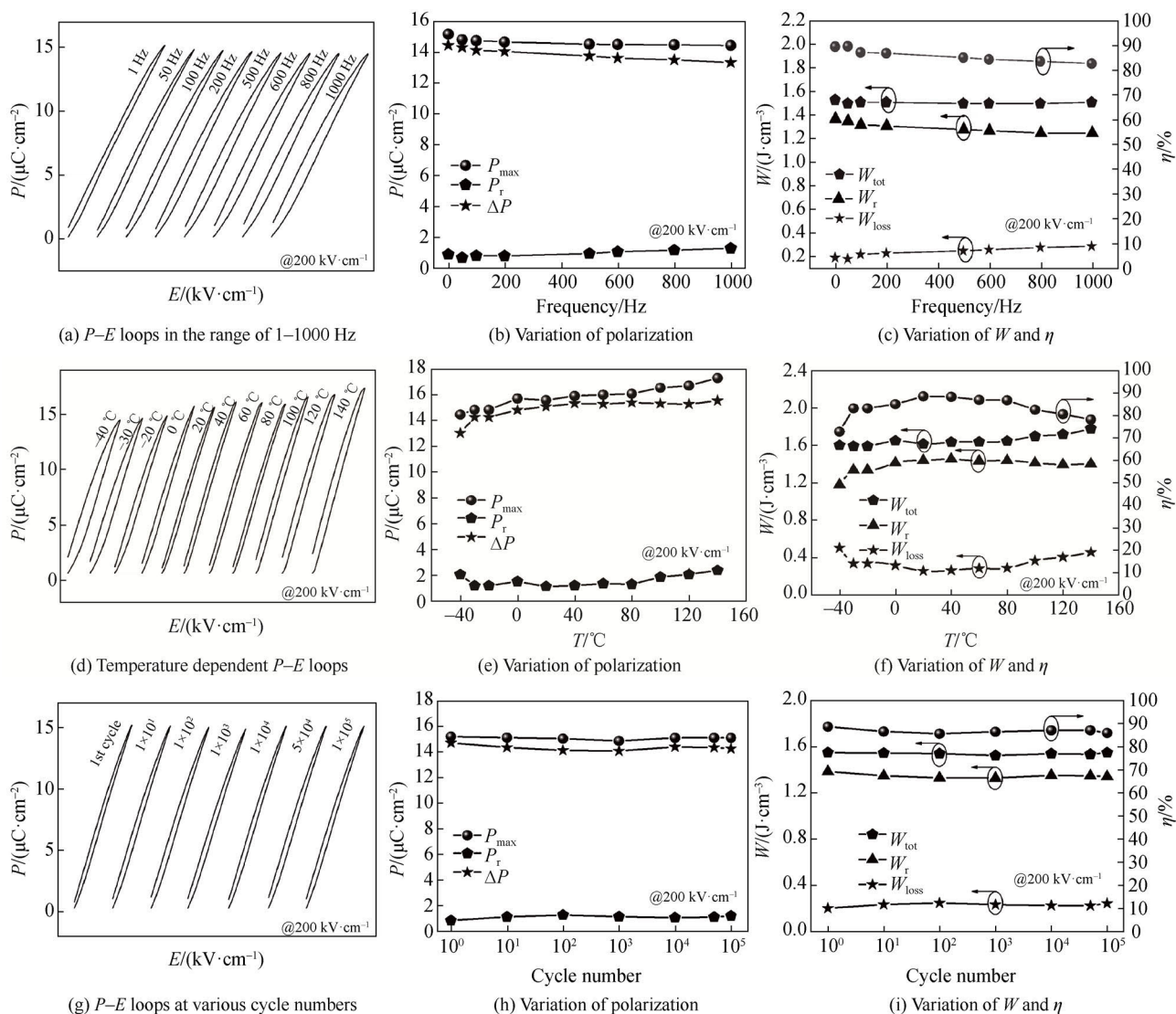


图 7 0.54BF-0.3BT-0.16SAN 陶瓷在各频率、温度和循环次数下的 P - E 线、 P 、 W 和 η

Fig. 7 P - E loops of 0.54BF-0.3BT-0.16SAN ceramic at various frequency, temperature and cycle and corresponding P , W and η

3 结论

采用两步烧结法成功制备了一系列 $(0.7-x)\text{BF}-0.3\text{BT}-x\text{SAN}$ 弛豫铁电陶瓷, 且 0.54BF-0.3BT-0.16SAN 在 370 kV/cm 的 E_b 下同时获得了 W_r 高达 3.90 J/cm^3 和 η 高达 85.5% 的优异能量存储性能。0.54BF-0.3BT-0.16SAN 弛豫铁电陶瓷中大 E_b 主要源于其小的晶粒尺寸、适当的介电常数和电场作用

下高活性纳米畴的协同作用。 $(0.7-x)\text{BF}-0.3\text{BT}-x\text{SAN}$ 弛豫铁电陶瓷展现了伪立方相结构, 且随着 x 增加, 陶瓷的晶胞体积逐渐减小, A-O 键和 B-O 键键强减弱, BO_6 八面体中局部结构无序性增强, 陶瓷的晶粒尺寸明显减小。介电测试结果表明, $(0.7-x)\text{BF}-0.3\text{BT}-x\text{SAN}$ 陶瓷具有强的弛豫特性。0.54BF-0.3BT-0.16SAN 弛豫铁电陶瓷还展现出良好的频率 ($1 \sim 1000 \text{ Hz}$)、温度 ($-20 \sim 100^\circ\text{C}$) 和循环

(1~10⁵ 次循环)稳定性。该研究为无铅弛豫铁电陶瓷储能性能提升提供了研究思路和理论基础。

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作者贡献声明:

赵钦福: 论文构思、撰写初稿、分析/综合数据并推导结论、获取资助

张攀升: 设计研究方法和实验方案、数据管理、绘制图表

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康 芳: 监督指导、审阅与修订、提供资源、获取资助

Energy Storage Performance of BiFeO_3 -Based Relaxor Ferroelectric Ceramics Modified with $\text{SrAl}_{0.5}\text{Nb}_{0.5}\text{O}_3$

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Extended Abstract

Introduction Dielectric capacitors are indispensable for pulsed power systems due to their high power density, ultrafast charge/discharge capability ($>\mu\text{s}$), and excellent fatigue resistance. However, their widespread adoption is fundamentally limited by poor energy storage performance, characterized by inadequate recoverable energy density (W_{rec}) and efficiency (η). To meet the demands of high-performance applications, it is imperative to simultaneously enhance W_{rec} , η , and breakdown strength (E_b). Among environmentally friendly candidates, BiFeO_3 - BaTiO_3 (BF-BT) relaxor ferroelectric ceramics stand out due to their high Curie temperature ($T_C \approx 830^\circ\text{C}$) and large maximum polarization (P_{max}). However, the intrinsic low E_b of BF-BT ceramics caused from the volatilization of Bi^{3+} and the change in the valence state of Fe^{3+} hinder their energy storage potential. To address these challenges, this work was to use a dual-strategy approach with compositional tailoring and two-step sintering for the preparation of $(0.7-x)\text{BF}-0.3\text{BT}-x\text{SAN}$ relaxor ferroelectric ceramics. The introduction of $\text{Sr}(\text{Nb}_{0.5}\text{Al}_{0.5})\text{O}_3$ into the $0.7\text{BF}-0.3\text{BT}$ system was to enhance relaxor behavior and refine the grain size, synergistically boosting both E_b and polarization response. Furthermore, the effect of SAN on the microstructure, dielectric, and energy storage properties was systematically investigated. This could provide research ideas and theoretical basis for improving the energy storage performance of BF-BT ceramics based relaxor ferroelectric ceramics.

Methods The raw materials powders of Bi_2O_3 , Fe_2O_3 , BaCO_3 , TiO_2 , SrCO_3 , MnO_2 , Nb_2O_5 and Al_2O_3 were analytical purity. These powders were precisely weighed according to a stoichiometric ratio, then ground with ethanol in a ball mill at 400 r/min for 12 h prior to drying. The mixed powder with a small amount of sintering aids (MnO_2) was subsequently calcined at 850°C . The mixture was further ground for 12 h and dried. The dried powder was compacted by cold isostatic pressing (200 MPa, 2 min) into circular discs ($\phi 10\text{ mm} \times 1\text{ mm}$). These discs were placed in covered alumina crucibles to minimize Bi volatilization and thermally treated at 1050 – 1110°C for 2 min, and then sintered at 1020 – 1050°C . The ceramic sheet was polished for microstructure characterization. After polishing for microstructural analysis, silver electrodes were screen-printed on the both surfaces of the 0.7 mm thick sintered ceramics and fired at 700°C for 20 min for electrical characterization.

The crystal structure of the ceramics was analyzed by X-ray diffraction (XRD). The surface morphology and grain distribution were examined by field emission scanning electron microscopy (FE-SEM) and performed by a software named Nano Measure. The microscopic domain structure of the ceramics was characterized by piezoelectric force microscopy (PFM). The Raman spectra in the range of 90 – 900 cm^{-1} were determined by Raman spectroscopy. The polarization-electric field hysteresis loops (P - E) were measured by a ferroelectric tester on disk-shaped samples (with the sizes of $\phi 1.5\text{ mm} \times 0.08\text{ mm}$).

Results and discussion The XRD patterns reveal that all the $(0.7-x)\text{BF}-0.3\text{BT}-x\text{SAN}$ ceramics exhibit an asymmetric singlet pattern, indicating that the crystal structure is a pseudo-cubic structure. The content of the second phase gradually increases with the increase of x due to the solid solubility limitation of SAN in BF-BT ceramics. The addition of SAN causes the XRD diffraction peaks shifting to higher angles, indicating a significant contraction of the lattice volume. The Raman peaks of ceramics do not show a significant shift in the Raman full spectrum, but the peak half width gradually increases, which is attributed to the increase in structural disorder. The Raman fitting results further indicate that increasing SAN weakens both A—O and B—O bonds, thereby reducing unit cell polarity and increasing local disorder in the BO_6 octahedra. This enhanced disorder facilitates the establishment of local random electric fields, which in turn promotes the formation of polar nanoregions. The SEM images manifest that the SAN results in a significant grain size reduction, especially as the x exceeds 0.14. The PFM results demonstrate that ceramics of matrix and $0.54\text{BF}-0.3\text{BT}-0.16\text{SAN}$ exhibit both strong and weak piezoelectric response nanodomains, and the nanodomains in $0.54\text{BF}-0.3\text{BT}-0.16\text{SAN}$ exhibit a weaker piezoelectric response. All the ceramics exhibit significant frequency dispersion and diffusion phase transition in their dielectric results, which imply a strong relaxation behavior. Polar, which can be attributed to a synergistic effect from the fine grain size, moderates a dielectric constant, and the presence of highly active nanodomains. Moreover,

the measurements of P – E loops under varying frequency–electric field (P – E) hysteresis loops show a significant decrease in the polarization strength of the ceramic with the increase of SAN, which is attributed to the increase of relaxor characteristics. The Weibull distribution fitting results reveal that the breakdown strength (E_b) initially increases and then decreases with increasing x . Specifically, the 0.54BF–0.3BT–0.16SAN ceramic achieves the maximum E_b of 370 kV/cm. The results of cycling tests reveal that the ceramic exhibits robust frequency, thermal, and fatigue stability.

Conclusions The (0.7– x)BF–0.3BT– x SAN relaxor ferroelectric ceramics with a pseudo–cubic structure were prepared by a two–step sintering method. The addition of SAN led to a contraction of unit cell and a concurrent weakening of both A–O and B–O bonds, consequently reducing unit cell polarity and enhancing local disorder within the BO_6 octahedra. The results of dielectric test indicated that (0.7– x)BF–0.3BT– x SAN ceramics had strong relaxation properties. The 0.54BF–0.3BT–0.16SAN ceramic simultaneously achieved the superior energy storage performance (*i.e.*, W_{rec} of 3.90 J/cm³ and η of 85.5%) at E_b of 370 kV/cm. Furthermore, the 0.54BF–0.3BT–0.16SAN ceramic exhibited the excellent frequency (*i.e.*, 1–1000 Hz), temperature (*i.e.*, –20 °C to 100 °C), and cycling stability (*i.e.*, 10⁵ cycles).

Keywords bismuth ferrite-based ceramics; relaxor ferroelectrics; energy storage performance; domain evolution