

# (1-x)(0.75K<sub>0.5</sub>Bi<sub>0.5</sub>TiO<sub>3</sub>-0.25BiFeO<sub>3</sub>)-xNa<sub>0.73</sub>Bi<sub>0.09</sub>NbO<sub>3</sub> 电介质陶瓷的 微观结构与储能性能

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**摘 要:** 为满足不断增长的高性能储能设备需求, 亟需研发能量存储性能出众的电介质电容器。采用传统固相反应法制备了 (1-x)(0.75Bi<sub>0.5</sub>K<sub>0.5</sub>TiO<sub>3</sub>-0.25BiFeO<sub>3</sub>)-xNa<sub>0.73</sub>Bi<sub>0.09</sub>NbO<sub>3</sub> (x=0~0.4) (简称 BKT-BF-xNBN) 样品。在 380 kV/cm 电场下, 样品表现出良好的储能性能, 可实现可回收能量密度  $W_{\text{rec}}=4.23 \text{ J/cm}^3$  和效率  $\eta=81.2\%$ 。NBN 的引入对 BKT 基陶瓷的微观结构与弛豫性产生了显著影响, 导致晶粒尺寸减小、陶瓷更加致密, 并诱导促使极性纳米区域的形成。此外, 样品还具有出色的充放电性能(放电时间  $t_{0.9}<75 \text{ ns}$ , 放电电流密度  $C_D=757.9 \text{ A/cm}^2$ , 放电功率  $P_D=94.7 \text{ MW/cm}^3$ )。这些结果表明 BKT-BF-xNBN 无铅铁电体在超级(电介质)储能电容器领域具有广阔的前景。

**关键词:** 钛酸铋钾; 无铅; 介电陶瓷; 弛豫铁电体; 储能电容器

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在储能领域, 铅基电介质电容器一直占据主导地位。然而, 随着环保意识的提升, 实现器件的无铅化已经成为一种趋势<sup>[1-3]</sup>。与铅基陶瓷相比, 无铅陶瓷相对而言其储能能量密度与储能效率都不太理想。储能相关的公式为:

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

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

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

其中:  $W$  为总储能密度;  $W_{\text{rec}}$  为可回收储能密度;  $\eta$  为效率;  $E$  为电场;  $P_{\text{max}}$  为最大极化强度;  $P_r$  为剩余极化强度<sup>[4-9]</sup>。为了提高电介质的可回收储能密度和效率, 需要同时提高  $\Delta p$  ( $\Delta p = P_{\text{max}} - P_r$ ) 和击穿强度  $E_b$ <sup>[10-13]</sup>。由于  $P_{\text{max}}$  通常是电介质的固有属性, 难以

改变, 因此可选择具有高  $P_{\text{max}}$  的材料作为基底; 然而, 通常情况下,  $P_{\text{max}}$  较高的基底也伴随着较大的  $P_r$ , 这个问题可以引入弛豫铁电体来进行改善。此外, 可通过控制晶粒的尺寸以提高陶瓷密度来提高  $E_b$ 。采用多种策略同时提高  $\Delta p$  与  $E_b$  是提升电介质储能性能的关键策略, 可以首先进行复合来获得高  $P_{\text{max}}$  的陶瓷, 然后引入弛豫性强和高带宽的铁电体, 以减小  $P_r$ 、提高耐压, 从而实现高储能密度的陶瓷。

Bi<sub>0.5</sub>K<sub>0.5</sub>TiO<sub>3</sub> (BKT) 是一种潜力巨大的电介质基底, 其自发极化强度  $P$  可达  $52 \mu\text{C/cm}^2$ 。然而, BKT 基陶瓷具有较大  $P_r$  以及较小  $E_b$ , 导致其储能性能不佳 ( $W_{\text{rec}} < 3 \text{ J/cm}^3$ ,  $\eta < 80\%$ )<sup>[14-15]</sup>。因此, 关键在于提高 BKT 基陶瓷样品的  $E_b$ , 同时减小  $P_r$ 。文献[16]报道将 BaTiO<sub>3</sub> 和 NaNbO<sub>3</sub> 引入 BKT 中可回收储能密度达到  $7.5 \text{ J/cm}^3$ 。这说明 BKT 基陶瓷具有很

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大的储能潜力, 尽管效率仍有改进的余地。减小  $P_r$ , 即细化电滞回线破坏长程铁电序, 被认为是一种有效策略。同时, 通过控制晶粒的生长以形成均匀的小晶粒和致密的微观结构, 可以提高  $E_b$ 。

综上所述, 可采用多重策略, 如控制晶粒尺寸和破坏长程铁电序诱导以形成极性纳米区域 (PNRs), 可以提升 BKT 电介质的储能性能<sup>[4, 17–20]</sup>。在本工作中, 弛豫铁电体  $\text{Na}_{0.73}\text{Bi}_{0.09}\text{NbO}_3$  被引入  $0.75\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3\text{--}0.25\text{BiFeO}_3$  ( $0.75\text{BKT--}0.25\text{BF}$ ) 中来改善陶瓷的储能行为。这一设计基于以下几点考虑: 1)  $0.75\text{BKT--}0.25\text{BF}$  中 BF 的摩尔分数为 25%, 位于相变界限 (MPB), 此时  $P$  最大化; 2) 引入的  $\text{Na}^+$  可能会进入原来的晶格中, 会破坏长程铁电序, 诱导 PNRs 的形成; 3) Bi 的加入可以补偿易挥发的 Bi 并且高价掺杂的  $\text{Nb}^{5+}$  有助于提高  $E_b$ ; 4)  $\text{Na}_{0.73}\text{Bi}_{0.09}\text{NbO}_3$  (NBN) 可能还会抑制晶粒的生长, 提高陶瓷的密度, 从而提高  $E_b$ 。

在本工作中, 设计了  $\text{BKT--BF--}x\text{NBN}$  的方案, 降低了  $P_r$  并提高了  $E_b$ , 获得了令人满意的结果 ( $W_{\text{rec}}=4.23 \text{ J/cm}^3$ ,  $\eta=81.2\%$ ), 并对相关机制进行了研究。

## 1 实验

### 1.1 样品的制备

使用传统固相反应法合成了样品  $\text{BKT--BF--}x\text{NBN}$  ( $x=0, 0.1, 0.2, 0.3, 0.4$ ) 陶瓷。制备所需的分析纯级别原料如下:  $\text{Bi}_2\text{O}_3$  (99.5%, 质量分数, 下同, 蜀都)、 $\text{K}_2\text{CO}_3$  (99.5%, Aladdin)、 $\text{TiO}_2$  (99.5%, 中星)、 $\text{Fe}_2\text{O}_3$  (99.5%, Aladdin)、 $\text{Na}_2\text{CO}_3$  (99.8%, Aladdin) 和  $\text{Nb}_2\text{O}_5$  (99.5%, 国药)。原料经过干燥处理后, 按照化学计量比称量, 然后将其直接置于球磨罐中, 并放入适量酒精, 进行球磨 12 h。混合均匀的物料在烘干后被放入坩埚中, 然后在  $850^\circ\text{C}$  进行预烧 5 h, 接着进行 12 h 的湿磨。在初步反应物中添加了 0.5% (质量分数) 的聚乙烯醇 (PVA), 然后将其放入直径为 12 mm 的模具中, 施加压力, 形成厚度约 0.8 mm 的圆片。生胚在炉子中升温排胶后, 在  $1050\sim1085^\circ\text{C}$  和  $1000\sim1035^\circ\text{C}$  烧结 3 h。

### 1.2 样品的表征

采用日本 Rigaku 公司生产的 MiniFlex 600 型衍射分析仪 ( $\text{Cu K}\alpha$  辐射) 进行晶体结构分析, 使用法国 Horiba 生产的 Raman 光谱仪 (LabRAM300, 532 nm)

测定相结构; 用扫描电子显微镜 (日本 JEOL JSM6460) 表征陶瓷的表面形貌; 利用阻抗分析仪 (美国 Keysight E4990A) 测量了介电温谱; 铁电分析仪 (美国 Radiant Technologies InC RT1-Premier II,) 测试了电滞回线以及一阶反转曲线。铁电测试样品的厚度约为  $100 \mu\text{m}$ , 电极采用金, 电极面积约为  $0.007922 \text{ cm}^2$ ; 击穿强度采用耐压测试仪 (南京民盛 Ms267IP-IIA (B)) 测试; 此外, 使用充放电平台 (上海同果智能科技 CFD-003) 评估了充放电性能, 测试样品的厚度约为  $100 \mu\text{m}$ , 电极采用银, 电极面积约为  $0.0314 \text{ cm}^2$ 。

## 2 结果与讨论

### 2.1 物相分析

图 1a 为样品  $\text{BKT--BF--}x\text{NBN}$  在室温测试而得的 XRD 谱。所有样品的 (100)、(110)、(111)、(200)、(202)、(211)、(220)、(310) 特征衍射峰都是明显且尖锐的, 表明  $\text{Na}_{0.73}\text{Bi}_{0.09}\text{NbO}_3$  已成功掺入原有的  $\text{BKT--BF}$  体系中<sup>[14, 21–22]</sup>。然而,  $x\geq 0.1$  的样品测试出了  $\text{Na}_2\text{Nb}_8\text{O}_{21}$  (JCPDS 13–0329) 杂质相。为了更深入地研究引入 NBN 后  $\text{BKT--BF}$  结构的变化, 对样品测试了 Raman 光谱。图 1b 为通过 PeakFit 软件进行反卷积的 Gaussian–Lorentz 模态展示的 Raman 光谱。不同的波数段展示不同的结构变化: 低波数区 ( $<200 \text{ cm}^{-1}$ ) 与 A 位 ( $\text{Bi}^{3+}$ 、 $\text{K}^+$  和  $\text{Na}^+$ ) 阳离子的振动有关; 中波数区域 ( $200\sim400 \text{ cm}^{-1}$ ) 是与 B–O 键振动密切联系; 高波数区域 ( $>700 \text{ cm}^{-1}$ ) 与光学重叠带相关<sup>[15, 23]</sup>。引入 NBN 后, 模态  $\nu_4$  和  $\nu_5$  逐渐分离, 说明 A 位和 B 位的阳离子共存形成了密集无序结构。此外, 随着 NBN 引入量的增加, 位于  $600 \text{ cm}^{-1}$  位置的  $\nu_3$  模态发生红移, 表明氧八面体 ( $\text{BO}_6$ ) 结构发生了倾斜以及 PNRs 的减小<sup>[24]</sup>。

### 2.2 显微结构分析

图 2 为样品  $\text{BKT--BF}$  以及储能优化组分样品  $\text{BKT--BF--}0.3\text{NBN}$  的表面形貌照片。由图 2 可见, 所有陶瓷样品的晶粒都是致密且形态一致的, 这意味着没有明显的衍生物产生。这 2 个组分的微观形貌最大的区别在于晶粒大小的差异, 优化组分的晶粒尺寸明显小于纯的组分。有相关论文也报道过, 可能是 NBN 的引入抑制了晶粒的生长, 这有助于提高陶瓷的电场击穿强度<sup>[3, 25–26]</sup>。晶粒尺寸的减小归因于金属阳离子 ( $\text{Na}^+$ 、 $\text{Bi}^{3+}$  和  $\text{K}^+$ ) 在 A 位的随机分布, 从而破坏了内部结构<sup>[3]</sup>。

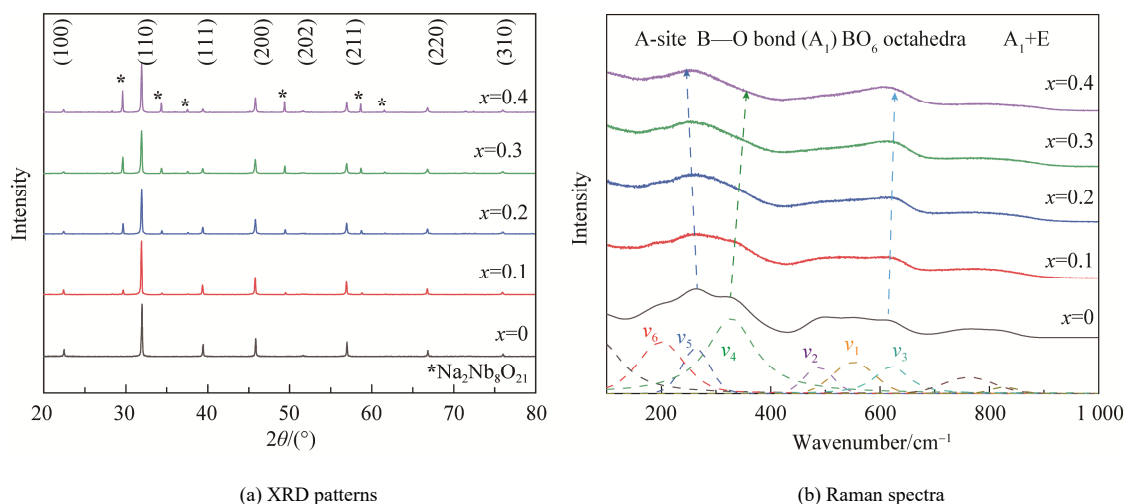
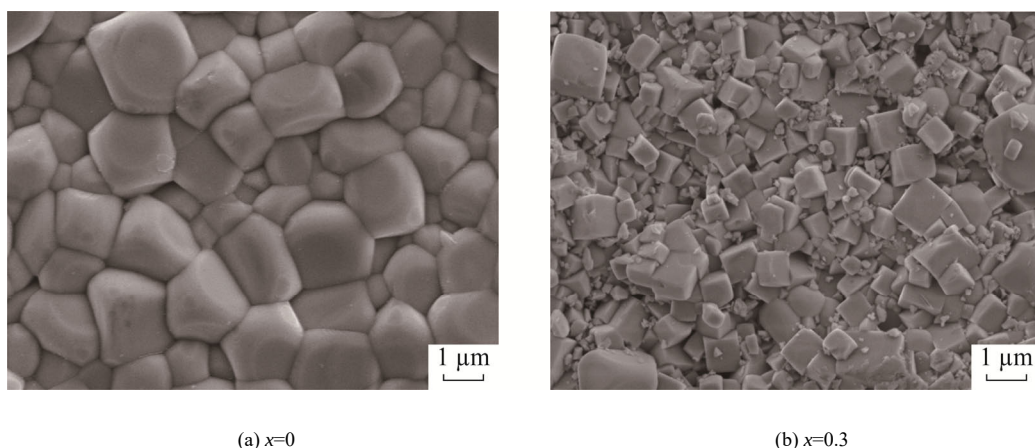


图 1 样品 BKT-BF-xNBN 的 XRD 谱和 Raman 光谱  
Fig. 1 XRD patterns and Raman spectra of BKT-BF-xNBN samples



(a)  $x=0$  (b)  $x=0.3$

图 2 样品 BKT-BF-xNBN 的 SEM 照片  
Fig. 2 SEM images for BKT-BF-xNBN samples

### 2.3 介电性能分析

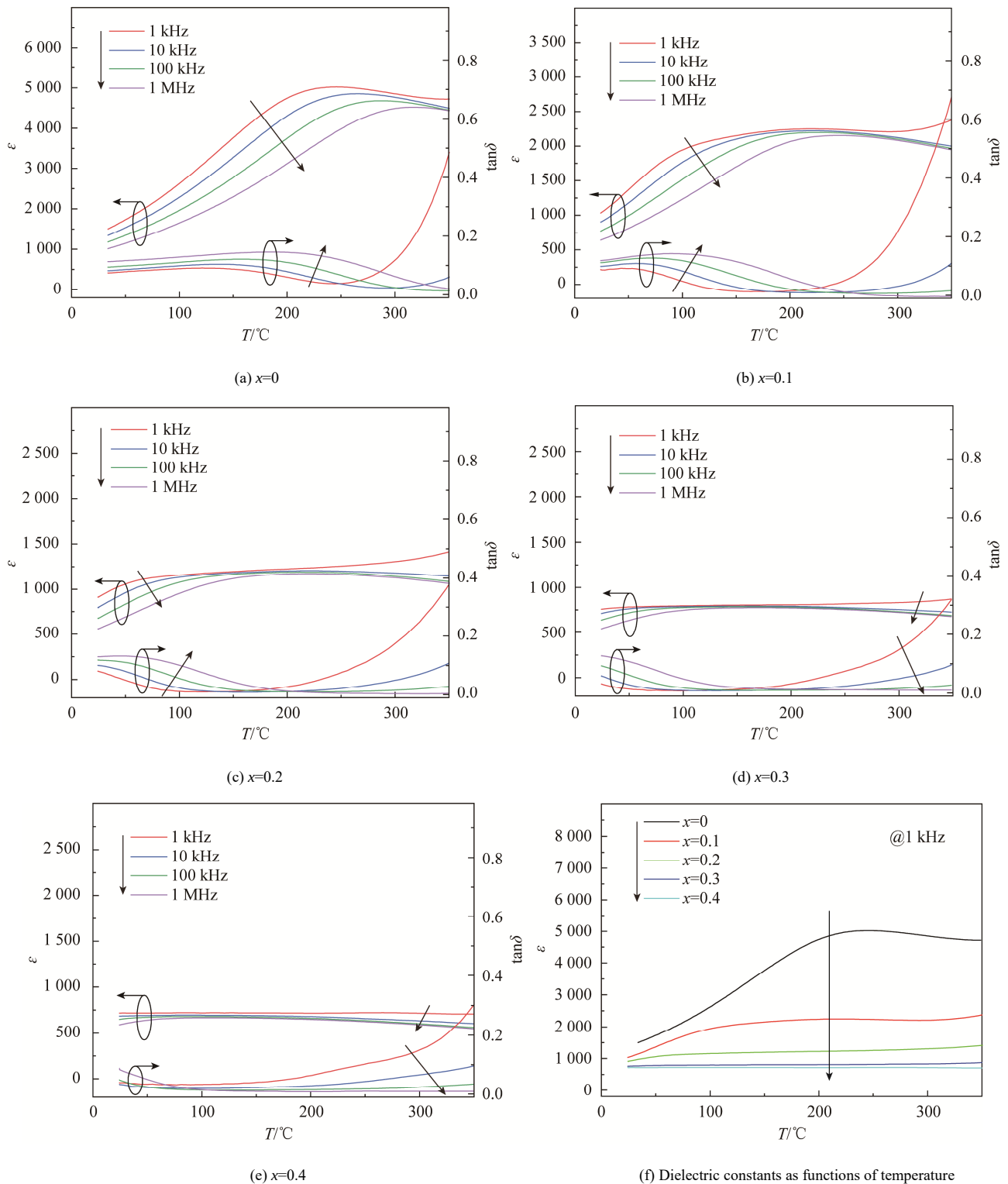
图 3a~图 3e 为样品 ( $x = 0 \sim 0.4$ ) 在不同温度下的介电常数。显然, 随着 NBN 引入量的增加, 样品的 Curie 温度逐渐降低, 朝着室温方向移动; 同时, 介电峰不断的宽平化, 表明陶瓷样品的弛豫性变强了<sup>[27-29]</sup>。随着 NBN 掺杂量的增加, 温度相关的介电常数曲线呈现出如图 3f 所示的平缓特征。当  $x$  的值达到 0.3 后, 介电常数值呈现出较强的温度稳定性, 几乎表现为一条直线, 这被认为与 NBN 陶瓷介电响应的温度不相关性存在联系, 并为储能场景下的稳定应用提供了支撑。样品 BKT-BF-0.3NBN 在 1 kHz 的室温介电损耗是 0.015, 而其他 3 组样品的值均大于 0.05, 该现象有助于优化组分获得良好的储能性能。同时, 随着掺杂量的增加, 样品的介电损耗也出现了对温

度不敏感的平台, 表明 NBN 的引入有助于提高陶瓷的温度稳定性。

为了定量分析陶瓷样品的弛豫性, 采用 Curie-Weiss 定律计算了弛豫度, 弛豫因子  $\gamma$  可由式 (4) 计算得出:

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

其中:  $\epsilon_r$  为相对介电常数;  $\epsilon_m$  为最大介电常数;  $T$  为温度;  $T_m$  为  $\epsilon_m$  相对应的温度;  $C$  为常数<sup>[28]</sup>。由图 4a~图 4e 可见, 样品 BKT-BF-0.3NBN 的弛豫因子  $\gamma=2.2$ , 显现出较强的弛豫性。为了更好地分析样品的温度稳定性, 图 4f 中的电容温度系数  $\alpha_C[\alpha_C = \Delta C/C(25^\circ\text{C})]$ , 电子工业协会 X8R 电容器标准计算方式] 的变化率小于  $\pm 15\%$ , 表明样品 BKT-BF-0.3NBN 良好的温度稳定性。

图3 样品 BKT-BF- $x$ NBN 的介电常数( $\epsilon$ )及损耗( $\tan\delta$ )Fig. 3 Dielectric constant ( $\epsilon$ ) and loss ( $\tan\delta$ ) of BKT-BF- $x$ NBN samples at different temperature

## 2.4 储能性能分析

样品 BKT-BF- $x$ NBN 在 140 kV/cm 电场下测试的双向电滞回线( $P$ - $E$ )以及电流密度曲线( $J$ - $E$ )如图 5a 和图 5b 所示。显然, 纯的组分的双向电

滞回线是饱和的, 电流密度曲线有 2 个凸起的尖峰, 显示出相对较强的铁电性, 这是由于电场的作用下长程铁电序的翻转引起的<sup>[30]</sup>;随着 NBN 量的增多, 样品的电滞回线变得更加纤细, 且没有

明显的尖峰翻转电流峰,说明弛豫性增强,这是因为样品长程铁电序被破坏、短程铁电序动态PNRs的形成<sup>[8, 31-33]</sup>。为了更深入地研究样品的动态响应,测试了陶瓷的一阶反转曲线(FORC)。图5c和图5d是2个样品的FORC循环图,这些曲线完整且光滑,其具有一定的可靠性。图5e和图

5f是从FORC数据中获取的 $P(\alpha, \beta)$ 数据,纯BKT-BF陶瓷在靠近中心点的地方有1个高度集中的区域,这表明在中等电场下微畴发生了密集的翻转<sup>[34-35]</sup>。而样品BKT-BF-0.3NBN的分布较为均匀,没有明显的集中区域,意味着转变成了弛豫状态<sup>[36]</sup>。

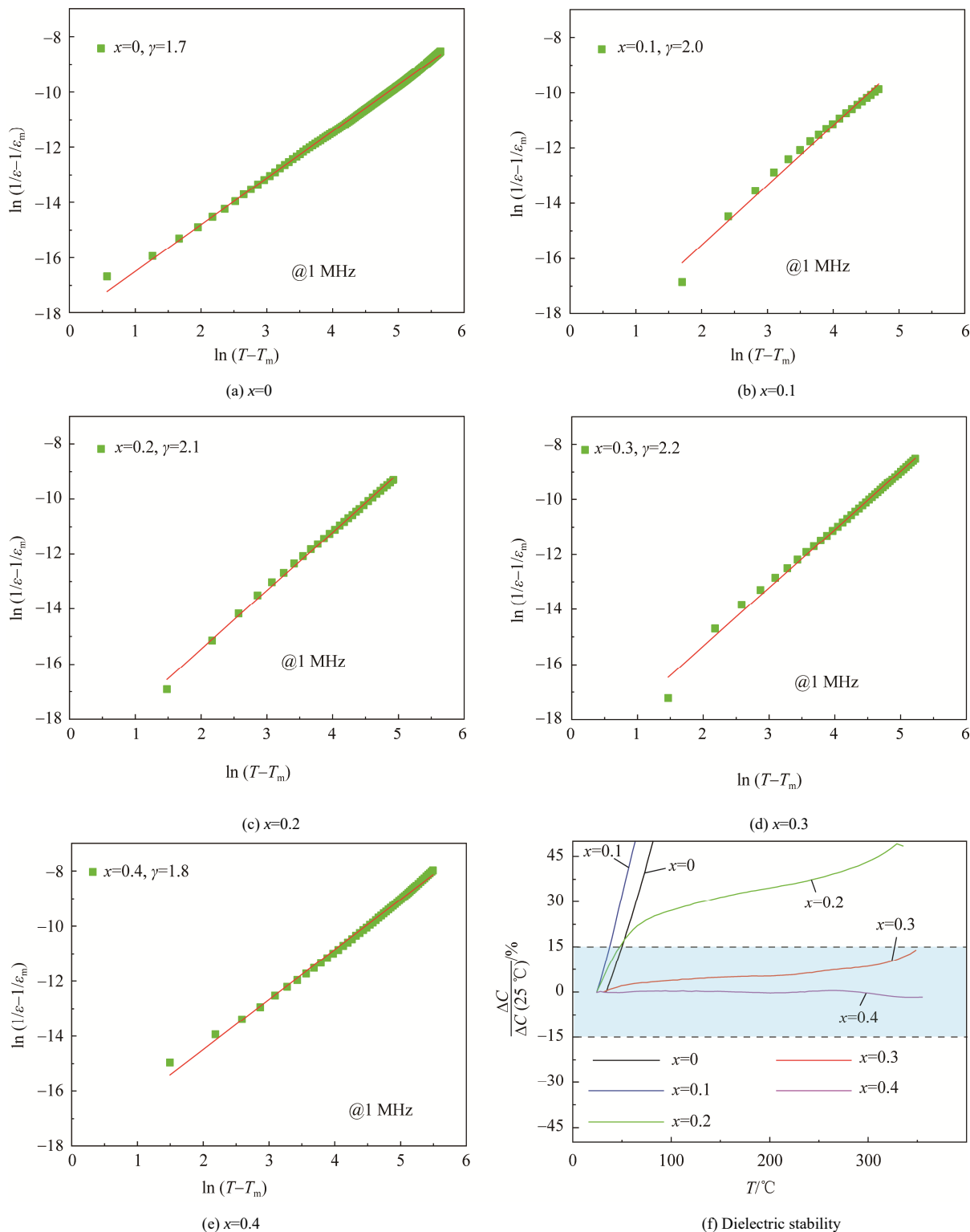


图4 样品BKT-BF-xNBN的弛豫性和介电稳定性

Fig. 4  $\ln(1/\epsilon - 1/\epsilon_m)$  and  $\ln(T - T_m)$  for BKT-BF-xNBN samples and temperature-dependent  $\Delta C/C(25^\circ\text{C})$  for BKT-BF-xNBN

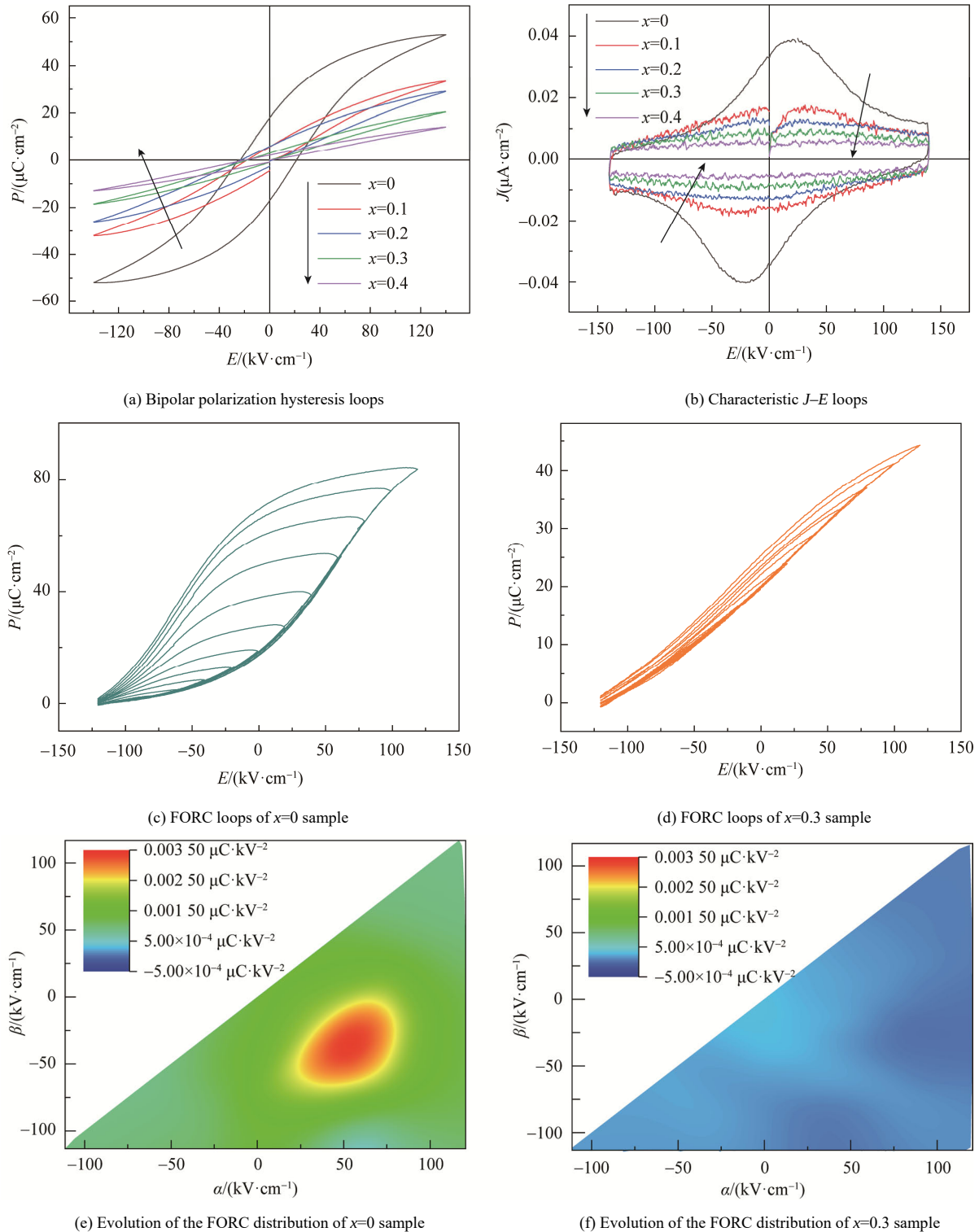


图5 样品 BKT-BF- $x$ NBN 在 140 kV/cm 外电场下的双向电滞回线( $P-E$ )、电流密度-电压( $J-E$ )曲线、FORC 循环和 FORC 分布  
Fig. 5 Bipolar polarization hysteresis ( $P-E$ ) loops and the characteristic  $J-E$  loops of BKT-BF- $x$ NBN samples at 140 kV/cm; first order reversal curve (FORC) loops and evolution of the FORC distribution for BKT-BF- $x$ NBN samples

图 6a 为 5 个组分测试统计的 Weibull 分布图, 所有样品的形状因子  $\beta$  值都大于 10, 这说明测试数据的可靠性<sup>[37–38]</sup>.  $E_b$  与  $\beta$  是通过式(5)计算而得:

$$X_i = \ln(E_i); Y_i = \ln(\ln(1/(1-i/(n+1)))) \quad (5)$$

其中:  $E_i$  为不同样品的击穿强度,  $i$  表示样品序号;  $n$

为被测试样品的总数<sup>[5]</sup>. 由图 6 可见,  $x$  越大的组分的击穿强度越强. 纯的组分击穿强度只有 204 kV/cm, 而优化组分的击穿强度则达到 383 kV/cm, 击穿强度的提高可能是因为添加了 Bi, 从而补充了挥发的 Bi, 并且  $Nb^{5+}$  高价掺杂可以平衡电荷<sup>[39–40]</sup>. 图 6b 为

$x=0\sim 0.4$  样品的单向电滞回线, 所有样品都是在其最大耐压下测试得到的。NBN 的引入有助于提高样品的击穿强度, 与图 6a 的 Weibull 分布相互印证。由图 6c 可得所有组分陶瓷的总储能密度  $W$ , 可回收储能

密度  $W_{\text{rec}}$  及储能效率  $\eta$ , 优化组分的陶瓷的可回收储能密度达  $4.23 \text{ J/cm}^3$ , 并且其效率高达 81.2%。可回收储能密度的提高可能是因为击穿强度的提高。

图 7a 为样品 BKT-BF-0.3NBN 在室温测试得到

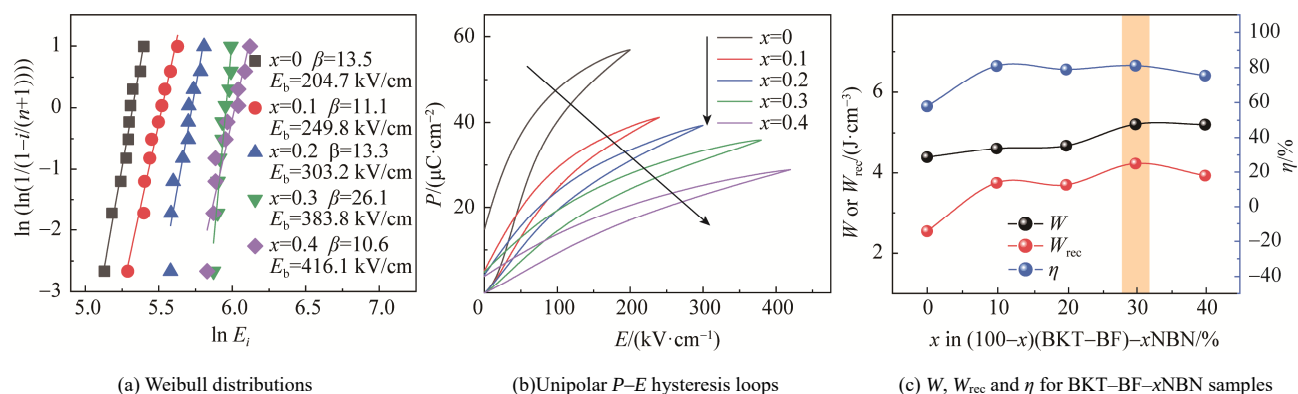


图 6 BKT-BF- $x$ NBN 陶瓷的 Weibull 分布图、单向  $P-E$  电滞回线和相应的  $W$ ,  $W_{\text{rec}}$  和  $\eta$  值

Fig. 6 Weibull distributions, unipolar  $P-E$  hysteresis loops and corresponding total energy storage density ( $W$ ), recoverable energy storage density ( $W_{\text{rec}}$ ) and energy storage efficiency ( $\eta$ ) for the BKT-BF- $x$ NBN samples

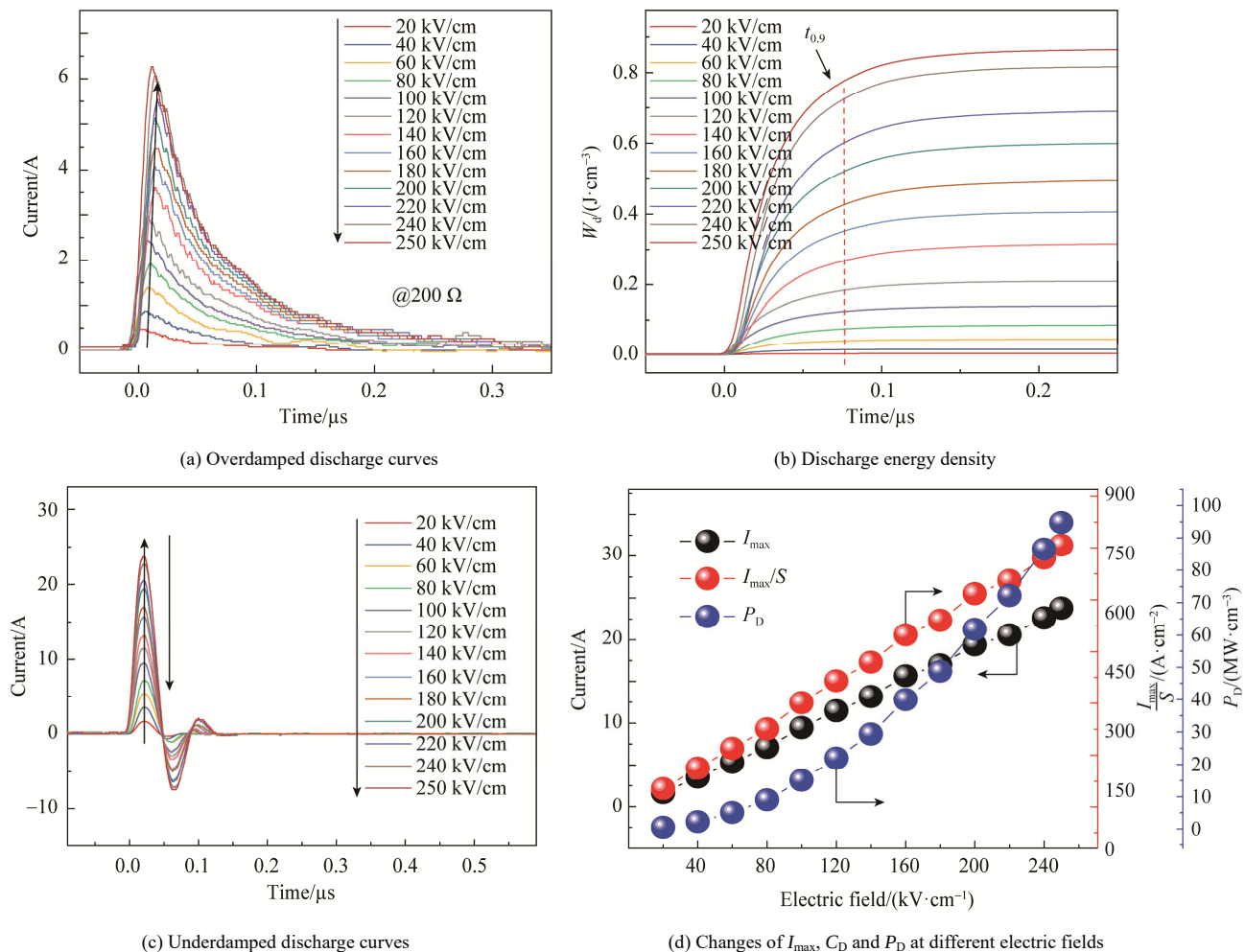


图 7 样品 BKT-BF-0.3NBN 在不同电场下的过阻尼放电电流波形、放电能量密度  $W_d$ 、欠阻尼放电电流波形, 和  $I_{\text{max}}$ ,  $C_D$ ,  $P_D$  的统计数据

Fig. 7 Overdamped discharge curves of BKT-BF-0.3NBN sample at different electric fields; discharge energy density of BKT-BF-0.3NBN sample; underdamped discharge curves of BKT-BF-0.3NBN sample; changes of maximum current ( $I_{\text{max}}$ ), current density ( $C_D$ ) and power density ( $P_D$ ) at different electric fields

的过阻尼放电曲线；样品的充放电相关性能测试涉及的公式为：

$$W_d = R \int I(t)^2 dt / V \quad (6)$$

其中： $W_d$ 为放电能量密度； $R$ 为负载电阻(本工作中 $R=200\ \Omega$ )； $I$ 为电流； $V$ 为样品的体积<sup>[3]</sup>。

图 7b 为优化组分不同电场下测得的不同时间下的放电能量密度。显然，所有样品的  $t_{0.9}$  ( $t_{0.9}$  指的是放电能量密度达到其最大值的 90%所需的时间)都小于 75 ns，这表明样品具有非常短的放电时间和高的放电能量密度。不同时间下测得的不同电场的欠阻尼放电电流曲线如图 7c 所示。在 250 kV/cm 电场下，样品的放电电流峰值  $I_{\max}$  高达 23.8 A。为了进一步了解优化组分的充放电性能，对样品进行了在不同电场下电流数值、电流密度和功率体积密度数据的测试，并将统计结果汇总在图 7d。样品 BKT-BF-0.3NBN 的电流密度  $C_D=757.9\text{ A/cm}^2$  ( $C_D=I_{\max}/S$ ,  $S$  为电极面积)，功率密度  $P_D=94.7\text{ MW/cm}^3$  ( $P_D=E \cdot I_{\max}/2S$ ,  $E$  为电场)，意味着优化组分具有应用在大功率场合的潜力<sup>[28, 41–42]</sup>。

### 3 结论

采用固相反应法制备了 BKT-BF- $x$ NBN 无铅铁电体。 $\text{Na}_{0.73}\text{Bi}_{0.09}\text{NbO}_3$  的引入改善了陶瓷的微观结构，增强了击穿强度，也改善了样品的弛豫性，并诱导形成了 PNRs。当  $x=0.3$  时，综合性能达到最佳，可回收储能密度  $W_{\text{rec}}=4.23\text{ J/cm}^3$ ，效率  $\eta=81.2\%$ ，同时击穿强度达到最大值。此外，样品 BKT-BF-0.3 NBN 拥有出色的介电温度稳定性和卓越的充放电性能， $t_{0.9}<75\text{ ns}$ ， $C_D=757.9\text{ A/cm}^2$ ， $P_D=94.7\text{ MW/cm}^3$ 。这些结果表明样品 BKT-BF-0.3NBN 陶瓷在高性能储能电容器方面具有广阔的应用前景。

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## Microstructure and Energy Storage Performance of $(1-x)(0.75\text{K}_{0.5}\text{Bi}_{0.5}\text{TiO}_3-0.25\text{BiFeO}_3)-x\text{Na}_{0.73}\text{Bi}_{0.09}\text{NbO}_3$ Ceramics

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### Extended Abstract

**Introduction** Lead-free dielectric capacitors have attracted recent attention due to the super power density, fast charge-discharge rate and outstanding thermal stability. However, the recoverable energy density of lead-free ferroelectric ceramic is relatively lower, compared to ceramics containing lead. The introduction of strong relaxor ferroelectrics can realize the excellent energy storage performance via decreasing remanent polarization as well as enhancing impedance.  $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$  (BKT) is a promising candidate for dielectric capacitor due to the unique lone pair electronic  $6s^2$  configuration about Bi, leading to a large spontaneous polarization (i.e.,  $P = 52 \mu\text{C}/\text{cm}^2$ ). Nevertheless, the energy storage properties of BKT-based ceramics are poor (i.e.,  $W_{\text{rec}} < 3 \text{ J}/\text{cm}^3$ ,  $\eta < 80\%$ ) because

of the large remanent polarization and negative breakdown strength. Chen et al. reported that the recoverable energy storage density reached  $7.5 \text{ J/cm}^3$  through adding the  $\text{BaTiO}_3$  and  $\text{NaNbO}_3$  into BKT, indicating that BKT-based ceramics had a substantial prospect. The long-range ferroelectric order is broken to obtain a slim hysteresis loop, which can improve the energy storage performance. Simultaneously, the uniform small grain and compact microstructure of ceramic are essential, which can upgrade the breakdown strength for ferroelectric material. Thus, reducing grain size and breaking ferroelectric long-range order to generate polar nano-regions (PNRs) could improve the BKT-based specimens energy storage properties. In this paper, a relaxor ferroelectric material of  $\text{Na}_{0.73}\text{Bi}_{0.09}\text{NbO}_3$  (NBN) was induced into  $0.75\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3\text{--}0.25\text{BiFeO}_3$  (0.75BKT–0.25BF) to reinforce the ESP of ceramics. BF and NBN were selected to optimize ESP. The morphotropic phase boundary (MPB) of BKT–BF binary system was constructed.

**Methods** For the synthesis of BKT–BF– $x$ NBN ( $x=0, 0.1, 0.2, 0.3$  and  $0.4$ ) ceramics,  $\text{Bi}_2\text{O}_3$  (99.5%, in mass fraction, the same below),  $\text{K}_2\text{CO}_3$  (99.5%),  $\text{TiO}_2$  (99.5%),  $\text{Fe}_2\text{O}_3$  (99.5%),  $\text{Na}_2\text{CO}_3$  (99.8%) and  $\text{Nb}_2\text{O}_5$  (99.5%) were used as raw materials. The dried oxides were weighted and mixed according to stoichiometric ratios in a polyethylene container, and then the mixed materials with alcohol were ground in a ball mill for 12 h. After drying, the mixture was calcined at  $850^\circ\text{C}$  for 5 h, and the powder was further ground under the same condition. Sequentially, the dried powder with 0.5% (in mass fraction) polyvinyl alcohol (PVA) was pressed into discs with a thickness of 0.8 mm and a diameter of 12 mm. Finally, the green plates were sintered at  $1000\text{--}1035^\circ\text{C}$  for 3 h.

**Results and discussion** The results show that an optimum recoverable energy storage density ( $W_{\text{rec}}$ ) of  $4.23 \text{ J/cm}^3$  and an improved energy storage efficiency ( $\eta$ ) of 81.2% at  $380 \text{ kV/cm}$  are achieved. The microstructure of the specimens is compact due to the refined size of grain, leading to a boosted breakdown strength ( $E_b$ ). In addition, an enhanced efficiency of the specimen with  $x$  of 0.3 can be obtained, which arose from the negligible remanent polarization ( $P_r$ ). Based on the analysis of dielectric relaxation, the dispersion coefficient ( $\gamma$ ) of the BKT–BF–0.3NBN is 2.2, implying a short-range ferroelectric order, which can increase the polar nanometer regions. To better understand the reason for the decreased  $P_r$ , the first order reversal curve (FORC) distribution of ceramics was measured. The optimized composition has a distinguished dielectric thermal stability and a superior charge–discharge performance (*i.e.*,  $t_{0.9}$  (the time for releasing 90% of all storage energy)  $< 75 \text{ ns}$ , current density ( $C_D$ ) of  $757.9 \text{ A/cm}^2$  and power density ( $P_D$ ) of  $94.7 \text{ MW/cm}^3$ ), indicating a promising prospect in the applications for high-power dielectric capacitors. These results illustrate that the composition design for BKT–BF– $x$ NBN is effective to refine the energy storage performance of ceramic.

**Conclusions** Lead-free BKT–BF– $x$ NBN ceramics with  $x$  of 0, 0.1, 0.2, 0.3 and 0.4 were synthesized. The introduction of  $\text{Na}_{0.73}\text{Bi}_{0.09}\text{NbO}_3$  improved the microstructure of ceramics, boosted the breakdown strength, enhanced the ceramics relaxation and resulted in the appearance of PNRs. As a result, the BKT-based ceramic with  $x$  of 0.3 had the optimum properties (*i.e.*,  $W_{\text{rec}}$  of  $4.23 \text{ J/cm}^3$  and  $\eta$  of 81.2%). Moreover, the superior dielectric thermal stability as well as charge–discharge performance (*i.e.*,  $t_{0.9} < 75 \text{ ns}$ ,  $C_D = 757.9 \text{ A/cm}^2$ ,  $P_D = 94.7 \text{ MW/cm}^3$ ) were achieved. This work indicated that BKT–BF–0.3NBN ceramic could have a promising application potential in cutting-edge performance dielectric capacitor.

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