

稀土 Ce^{4+} 掺杂对 BCT-BZNT 陶瓷结构和储能性能的影响

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摘 要: 电介质电容器由于具有超高的功率密度、超快的充放电速率, 被广泛应用于脉冲功率电子设备。利用传统固相反应法合成了 $(1-x)\{0.88(\text{Ba}_{0.6}\text{Ca}_{0.4})\text{TiO}_3-0.12\text{Bi}[\text{Zn}_{2/3}(\text{Nb}_{0.85}\text{Ta}_{0.15})_{1/3}]\text{O}_3\}-x\text{CeO}_2$ 陶瓷(BCT-BZNT- $x\text{Ce}$, $x=0, 0.010, 0.015, 0.020, 0.025$)。研究了稀土 Ce 对 $0.88(\text{Ba}_{0.6}\text{Ca}_{0.4})\text{TiO}_3-0.12\text{Bi}[\text{Zn}_{2/3}(\text{Nb}_{0.85}\text{Ta}_{0.15})_{1/3}]\text{O}_3$ 陶瓷相结构、微观形貌、介电和储能性能的影响。结果表明: 随着 Ce 含量的增加, 陶瓷的晶粒得到细化, 介电常数和介电损耗减小。此外, Ce 的引入显著增强了样品的饱和极化和击穿电场强度。当 $x=0.02$ 时, 陶瓷在 600 kV/cm 的电场强度下获得了极高的可回收储能密度 5.49 J/cm^3 和储能效率 89.4% , 同时具有超快的充放电速率($t_{0.9}=23.8\text{ ns}$)。样品 BCT-BZNT- 0.02Ce 呈现出优异的综合性能, 使其在脉冲功率领域具有很好的发展潜力。

关键词: 钛酸钡; 弛豫铁电体; 储能性能; 充放电速率

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由各种原因引起的全球性问题不断加剧, 导致能源匮乏, 可再生、可持续能源的发展受到广泛关注。目前, 广泛研究的储能材料有: 电池、电化学电容器、燃料电池以及介质电容器^[1-2]。介质陶瓷电容器由于具有高功率密度、快速充放电能力以及良好的稳定性能而被广泛应用于高能脉冲领域, 但与其它电容器相比它的储能密度较低, 这限制了其在储能领域的发展^[3-4]。介质电容器仍然是以铅基材料为主, 但铅具有挥发性, 在样品制备、使用和废弃过程会对人体以及环境造成严重危害^[5]。因此, 迫切需要开发具有高储能性能的无铅介电储能陶瓷。介电陶瓷的储能性能一般由可回收储能密度(W_{rec})和储能效率(η)来评估, 其计算公式为^[6-7]:

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

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

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

其中: P_{max} 、 P_r 和 P 分别为饱和极化、剩余极化和极化强度; E 为电场强度; W 为总储能密度。从式

(1)~式(3)可以看出, 增大极化差 $\Delta P (P_{\text{max}}-P_r)$ 和击穿电场强度(BDS)是实现高的 W_{rec} 和 η 的有效途径。

介电储能陶瓷一般分为线性介质、铁电体、反铁电体、弛豫铁电体 4 类^[8]。然而, 线性介质的饱和极化不利于获得高的储能密度^[9]。大部分反铁电陶瓷材料含有贵金属以及重金属等元素, 不仅增加了成本而且破坏了生态环境^[8]。此外, 反铁电陶瓷的铁电-反铁电相变发生在高电场下, 随着内应力的不断集中和失效, 反铁电陶瓷材料会出现不同程度的体积膨胀和裂纹, 从而降低了使用寿命^[10]。铁电体的剩余极化和饱和极化都很大, 击穿场强较低, 因此储能效率一般不理想。弛豫铁电体的电滞回线细长, 剩余极化很小, 有利于获得较高的储能密度和储能效率, 在储能领域有着广泛的应用前景。

具有钙钛矿结构的钛酸钡(BaTiO_3)陶瓷为典型的铁电体, 具有良好的介电性能和绝缘性能, 但 BaTiO_3 基陶瓷的 BDS 较低、 P_r 较大, 不利于 BaTiO_3 在储能领域的发展。研究发现, 利用多元固溶和离子掺杂相结合的方式诱导 BaTiO_3 陶瓷由铁电体转变为弛豫铁电体, 产生极性纳米微区(PNRs), 从而有助于 P_r 的降低, 提高其储能性能。如, Ca^{2+} 引入 $(\text{Ba}_{0.65}\text{Sr}_{0.245}\text{Bi}_{0.007})\text{TiO}_3$ 陶瓷, 起到了降低介电损耗

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和减小晶粒尺寸的作用,从而可以承受更高的加载电场^[2]。Bi(Zn_{2/3}Nb_{1/3})O₃引入(Ba_{0.8}Sr_{0.2})TiO₃增加了阳离子的无序性,降低了介电损耗,从而使得 $P-E$ 曲线变细,改善了储能性能^[11]。ZnTa₂O₆ (ZT)引入 Na_{0.3}Bi_{0.3}Ba_{0.04}Sr_{0.36}TiO₃ (BNBST),破坏了 BNBST 陶瓷的铁电有序性、降低剩余极化以及增强了弛豫行为^[12]。Nb₂O₅ 引入 0.46Bi_{1.02}FeO₃–0.29BaTiO₃–0.25Bi_{0.5}Na_{0.5}TiO₃ (BF–BT–BNT),增加了 BF–BT–BNT 陶瓷的局部结构无序性、饱和极化以及电阻率,从而使得 W_{rec} 显著提升^[13]。稀土掺杂主要受到离子尺寸大小的影响,尺寸较小的离子通常取代 B 位而较大的离子取代 A 位,而中等大小的稀土离子根据 A/B 的比例而取代 A 位或者 B 位也能够起到改善 BaTiO₃ 基陶瓷的弛豫行为和 BDS 的作用,提高陶瓷的储能性能^[14–15]。比如, Huang 等^[3]通过传统固相反应法制备了稀土(Re=La, Nd, Sm, Gd, Dy, Er, Yb)掺杂的 0.7BaTiO₃–0.3Sr_{0.7}Bi_{0.2}TiO₃–0.0015Re₂O₃ (BT–SBT–Re)陶瓷,降低介电损耗的同时提高陶瓷的电阻率,使得 BT–SBT–Gd 陶瓷在 330 kV/cm 的电场强度下获得了优异的储能性能($W_{\text{rec}}=3.20 \text{ J/cm}^3$, $\eta=91.5\%$)。Zeng 等^[16]通过在 0.65BaTiO₃–0.35Sr_{0.7}Bi_{0.2}TiO₃ 引入 CeO₂,制备了 BT–SBT– x Ce 陶瓷,同样改善了该体系陶瓷的弛豫行为,在 $x=0.02$ 时获得了最优的储能密度,其中 $W_{\text{rec}}=2.57 \text{ J/cm}^3$, $\eta=81.3\%$ 。上述研究表明,稀土 Ce 掺杂有助于改善弛豫行为和 BDS,提高陶瓷的储能性能。

本工作通过稀土 Ce 掺杂,采用传统的高温固相反应法制备了 $(1-x)\{0.88(\text{Ba}_{0.6}\text{Ca}_{0.4})\text{TiO}_3-0.12\text{Bi}[\text{Zn}_{2/3}(\text{Nb}_{0.85}\text{Ta}_{0.15})_{1/3}]\text{O}_3\}-x\text{CeO}_2$ (简称 BCT–BZNT– x Ce, $x=0, 0.010, 0.015, 0.020, 0.025$)陶瓷,并详细研究了 Ce 掺杂对 BCT–BZNT– x Ce 陶瓷相结构、微观形貌、介电和铁电性能的影响。Ce 离子的引入大幅提高了陶瓷的 BDS 和 ΔP ,为 BaTiO₃ 储能陶瓷的发展提出了新的设计思路。

1 实验

1.1 样品制备

以 BaCO₃ (99.95%, 质量分数, 下同, Aladdin), CaCO₃ (99.50%, Alfa Aesar), TiO₂ (99.90%, Aladdin), Bi₂O₃ (99.90%, Aladdin), ZnO (99.99%, Aladdin), Nb₂O₅ (99.98%, Aladdin), Ta₂O₅ (99.50%, Aladdin) 和 CeO₂ (99.99%, Aladdin) 为原料,采用传统的高温固相反应法制备了 BCT–BZNT– x Ce 陶瓷。首先,将根据化学计量比称取的药品进行一次球磨,然后在

900 °C 预烧 4 h,预烧后的粉末进行二次球磨,将造粒后的粉料压成直径为 10 mm 的圆片,在 1 200 °C 烧结 2 h,得到 BCT–BZNT– x Ce 陶瓷样品,将烧结好的样品减薄抛光至 0.05 mm,处理后的样品溅射直径为 1 mm 的金电极,进行储能性能测试。

1.2 样品表征

采用 SmartLab 型 X 射线衍射仪(XRD, 理学, 日本)在 20°~80°的 2θ 范围内研究了陶瓷样品的晶体结构,利用 inVia 型激光共聚焦 Raman 光谱仪(Raman, 雷尼绍, 英国)测试了 100~1 200 cm⁻¹ 范围内的 Raman 光谱。用 Merlin Compact 型场发射扫描电子显微镜(FE–SEM, Zeiss, 德国)表征了陶瓷表面的微观形貌以及元素分析。使用 HCT1821 型高温介电测试系统(同果科技, 上海)在–150~350 °C 的温度范围、1~1 000 kHz 的频率范围内对样品的介电性能进行了研究,采用 TF2000 型铁电分析仪(aixACCT, 德国)对样品的铁电性能进行了研究,利用 CFD-003 型高压充放电测试仪(同果科技, 上海)研究了样品的充放电性能。

2 结果与讨论

2.1 结构及显微形貌分析

BCT–BZNT– x Ce 陶瓷在 20°~80°范围内的 XRD 谱如图 1 所示。由图 1a 可见,样品并非是单一相结构,主晶相为四方相,与 BaTiO₃ 的标准卡片 JCPDS 74–1956 相对应。另外,在 2θ 为 33.0°、47.5°、59.0° 附近观察到了第二相的衍射峰,与正交相的 CaTiO₃ (JCPDS 82–0228)相对应。正交相 CaTiO₃ 的产生是由于该体系中过量的 Ca²⁺造成的,这与前期的研究工作相一致^[17]。当 $x=0.025$ 时, 2θ 在 28.5°处的衍射峰是由过量的 Ce⁴⁺引起的。由图 1b 可见, (200) 衍射峰随着 Ce 掺杂量的增加向低角度偏移,这是由于离子半径较大的 Ce⁴⁺ (配位数为 6, 离子半径为 0.870 Å)取代了离子半径较小的 Ti⁴⁺ (配位数为 6, 离子半径 0.605 Å)引起的晶格膨胀造成的。

图 1c 为 BCT–BZNT– x Ce 陶瓷的 Raman 光谱,在 100~1 200 cm⁻¹ 范围分成了 4 个主要区域:分别为与 A 位阳离子振动有关的低波数范围(100~200 cm⁻¹),与 Ti–O 键的振动有关的中波数范围(200~400 cm⁻¹),与 TiO₆ 八面体振动有关的高波数范围(400~700 cm⁻¹)以及 A 和 E 纵向光学带重叠的 Raman 峰范围(>700 cm⁻¹)^[18]。240 cm⁻¹ 附近的 Raman 峰主要由正交相的 CaTiO₃ 引起的,进一步说明了 BCT–BZNT– x Ce 陶瓷中 CaTiO₃ 相的存在^[19]。当 $x=$

0.025 时, 在 470 cm^{-1} 处观察到的 Raman 峰可能与出现的 CeO_2 有关, 这与 XRD 的结果一致。在 740 cm^{-1} 处观察到的 Raman 峰 [$A_1(\text{LO})$] 与局部短程

有序结构密切相关^[20]。在 780 cm^{-1} 处的 A_{1g} Raman 峰归因于不同离子占据了钙钛矿结构的 B 位^[4]。

图 2a~图 2e 为 BCT-BZNT- $x\text{Ce}$ 陶瓷表面的

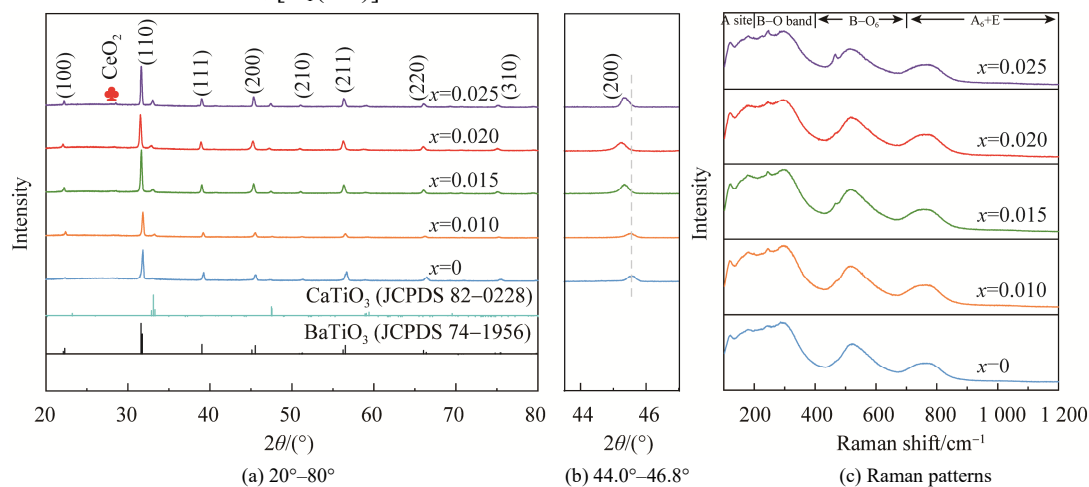


图 1 BCT-BZNT- $x\text{Ce}$ 陶瓷的 XRD 谱及 Raman 谱

Fig. 1 XRD and Raman patterns of BCT-BZNT- $x\text{Ce}$ ceramics

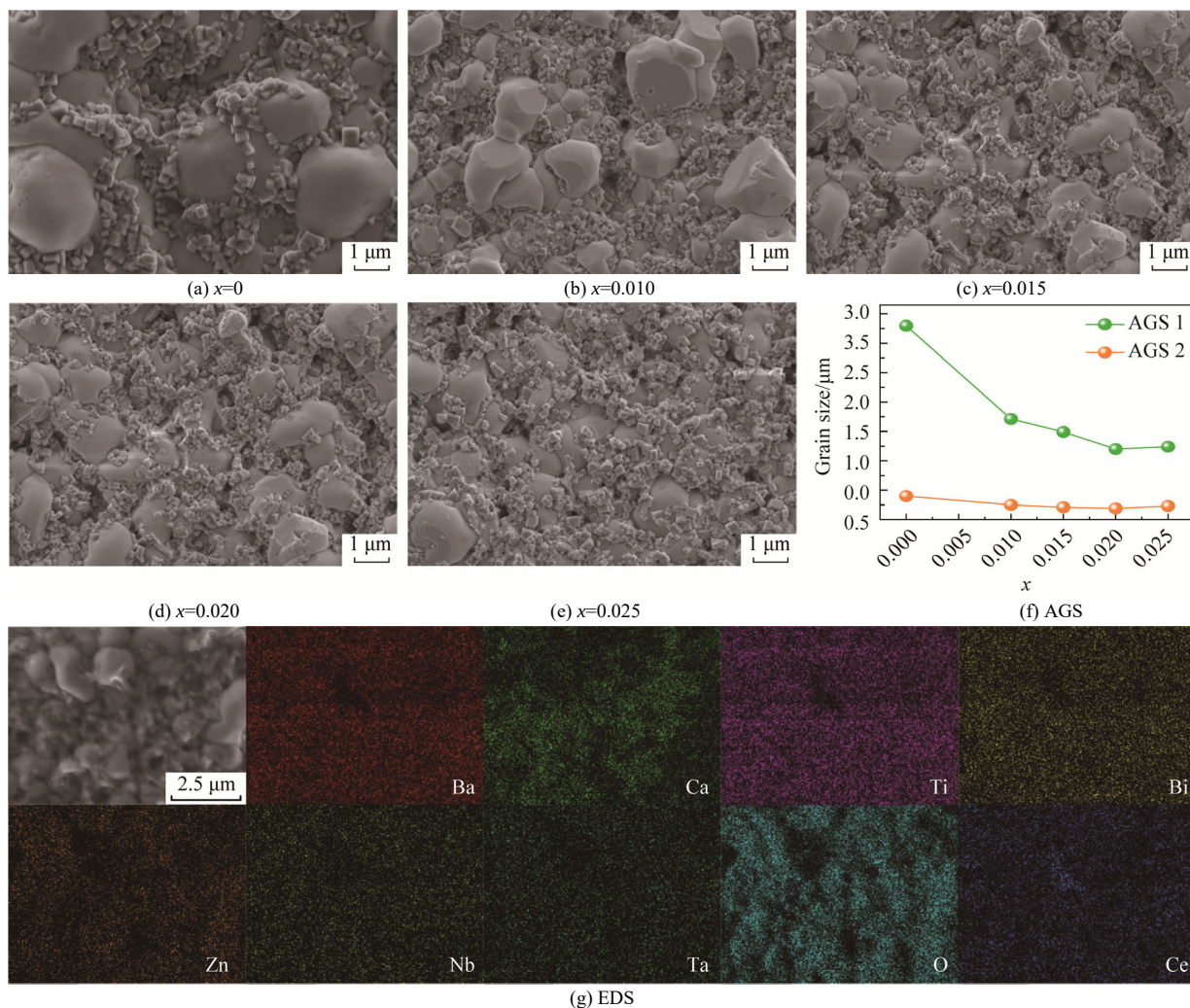


图 2 BCT-BZNT- $x\text{Ce}$ 陶瓷的 SEM 照片和平均晶粒尺寸(AGS 1 和 AGS 2 分别为粗晶粒和细晶粒)和样品 BCT-BZNT-0.02Ce 的元素分布图

Fig. 2 SEM images, average grains size (AGS) of the coarse and fine grains of BCT-BZNT- $x\text{Ce}$ ceramics (AGS 1 and AGS 2 are coarse and fine grains respectively) and element distribution images of BCT-BZNT-0.02Ce sample

SEM 照片, 可以观察到所有样品都是由 2 种不同尺寸的晶粒形成的, 粗晶粒(主晶相)和细晶粒(第二相的异常晶粒)。图 2f 为利用 Nano Measurer 对晶粒进行评估得到的结果。由图 2f 可见, Ce 的引入明显降低了样品粗晶粒的尺寸, 细晶粒也略有减小。当 $x=0.02$ 时不论是粗晶还是细晶, 平均晶粒尺寸(AGS)都达到了最小, 这也是样品 BCT-BZNT-0.02Ce 获得最高 BDS 原因。因为晶粒越小晶界越多, 有利于获得更高的绝缘性能, 从而增加 BDS。为了进一步

研究 2 种晶粒的成分, 对样品 BCT-BZNT-0.02Ce 进行了能谱(EDS)分析, 结果如图 2g 所示。由图 2g 可见, 细晶中 Ca 的分布明显较多, 而在粗晶中 Ba 的分布较多。Ti、Bi、Zn、Nb、Ta、Ce 在粗晶和细晶中的分布基本一致。说明粗晶是以 BaTiO_3 为主而细晶是以 CaTiO_3 为主的。

2.2 介电性能分析

图 3 为在不同测试频率下 BCT-BZNT- x Ce 陶瓷的介电温谱, 所有陶瓷样品的介电常数(ϵ_r)和介电

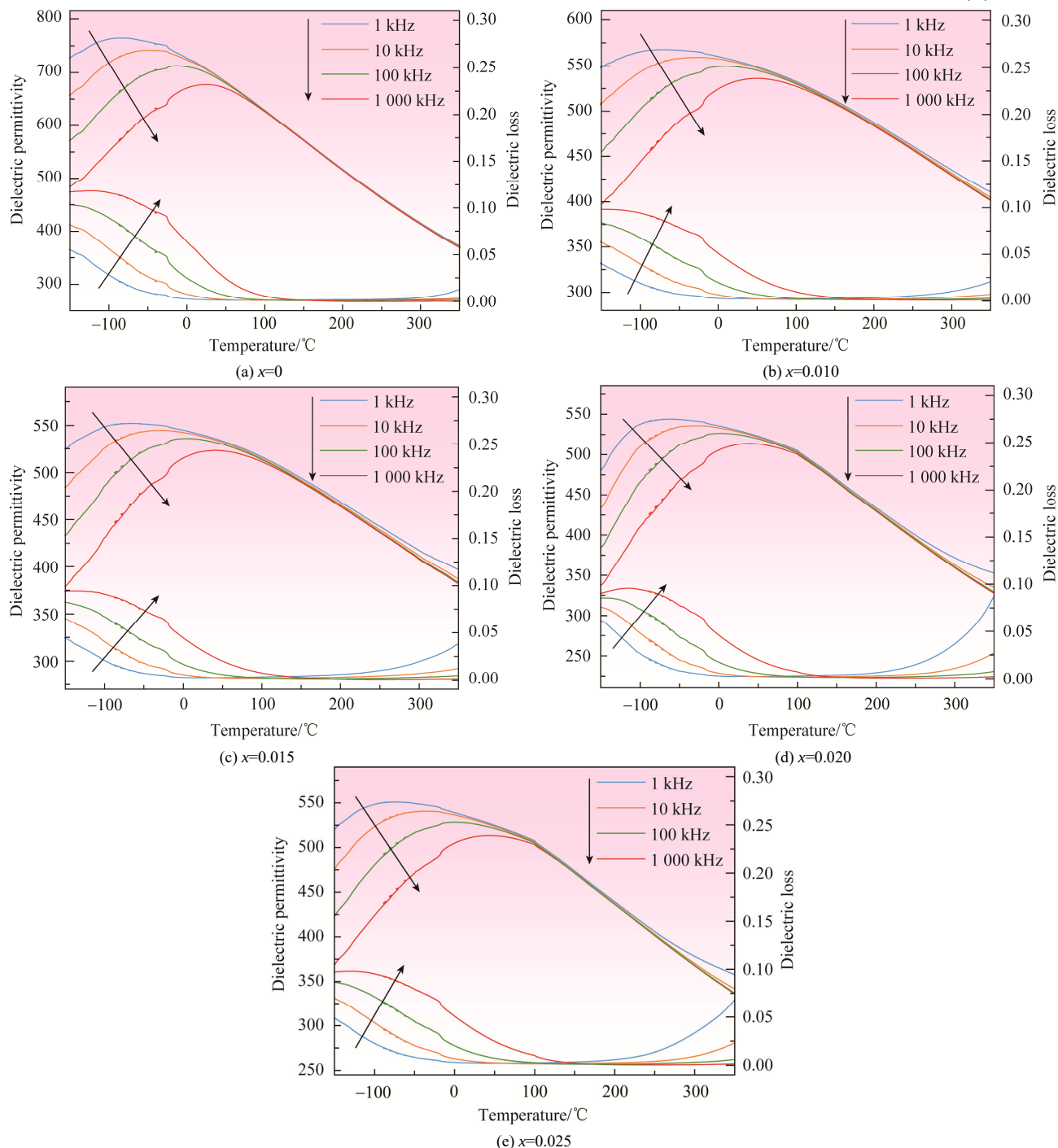
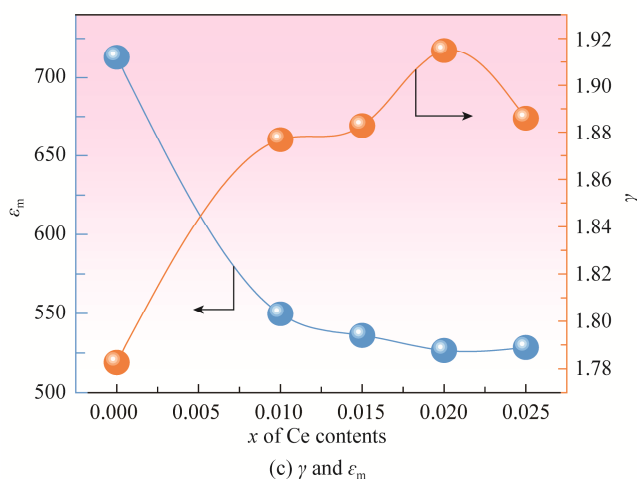
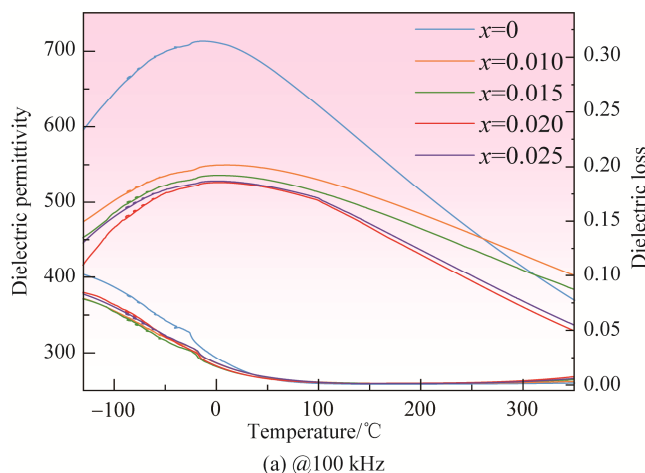


图 3 BCT-BZNT- x Ce 陶瓷的介电常数和介电损耗随温度的变化曲线

Fig. 3 Temperature dependences of dielectric permittivity and dielectric loss for BCT-BZNT- x Ce ceramics

损耗($\tan\delta$)随着频率的升高而降低。呈现出频率色散和扩散相变, 表现出了典型的弛豫行为, 这是因为 A 位和 B 位离子之间较大的价差诱导产生 PNRs^[3, 21]。图 4a 为 BCT-BZNT- $x\text{Ce}$ 陶瓷所有样品的 ϵ_r 和 $\tan\delta$ 在 100 kHz 条件下随温度变化的曲线。可以观察到 Ce 掺杂后 BCT-BZNT- $x\text{Ce}$ 陶瓷的 ϵ_r 和 $\tan\delta$ 都明显降低, 适当的 ϵ_r 有助于 BCT-BZNT- $x\text{Ce}$ 陶瓷获得较高的电场^[22]。为了进一步研究 BCT-BZNT- $x\text{Ce}$ 陶瓷的介电弛豫性能, 引入了修正的 Curie-Weiss 定律^[23]:

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



其中: ϵ_m 为最大介电常数; T_m 为当介电常数为 ϵ_m 时的温度; C 为 Curie-Weiss 常数。由此得到的 γ 值如图 4b 所示。一般认为 $\gamma=1$ 时为理想的铁电体, $\gamma=2$ 为理想的弛豫铁电体^[21]。由图 4b 的拟合结果可知, 没有掺杂 Ce 的陶瓷弛豫系数仅为 1.783, 弛豫系数随着 Ce 含量的增加而增加, 特别是样品 BCT-BZNT-0.02Ce 的 γ 值达到了最大(1.917), 接近理想的弛豫铁电体, 说明 Ce 掺杂可以进一步提高 BCT-BZNT- $x\text{Ce}$ 陶瓷的弛豫性能。从图 4c 中可以明显的观察到 ϵ_m 和 γ 随 Ce 掺杂量增加的变化趋势, 当 $x=0.02$ 时, ϵ_m 最低, γ 最大, 这有利于实现高的 BDS, 从而可以获得具有优异储能性能的介电陶瓷^[20]。

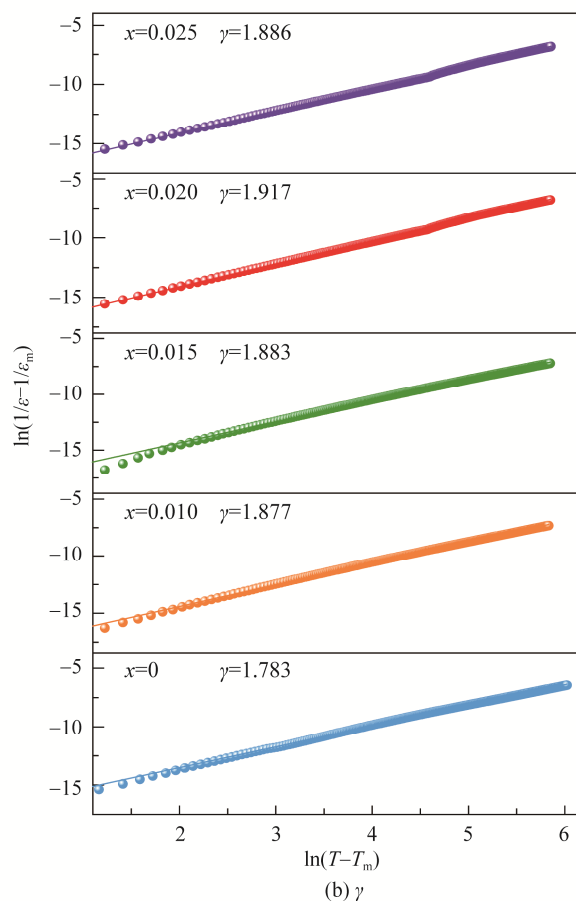


图 4 BCT-BZNT- $x\text{Ce}$ 陶瓷在 100 kHz 条件下的介电温谱, ϵ_m 和弥散系数(γ)随 x 的变化曲线

Fig. 4 Temperature dependences of dielectric permittivity and dielectric loss, the variation of maximum dielectric constant (ϵ_m) and diffuseness parameter (γ) values with x of BCT-BZNT- $x\text{Ce}$ ceramics under 100 kHz

2.3 铁电性能分析

图 5a~图 5c 为 BCT-BZNT- $x\text{Ce}$ 陶瓷在 BDS 下的 P - E 曲线及其对应的储能性能。所有样品的 P - E 曲线细长, 表现出良好的弛豫特性。随着 Ce 含量的增加, BDS 呈现先增大后减小的趋势, BDS 增大可归因于介电常数的降低以及晶粒尺寸的减

小, 这有助于储能性能的提升^[24]。BDS 和 ΔP ($P_{\max} - P_r$) 均在 $x=0.02$ 时达到最大, 分别为 600 kV/cm 和 24.50 $\mu\text{C}/\text{cm}^2$, 如图 5b 所示, 这说明 Ce 的引入对改善 BDS 和 ΔP 有着重要作用。陶瓷样品的 W_{rec} 和 η 可根据 P - E 曲线利用式(1)~式(3)计算得到。由图 5c 可见, 随着 Ce 含量的增加, BCT-BZNT- $x\text{Ce}$

陶瓷的 W_{rec} 先增加后减小。当 $x=0.02$ 时, 获得了最优的储能性能($W_{\text{rec}}=5.49 \text{ J/cm}^3$, $\eta=89.4\%$), 这与较高的 BDS 和 ΔP 密切相关。图 5d 为在不同电场下测得的样品 BCT-BZNT-0.02Ce 陶瓷的 $P-E$ 曲线, 可以看到 P_{max} 随着 BDS 的增加明显增大, 表现出细长的曲线, 表明样品 BCT-BZNT-0.02Ce 具有较高

的储能密度和储能效率。图 5e 为本工作与近期研究的关于 BT 基^[17, 22, 25–26]、BNT 基^[12, 27–29]、BF 基^[30–33]、NN 基^[34–37]陶瓷的储能性能的比较, 可以看到样品 BCT-BZNT-0.02Ce 的储能性能优于近期报道的大多数储能陶瓷材料, 在储能领域表现出较大的发展潜力。

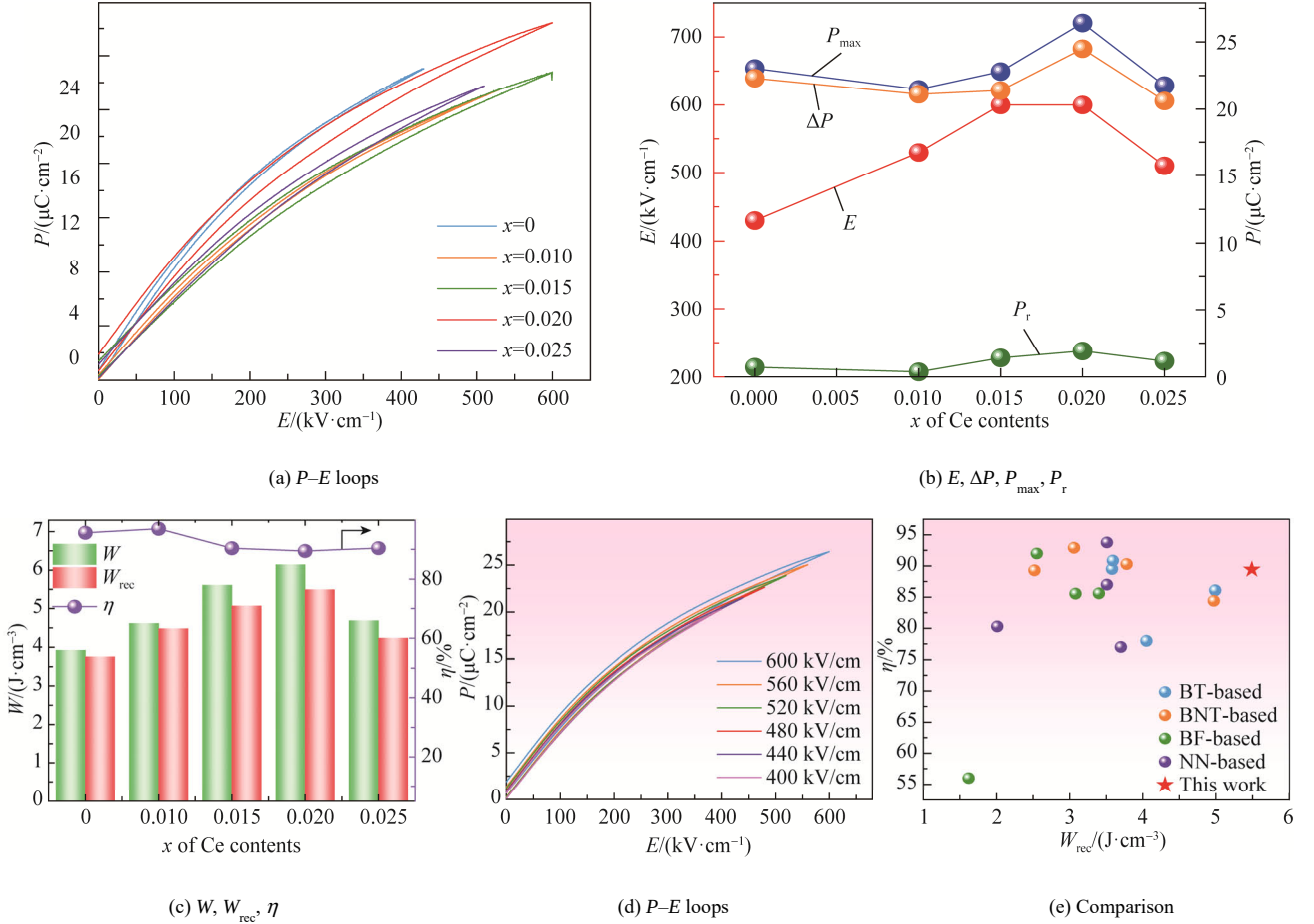


图 5 BCT-BZNT- x Ce 陶瓷在击穿电场下的 $P-E$ 曲线及其对应的储能性能, 样品 BCT-BZNT-0.02Ce 陶瓷的 $P-E$ 曲线, 样品 BCT-BZNT-0.02Ce 与其他陶瓷材料储能性能的对比如 Fig. 5

$P-E$ loops and energy storage performance of BCT-BZNT- x Ce ceramics under breakdown field, $P-E$ loops of BCT-BZNT-0.02Ce sample, comparison of energy storage performance of BCT-BZNT-0.02Ce sample and other ceramic materials

2.4 充放电性能

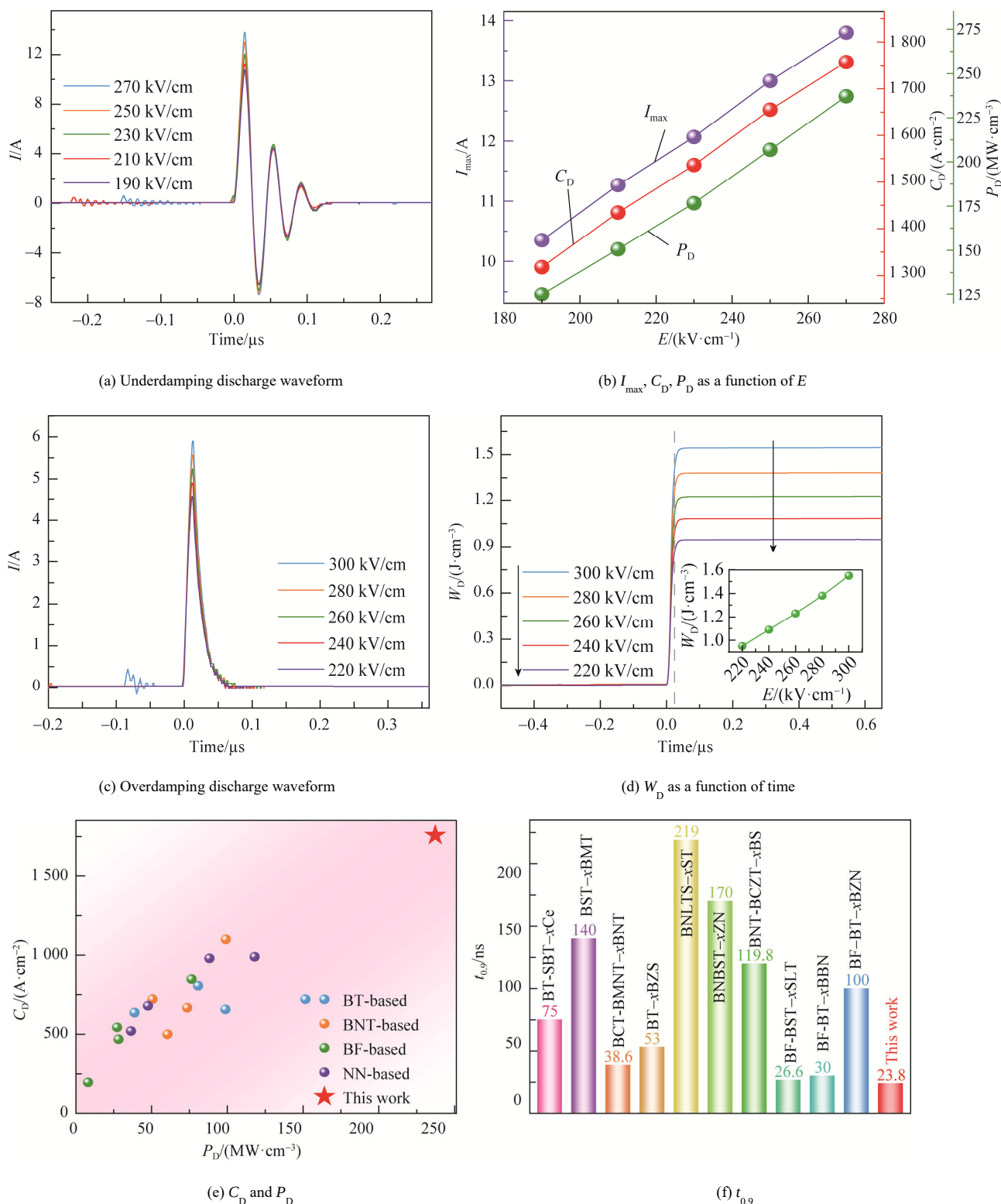
为了进一步研究样品 BCT-BZNT-0.02Ce 的实用性, 对样品的充放电性能进行了研究, 结果如图 6 所示。电流密度(C_D)、功率密度(P_D)和放电能量密度(W_D)是表征充放电性能的重要参数, 其计算公式为^[38–39]:

$$C_D = \frac{I_{\text{max}}}{S} \quad (5)$$

$$P_D = \frac{EI_{\text{max}}}{2S} \quad (6)$$

$$W_D = \frac{R}{V} \int I^2(t) dt \quad (7)$$

式中: I_{max} 为最大电流; S 为电极面积; V 为样品的有效体积; R 为电阻(187Ω)。图 6a 为欠阻尼条件下的放电波形, 可以看出电流随着电场强度的增加而逐渐增加。根据图 6a 计算得到的 I_{max} 、 C_D 、 P_D 值如图 6b 所示。由图 6b 可见, 随着 E 从 190 kV/cm 增加到 270 kV/cm , C_D 、 P_D 值分别从 1317.80 A/cm^2 、 125.19 MW/cm^3 增加到了 1757.07 A/cm^2 、 237.20 MW/cm^3 。图 6c 和图 6d 为在过阻尼条件下的充放电性能, 电流随着电场强度的增加而增加, 如图 6c 所示。图 6d 为 W_D 随电场强度变化的曲线, 可以看到随着 E 从 220 kV/cm 增加到 300 kV/cm , W_D 从 0.95 J/cm^3



C_D is current density; P_D is power density; W_D is discharged energy density.

图 6 样品 BCT-BZNT-0.02Ce 欠阻尼条件下的充放电性能, 过阻尼条件下的充放电性能以及与其他陶瓷材料充放电性能的对比

Fig. 6 Charge-discharge performance of BCT-BZNT-0.02Ce sample under underdamping, under overdamping and comparison of charge-discharge performance of BCT-BZNT-0.02Ce sample and other ceramic materials

增加到了 $1.55 J/cm^3$ 。可见 W_D 相较于 W_{rec} 小很多, 从动力学角度分析, 畴壁运动在较高频率下的贡献

较小^[40-41]。一般将释放 90% 的 W_D 所需要的时间 $t_{0.9}$ 称为充放电时间, $t_{0.9}$ 是评价介质电容器的一个重要

参数。样品 BCT–BZNT–0.02Ce 在 300 kV/cm 下测得的 $t_{0.9}$ 为 23.8 ns, 图 6d 中虚线表明该陶瓷具有超快的放电速率。调查比较了近期 BT 基^[16–17, 25–26]、BNT 基^[12, 27, 29]、BF 基^[31–33]陶瓷材料的充放电性能, 如图 6e~图 6f 所示, 观察到样品 BCT–BZNT–0.02Ce 的 $t_{0.9}$ 、 C_D 和 P_D 远优于大部分陶瓷材料。这进一步证明了样品 BCT–BZNT–0.02Ce 在脉冲电容器领域具有良好的发展前景。

3 结论

稀土元素 Ce 的引入, 细化了 BCT–BZNT–xCe 陶瓷的晶粒尺寸, 大幅提升了样品的 BDS。同时提升了 BCT–BZNT–xCe 陶瓷的弛豫性, 在 $x=0.02$ 时, 样品的弛豫系数 γ 达到了 1.917, 为典型的弛豫铁电体。室温下, 该样品在 600 kV/cm 的场强作用下获得了优异的储能性能, W_{rec} 和 η 分别为 5.49 J/cm³、89.4%, 这得益于 BDS 的提升和 P_{max} 的增加。此外, 样品 BCT–BZNT–0.02Ce 还具有良好的充放电性能, 在欠阻尼状态获得了高的 C_D 和 P_D , 分别为 1 757.07 A/cm² 和 237.20 MW/cm³; 同时, 样品 BCT–BZNT–0.02Ce 获得了超快的充放电速率 ($t_{0.9}=23.8$ ns)。样品 BCT–BZNT–0.02Ce 所具有的优异综合性能使其在脉冲电容器领域具有巨大的应用前景。

参考文献:

- WENG N, ZHANG J, WANG J, et al. Electrostatic energy storage performances of La(Ni_{2/3}Ta_{1/3})O₃-modified Na_{0.5}Bi_{0.5}TiO₃ lead-free ceramics[J]. J Am Ceram Soc, 2023, 106(5): 2963–2971.
- LI Y, TANG M, ZHANG Z, et al. BaTiO₃-based ceramics with high energy storage density[J]. Rare Metals, 2023, 42(4): 1261–1273.
- HUANG Q, SI F, TANG B. The effect of rare-earth oxides on the energy storage performances in BaTiO₃ based ceramics[J]. Ceram Int, 2022, 48(12): 17359–17368.
- LONG C, ZHOU W, LIU L, et al. Achieving excellent energy storage performances and eminent charging–discharging capability in donor (1–x)BT–x(BZN–Nb) relaxor ferroelectric ceramics[J]. Chem Eng J, 2023, 459: 141490.
- QIN W, ZHAO M, LI Z, et al. High energy storage and thermal stability under low electric field in Bi_{0.5}Na_{0.5}TiO₃-modified BaTiO₃–Bi(Zn_{0.25}Ta_{0.5})O₃ ceramics[J]. Chem Eng J, 2022, 443: 136505.
- YAN F, GE G, QIAN J, et al. Gradient-structured ceramics with high energy storage performance and excellent stability[J]. Small, 2023, 19(6): e2206125.
- WEI F, YANG Y, ZHANG L, et al. Simultaneously achieving high energy storage performance and low electrostrictive strain in BT-based ceramics[J]. J Am Ceram Soc, 2023, 106(6): 3491–3500.
- HU Y C, DANG S T, CAO J Q, et al. Improved energy storage performance of BST–BNT ceramics via composition modification[J]. Solid State Commun, 2023, 362: 115100.
- 贺薪瑜, 管泽浩, 王晓智, 等. K_{0.5}Na_{0.5}NbO₃–xBiMg_{0.5}Ti_{0.5}O₃ 电介质陶瓷的结构与储能性能[J]. 硅酸盐学报, 2019, 47(2): 288–292. HE Xinyu, GUAN Zehao, WANG Xiaozhi, et al. J Chin Ceram Soc, 2019, 47(2): 288–292.
- WANG W, ZHANG L, JING R, et al. Enhancement of energy storage performance in lead-free barium titanate-based relaxor ferroelectrics through a synergistic two-step strategy design[J]. Chem Eng J, 2022, 434: 134678.
- ZHANG L, PANG L, LI W, et al. Extreme high energy storage efficiency in perovskite structured (1–x)(Ba_{0.8}Sr_{0.2})TiO₃–xBi(Zn_{2/3}Nb_{1/3})O₃ (0.04≤x≤0.16) ceramics[J]. J Eur Ceram Soc, 2020, 40(8): 3343–3347.
- JIANG Z, YUAN Y, YANG H, et al. Superior thermal stability and energy storage properties of (1–x)Na_{0.3}Bi_{0.3}Ba_{0.04}Sr_{0.36}TiO₃–xZnTa₂O₆ lead-free ceramic[J]. J Alloy Compd, 2022, 906: 164345.
- WANG M, XIE A, FU J, et al. Energy storage properties under moderate electric fields in BiFeO₃-based lead-free relaxor ferroelectric ceramics[J]. Chem Eng J, 2022, 440: 135789.
- LI Y, HAO Y, WANG X, et al. Studies of dielectric properties of rare earth (Y, Gd, Yb) doped barium titanate sintered in pure nitrogen[J]. Ferroelectrics, 2010, 407(1): 134–139.
- SRIKANTH K S V, RAHUL. Enhanced electrocaloric, pyroelectric and energy storage performance of BaCe_xTi_{1–x}O₃ ceramics[J]. J Eur Ceram Soc, 2017, 37(13): 3927–3933.
- ZENG X, LI Y, DONG J, et al. The polarization contribution and effect mechanism of Ce-doped 0.65BaTiO₃–0.35Sr_{0.7}Bi_{0.2}TiO₃ Pb-free ferroelectric ceramics for dielectric energy storage[J]. Ceram Int, 2021, 47(22): 32015–32024.
- SUN M, WANG X, LI P, et al. Realizing ultrahigh breakdown strength and ultrafast discharge speed in novel barium titanate-based ceramics through multicomponent compounding strategy[J]. J Eur Ceram Soc, 2023, 43(3): 974–985.
- KANG R, WANG Z, LOU X, et al. Energy storage performance of Bi_{0.5}Na_{0.5}TiO₃-based relaxor ferroelectric ceramics with superior temperature stability under low electric fields[J]. Chem Eng J, 2021, 410: 128376.
- HUONG D T M, NAM N H, VU L V, et al. Preparation and optical characterization of Eu³⁺-doped CaTiO₃ perovskite powders[J]. J Alloy Compd, 2012, 537: 54–59.
- SHI C, YAN F, GE G, et al. Significantly enhanced energy storage performances and power density in (1–x)BCZT–xSBT lead-free ceramics via synergistic optimization strategy[J]. Chem Eng J, 2021, 426(15): 130800.
- HU D, PAN Z, TAN X, et al. Optimization the energy density and efficiency of BaTiO₃-based ceramics for capacitor applications[J]. Chem Eng J, 2021, 409: 127375.
- YIN M, BAI G, LI P, et al. Achieving ultrahigh energy storage properties with superior stability in novel (Ba_(1–x)Bi_x)(Ti_(1–x)Zn_{0.5x}Sn_{0.5x})O₃ relaxor ferroelectric ceramics via chemical modification[J]. Chem Eng J, 2023, 460: 141724.
- LI Y, LIU Y, TANG M, et al. Energy storage performance of BaTiO₃-based relaxor ferroelectric ceramics prepared through a two-step process[J]. Chem Eng J, 2021, 419: 129673.
- ZHOU M, LIANG R, ZHOU Z, et al. Combining high energy efficiency and fast charge–discharge capability in novel BaTiO₃-based relaxor ferroelectric ceramic for energy-storage[J]. Ceram Int, 2019, 45(3): 3582–3590.

- [25] MA C, ZHANG R, ZHANG G, et al. Structural evolution and energy storage properties of $\text{Bi}(\text{Zn}_{0.5}\text{Zr}_{0.5})\text{O}_3$ modified BaTiO_3 -based relaxation ferroelectric ceramics[J]. *J Energy Storage*, 2023, 72: 108374.
- [26] REHMAN M, MANAN A, KHAN M, et al. Improved energy storage performance of $\text{Bi}(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_3$ modified $\text{Ba}_{0.55}\text{Sr}_{0.45}\text{TiO}_3$ lead-free ceramics for pulsed power capacitors[J]. *J Eur Ceram Soc*, 2023, 43(6): 2426–2441.
- [27] LU Y, LI P, DU J, et al. SrTiO_3 -modified $\text{Bi}_{0.5}\text{Na}_{0.47}\text{Li}_{0.03}\text{Ti}_{0.99}\text{Sn}_{0.01}\text{O}_3$ relaxor ferroelectric ceramics with high energy storage performance[J]. *Int J Appl Ceram Technol*, 2023, 20(4): 2350–2359.
- [28] ZHANG X, YANG F, MIAO W, et al. Effective improved energy storage performances of $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ -based relaxor ferroelectrics ceramics by A/B-sites co-doping[J]. *J Alloy Compd*, 2021, 883: 160837.
- [29] SHI P, ZHU X, LOU X, et al. Tailoring ferroelectric polarization and relaxation of BNT-based lead-free relaxors for superior energy storage properties[J]. *Chem Eng J*, 2022, 428: 132612.
- [30] WANG W, TANG X, JIANG Y, et al. Modified relaxor ferroelectrics in BiFeO_3 – $(\text{Ba},\text{Sr})\text{TiO}_3$ – BiScO_3 ceramics for energy storage applications[J]. *Sustainable Mater Technol*, 2022, 32: e00428.
- [31] BAI X, CHEN Z, ZHENG P, et al. High recoverable energy storage density in nominal $(0.67-x)\text{BiFeO}_3$ – 0.33BaTiO_3 – $x\text{BaBi}_2\text{Nb}_2\text{O}_9$ lead-free composite ceramics[J]. *Ceram Int*, 2021, 47(16): 23116–23123.
- [32] TANG M, YU L, WANG Y, et al. Dielectric, ferroelectric, and energy storage properties of $\text{Ba}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ -modified BiFeO_3 – BaTiO_3 Pb-free relaxor ferroelectric ceramics[J]. *Ceram Int*, 2021, 47(3): 3780–3788.
- [33] ZHAO J, BAO S, TANG L, et al. Improved energy storage performances of lead-free BiFeO_3 -based ceramics via doping $\text{Sr}_{0.7}\text{La}_{0.2}\text{TiO}_3$ [J]. *J Alloy Compd*, 2022, 898: 162795.
- [34] MA J, LIN Y, YANG H, et al. Achieved high energy storage property and power density in NaNbO_3 – $\text{Bi}(\text{Sn}_{0.5}\text{Ni}_{0.5})\text{O}_3$ ceramics[J]. *J Alloy Compd*, 2021, 868: 159206.
- [35] SUN C, CHEN X, SHI J, et al. Simultaneously with large energy density and high efficiency achieved in NaNbO_3 -based relaxor ferroelectric ceramics[J]. *J Eur Ceram Soc*, 2021, 41(3): 1891–1903.
- [36] WANG X, DONG Q, PAN Y, et al. Enhanced energy storage performances of $\text{Bi}(\text{Ni}_{1/2}\text{Sb}_{2/3})\text{O}_3$ added NaNbO_3 relaxor ferroelectric ceramics[J]. *Ceram Int*, 2022, 48(10): 13862–13868.
- [37] ZHANG S, LI W, ZHANG Y, et al. Large energy density and high efficiency achieved simultaneously in $\text{Bi}(\text{Mg}_{0.5}\text{Hf}_{0.5})\text{O}_3$ -modified NaNbO_3 ceramics[J]. *Results Phys*, 2023, 44: 106194.
- [38] NING Y, PU Y, WU C, et al. Achieving high energy storage performance below 200 kV/cm in BaTiO_3 -based medium-entropy ceramics[J]. *Ceram Int*, 2023, 49(12): 20326–20333.
- [39] WANG Q, XIE B, ZHENG Q, et al. $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ -based relaxor-ferroelectric ceramics for low-electric-field dielectric energy storage via bidirectional optimization strategy[J]. *Chem Eng J*, 2023, 452: 139422.
- [40] LI T, CHEN P, LI F, et al. Energy storage performance of $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ – SrTiO_3 lead-free relaxors modified by $\text{AgNb}_{0.85}\text{Ta}_{0.15}\text{O}_3$ [J]. *Chem Eng J*, 2021, 406: 127151.
- [41] LI F, ZHAI J, SHEN B, et al. Multifunctionality of lead-free BiFeO_3 -based ergodic relaxor ferroelectric ceramics: High energy storage performance and electrocaloric effect[J]. *J Alloy Compd*, 2019, 803: 185–192.

Effect of Rare-Earth Ce^{4+} Doping on Structure and Energy Storage Properties of BCT–BZNT Ceramics

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Extended Abstract

Introduction Dielectric ceramic capacitors are widely used in the field of high energy pulse because of their high power density, ultra-fast charge–discharge speed and good stability. However, compared with other capacitors, the low recoverable energy storage density (W_{rec}) affects its development in the field of energy storage. The typical ferroelectric BaTiO_3 (BT) with good dielectric and insulation properties is restricted in the development of energy storage field due to the low breakdown strength and large residual polarization. It is indicated that the combination of multi-component solid solution and ion doping induces the polar nanoregions (PNRs) and the transformation of BaTiO_3 ceramics from ferroelectrics to relaxation ferroelectrics due to the reduction of P_r and the improvement of energy storage performance. In addition, obtaining simultaneously the high W_{rec} and energy storage efficiency (η) is a challenge. In this paper, $(1-x)\{0.88(\text{Ba}_{0.6}\text{Ca}_{0.4})\text{TiO}_3$ – $0.12\text{Bi}[\text{Zn}_{2/3}(\text{Nb}_{0.85}\text{Ta}_{0.15})_{1/3}]\text{O}_3\}$ – $x\text{CeO}_2$ (abbreviated as BCT–BZNT– $x\text{Ce}$, $x = 0, 0.010, 0.015, 0.020, 0.025$) ceramics were prepared by a conventional solid-state reaction method. The structure and energy storage properties of the ceramics with different Ce^{4+} doping contents were investigated.

Methods High purity BaCO_3 , CaCO_3 , TiO_2 , Bi_2O_3 , ZnO , Nb_2O_5 , Ta_2O_5 and CeO_2 were used as raw materials. The raw materials were weighted and mixed according to stoichiometric ratio. The mixed raw materials were firstly ground in a ball mill, and then dried and calcined in air at 900°C for 4 h. Afterwards, the calcined powder was further ground, dried and pressed into discs with 10 mm in diameter. The discs were sintered at 1200°C for 2 h to obtain the ceramic samples. The ceramic samples were thinned and polished to 0.05 mm, and sputtered with Au electrodes for the energy storage properties.

The phase structure of the samples was analyzed by a model SmartLab X-ray diffractometer (XRD, Rigaku Co., Japan) in the

range of 20° – 80° . The Raman spectra of the samples were analyzed by a model Renishaw inVia Laser Confocal Raman Microspectroscopy (Renishaw Co., UK). The microstructure and elemental analysis (EDS) were determined by a model Merlin Compact Field Emission Scanning Electron Microscope (FE-SEM, Zeiss Co., Germany). The dielectric properties were analyzed by a model HCT1821 High-Low Temperature Dielectric Testing System (Tongguo Technology Co., China). The unipolar P – E curves were measured by a model TF2000 ferroelectric tester (aixACCT Co., Germany) to investigate the ferroelectric performance. The pulsed performance of the samples was examined by a model CFD-003 plus high-voltage charge–discharge measuring instrument (Tongguo Technology Co., China).

Results and discussion All the samples are a multiphase structure with a tetragonal phase BaTiO_3 (BT) as a main phase and an orthorhombic phase CaTiO_3 (CT) as a second phase. The excessive Ce^{4+} causes the appearance of the diffraction peak at 28.5° of 2θ when $x=0.025$. Also, the diffraction peaks move to a low angle from the magnified (200). The minimum average grain size (AGS) of both coarse and fine grains is obtained when $x=0.02$. The BCT–BZNT–0.02Ce ceramic obtains a high breakdown strength. The EDS analysis indicates that the coarse grains contain more Ba, while the fine grains contain more Ca.

The dielectric permittivity of samples decreases with increasing the frequency. A large valence difference between the A-site and B-site ions induces PNRs, having a typical relaxation behavior. Besides, the diffuseness parameter (γ) as $x=0.02$ is the maximum value (*i.e.*, 1.917), which is similar to that of the ideal relaxation ferroelectric. The unipolar P – E curves of all the samples are slender and exhibit good relaxation characteristics. The breakdown strength and maximum polarization strength (P_{max}) increase with the increase of Ce content, and reach the maximum values as $x=0.02$. A high W_{rec} of 5.49 J/cm^3 and a high η of 89.4% are obtained at 600 kV/cm in BCT–BZNT–0.02Ce ceramic, which is attributed to the increase of breakdown strength and P_{max} . Moreover, the superior charge–discharge performance is obtained in BCT–BZNT–0.02Ce ceramic. The ultra-high current density (*i.e.*, $C_D=1\,757.07 \text{ A/cm}^2$) and power density (*i.e.*, $P_D=237.20 \text{ MW/cm}^3$) are obtained at 270 kV/cm. Besides, a discharge energy density (W_D) of 1.55 J/cm^3 and an ultra-fast charge–discharge speed ($t_{0.9}$) of 23.8 ns are obtained simultaneously. The W_D is smaller than the W_{rec} due to the unremarkable contribution of domain wall motion at higher frequencies from the perspective of dynamics. The BCT–BZNT–0.02Ce ceramic with ultra-high W_{rec} (5.49 J/cm^3), η (89.4%), C_D ($1\,757.07 \text{ A/cm}^2$), P_D (237.20 MW/cm^3) and ultra-fast $t_{0.9}$ (23.8 ns) can be used in pulsed capacitors.

Conclusions The grains size of BCT–BZNT– x Ce ceramics was refined *via* the introduction of rare-earth element Ce. The γ of the BCT–BZNT– x Ce ceramics was improved, and the BCT–BZNT–0.02Ce ceramic showed a typical relaxation ferroelectric performance (*i.e.*, $\gamma=1.917$). The superior energy storage performance (*i.e.*, $W_{\text{rec}}=5.49 \text{ J/cm}^3$, $\eta=89.4\%$) of BCT–BZNT–0.02Ce ceramic was achieved at 600 kV/cm at room temperature due to the breakdown strength and P_{max} . Also, the BCT–BZNT–0.02Ce ceramic exhibited a superior charge–discharge performance (*i.e.*, $C_D=1\,757.07 \text{ A/cm}^2$, $P_D=237.20 \text{ MW/cm}^3$, and $t_{0.9}=23.8 \text{ ns}$). The BCT–BZNT–0.02Ce ceramic with the superior comprehensive properties could have a great application prospect in pulsed capacitors.

Keywords barium titanate; relaxor ferroelectrics; energy storage performance; charge–discharge speed