

Zr 掺杂对 $\text{Sr}_{0.7}\text{Bi}_{0.2}\text{TiO}_3$ 铁电陶瓷储能性能的影响刘建博¹, 郑 鹏¹, 白王峰², 盛林生³

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摘 要: 高功率、高能量密度的介质储能电容器在脉冲功率系统小型化和轻量化的过程中具有重要意义。采用固相反应法制备了无铅改性的 $\text{Sr}_{0.7}\text{Bi}_{0.2}\text{TiO}_3$ (SBT) 基储能陶瓷, 研究了掺杂不同含量 ZrO_2 对该陶瓷的相结构、微观结构、介电性能、铁电性能、击穿机制的影响。结果表明: Zr 元素部分以 Zr^{4+} 形式溶解于 SBT 晶格中, 其余以 ZrO_2 形式存在晶界和晶粒表面; 储能密度的提升主要依赖于介电击穿强度(E_b)的增强, 可能的物理机制, 包括晶粒尺寸、带隙、阻抗和激活能等, 协同促进了 E_b 的提高。在所研究的材料中, SBT-2% (质量分数) ZrO_2 陶瓷具有最好的储能性能, 可恢复储能密度 $W_{\text{rec}}=5.57 \text{ J/cm}^3$, 能量效率 $\eta=88.97\%$; 即使在经过 5×10^4 次循环后也能表现出良好的性能稳定性(W_{rec} 变化幅度 $< 1\%$), 是一种非常有前景的脉冲功率储能电容器候选材料。

关键词: 钛酸锶铋基陶瓷; 储能; 介电击穿强度; 物理机制

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随着现代工业水平迅速的进步, 自然资源的消耗逐渐增加, 化石能源的短缺也日益严重^[1-2]。新能源的开发即将缓解能源危机, 减少环境污染。总的来说, 为了实现长期的可持续发展, 希望新能源材料具有高性能、低成本、环保性的特点^[3]。大多数电子设备的正常运行取决于电池和电容器的存在^[2, 4-5], 因此, 储能器件已成为电力领域最具有活力的分支之一。电池具有高能量密度, 但不能提供足够的功率输出。与电池相比, 介电电容器内部没有化学反应, 具有高功率输出和快速的充放电速率, 在脉冲电源、激光武器、混合动力汽车等设备上具有很大的应用价值^[6-7]。然而, 电介质电容器的低能量密度限制了其实际应用, 提高可恢复储能密度是非常重要的任务^[8]。

介质电容器的可恢复储能密度(W_{rec})和能量效率(η)通常采用式(1)~式(3)计算^[9]:

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

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

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

其中: E 为施加的电场; P 为自发极化; P_{max} 为最大极化; P_r 为剩余极化。基于式(1)~式(3)可知, W_{rec} 由 P_{max} 、 P_r 和 E 确定, 其中 E 受到 E_b 的约束。需要增加放电曲线和极化轴的积分面积, 以提高 W_{rec} 的值。因此, 较高的 P_{max} 和较大的 E_b 可以增加 W_{rec} ^[10]。

电介质一般分为线性电介质、弛豫铁电体、普通铁电体和反铁电体^[11-13], 弛豫铁电材料具有较高的能量效率(η)、较高的饱和极化率(P_s)、较小的剩余极化率(P_r)以及在电场作用下不会因相变产生内

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应力,被认作是最具潜力的储能材料。 $\text{Sr}_{0.7}\text{Bi}_{0.2}\text{TiO}_3$ (SBT)陶瓷是一种经典的无铅遍历弛豫铁电体,由于 Bi^{3+} 偏离中心和 Sr 位空位^[14–15],并且 Bi 的 $6s^2$ 轨道和 O 的 $2p$ 轨道之间的杂化^[16–17], SBT 陶瓷在较宽的温度范围内具有优异的铁电弛豫行为,可以获得高介电常数和高的储能效率。但 SBT 基介电陶瓷相对较低的击穿强度限制了能量存储密度的提高^[14, 18–19]。Zhao 等^[14]报道了一种基于 SBT 的弛豫铁电陶瓷,其在 290 kV/cm^3 时具有 2.1 J/cm^3 的 W_{rec} 和 97.6% 的高 η ; Chao 等^[19]报道了弛豫铁电陶瓷 $(\text{Sr,Pb,Bi})\text{TiO}_3$ 在 50 kV/cm 时具有 0.228 J/cm^3 的 W_{rec} 和 94.2% 的 η 。可以看到这些报道的 SBT 陶瓷材料耐电强度都不高,因而无法获得高储能密度。进行 E_b 值的改善是解决储能密度受限的有效途径。

在许多研究中,已经证明添加一些氧化物可以有效抑制晶粒生长,增加 E_b ^[20]。在本工作中选择 ZrO_2 作为添加剂,在高温烧结时 Zr^{4+} 可以稳定 SBT 中的 Ti 的电荷,抑制氧的解离^[21],同时,部分 Zr^{4+} 会以氧化物的形式沉积在晶界,抑制晶粒生长^[22],以期通过选择适量的 ZrO_2 添加剂,在不降低介电常数的情况下提高耐电强度,提升材料的储能密度。

1 实验

1.1 样品制备

采用传统固相反应烧结法制备 SBT 陶瓷样品。以 Bi_2O_3 (99.5%, 蜀都), SrCO_3 (99.5%, Aladdin), TiO_2 (99.8%, 仙桃) 和 ZrO_2 (99.9%, Aladdin) 为原料,按照化学计量比称量各配料质量。配料后以无水乙醇和锆球为球磨介质球磨 12 h 并在烘箱中进行烘干,在 $850\text{ }^\circ\text{C}$ 预烧 5 h 后,按照相应质量比 $\text{Sr}_{0.7}\text{Bi}_{0.2}\text{TiO}_3+x\text{ZrO}_2$ (SBT- $x\text{Zr}$, $x=0, 0.5\%, 1.0\%, 2.0\%, 5.0\%$, 质量分数) 将原料二次球磨 24 h。将烘干的粉末压制厚度 0.8 mm 、直径 12.0 mm 的片状,然后以 $4\text{ }^\circ\text{C/min}$ 的速率升温到 $1200\sim 1250\text{ }^\circ\text{C}$,保温烧结 3 h,然后自然降温。

1.2 样品表征

通过 X 射线衍射仪 (XRD, MiniFlex600, Rigaku, 日本) 在 $20^\circ\sim 80^\circ$ 的角度范围内测试分析烧结样品的相结构,通过扫描电子显微镜 (FE-SEM, S-4200, Hitachi, 日本) 观察样品表面形貌。陶瓷的带隙 (E_g) 由紫外-可见分光光度计 (TU-1901, 普析通用仪器有限责任公司, 北京) 测定吸收光谱,然后计算得到;能量存储特性采用铁电测量系统 (RT1-Premier II, Radiant Technologies Inc, 美国) 测量并分析计算得

到;介电温谱采用阻抗分析仪 (4990 A, Agilent, 美国) 测得。采用充放电仪器 (CFD-003, 果果仪器, 上海) 测量陶瓷样品的充放电行为。

2 结果与讨论

2.1 物相及微观结构分析

图 1a 为室温 SBT- $x\text{Zr}$ 陶瓷在 $20^\circ\sim 80^\circ$ 区域的 XRD 谱。所有组分样品的 (200) 峰并没有发现劈裂,呈现为伪立方相^[16],表明不同掺杂量 Zr 的引入并未改变 SBT- $x\text{Zr}$ 陶瓷原有的晶体结构。放大后的 (110) 峰如图 1b 所示, (110) 峰值随着 ZrO_2 含量的增加逐渐向一个较低的衍射角略微偏移,这主要归因于 Zr^{4+} (0.072 nm) 取代了 Ti^{4+} (0.061 nm) 引起的晶格扩张^[23]。样品 SBT-2Zr 的元素分布如图 1c 所示,主要元素 Sr、Bi、Ti 和 O 是均匀分布的,而 Zr 元素在局部晶界及表面聚集,这表明该陶瓷为 0-3 型复合结构,而不是完全固溶体。

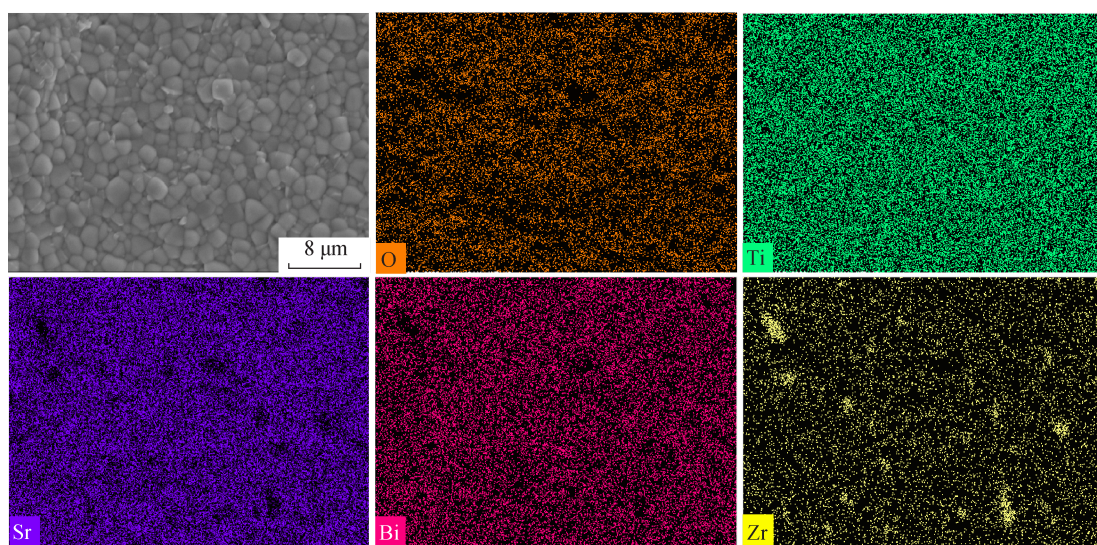
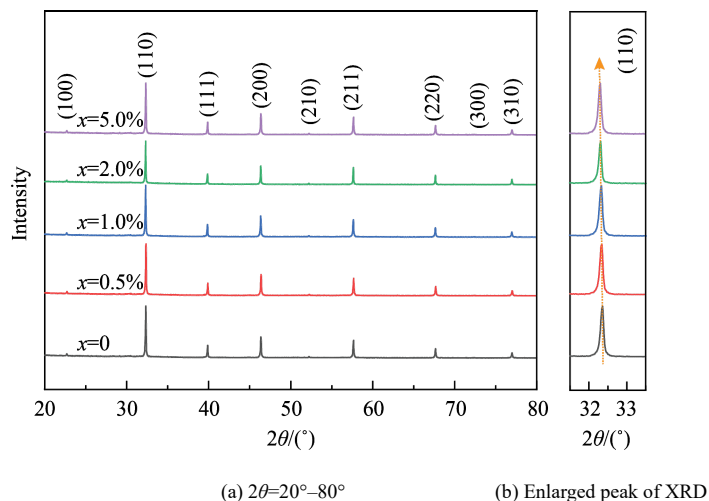
2.2 介电性能分析

图 2 为测试温度和频率对 SBT- $x\text{Zr}$ ($x=0, 2\%$) 陶瓷介电常数的影响。由图 2 可见, SBT 陶瓷中可以观察到频率色散行为,这是弛豫铁电体的典型特征^[23]。 ZrO_2 的加入略微降低了 SBT 陶瓷的介电常数,这主要是由于介电常数较小的 ZrO_2 添加剂的稀释效应所致。样品 SBT-2%Zr 相对于 SBT 陶瓷来说,介电损耗在宽的温度和频率范围内仍然可以稳定在低值,这对储能应用是有益的,因为介电损耗不仅会降低充放电效率,还会产生余热,从而导致热失控并缩短电容器的寿命。

2.3 储能性能分析

图 3a 为 SBT- $x\text{Zr}$ 陶瓷在 160 kV/cm 测得的双向极化-电场 (P - E) 电滞曲线。由图 3a 可见,随着 ZrO_2 含量的增加, P_m 逐渐降低。这是由于 Ti^{4+} 被 Zr^{4+} 部分取代,破坏了基体相的长程铁电顺序^[23]。由图 3b 可见,所有组分的电流密度-电场 (J - E) 曲线都呈现扁平的形状,表明良好的弛豫行为。

所有组分在 E_b 处的单向 P - E 电滞回线如图 4a 所示。伴随着 ZrO_2 含量的增加,样品的 E_b 值逐渐增大,最高值可达 580 kV/cm ,比纯 SBT 陶瓷高 27.6%,这有利于实现更高的储能密度。由图 4b 可见, W_{rec} 值从 $x=0$ 时的 4.07 J/cm^3 增加到 $x=2\%$ 时的 5.57 J/cm^3 ,而 η 值仍可以保持在 88.97%。然而,当 $x=5\%$ 时,尽管获得了高的 E_b 值,但过量的 ZrO_2 的引入导致 P_{max} 显著降低,因此无法获得最高的 W_{rec} 值。结合以上结果可以看出: W_{rec} 的提升主要来源于 E_b 值的显著增大。



(c) Element distribution diagram of SBT-2%Zr sample

图 1 SBT-xZr 陶瓷的 XRD 谱及元素分布图

Fig. 1 XRD patterns and elemental distribution maps of SBT-xZr ceramics

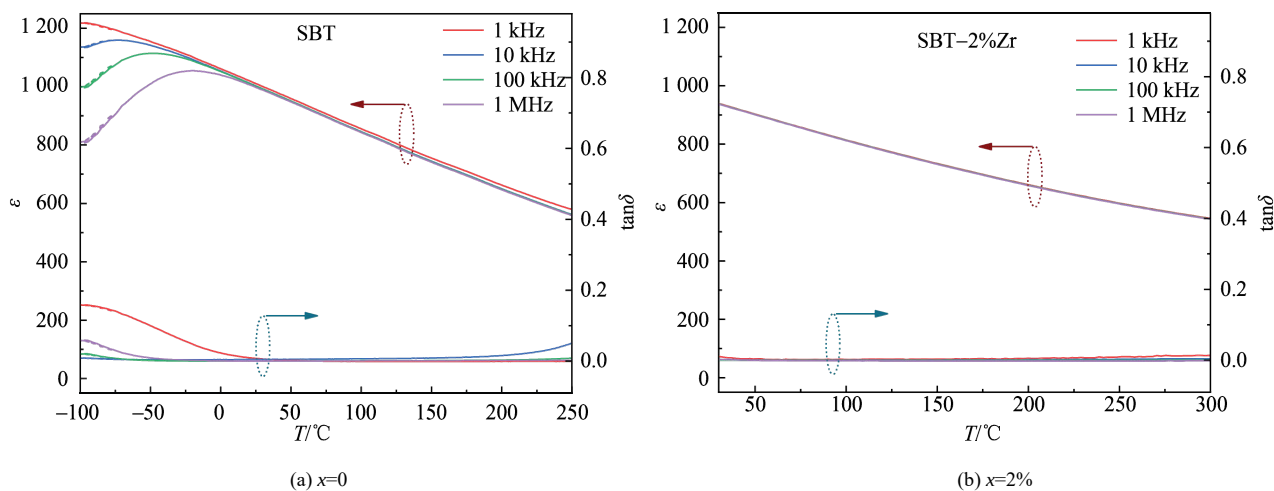
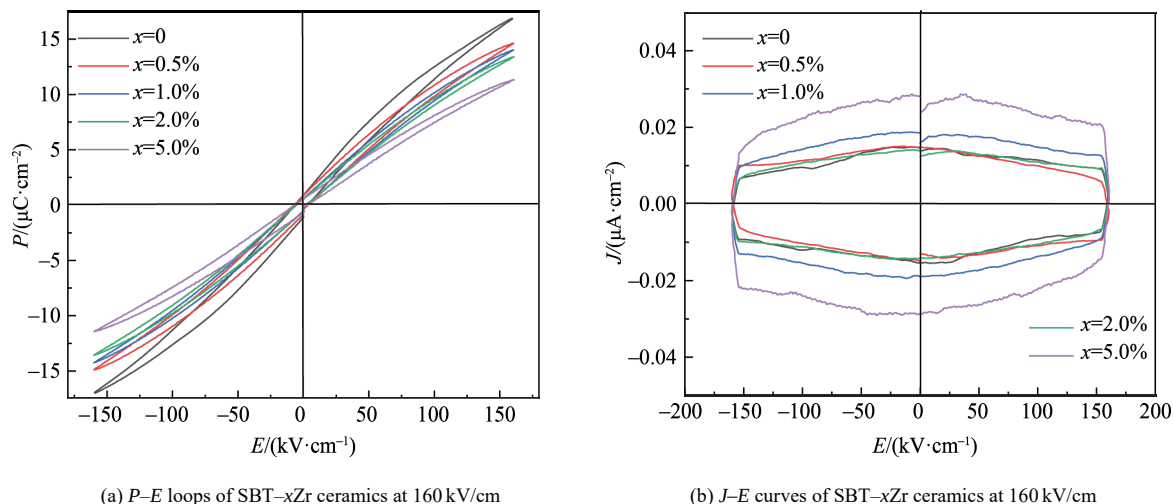
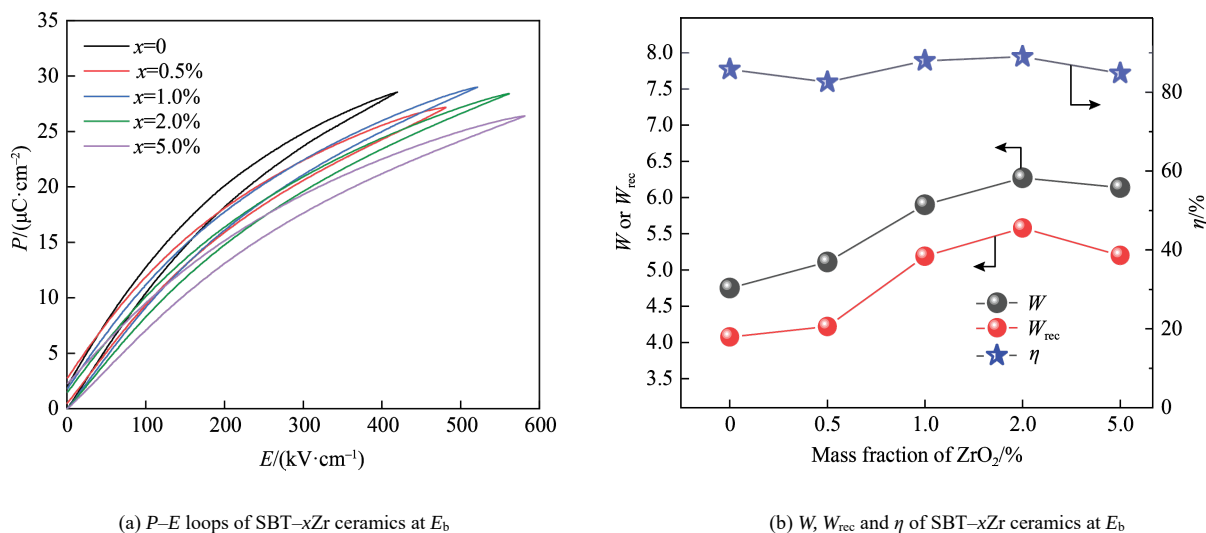


图 2 SBT-xZr 陶瓷随温度和频率变化的介电常数和介电损耗

Fig. 2 Dielectric constant and dielectric loss of SBT-xZr ceramics varying with temperature and frequency

图3 SBT-xZr 陶瓷 160 kV/cm 下的双向 P - E 电滞曲线及 J - E 曲线Fig. 3 Bidirectional polarization-electric field (P - E) hysteresis curves and current density-electric field (J - E) curves of SBT-xZr ceramics at 160 kV/cm图4 SBT-xZr 陶瓷在 E_b 处的单向 P - E 曲线及相应的总的储能密度(W), W_{rec} 和 η Fig. 4 Unidirectional P - E curves of SBT-xZr ceramics at E_b and corresponding total energy storage density (W), recoverable energy storage density (W_{rec}) and energy efficiency (η)

2.4 微观晶粒尺寸分析

如 2.3 节所述, E_b 成为提高 SBT-xZr 陶瓷储能性能的最重要的参数。陶瓷电容器的击穿机制来源于外在微观结构的贡献和内在电响应^[24-25]。外在贡献主要源于陶瓷的致密程度和粒径分布。图 5a~图 5e 为 SBT-xZr 陶瓷的 SEM 照片以及相对应的粒径分布。从表面显微照片可以看出, 所有组分的样品均展示了致密的显微结构, 无气孔产生。除此之外, 随着 ZrO_2 的增多, 该陶瓷的平均晶粒尺寸呈现逐渐减小的趋势。如图 5f 所示, 平均晶粒尺寸从 $2.30 \mu\text{m}$ 降低至 $1.31 \mu\text{m}$ 。与纯 SBT 陶瓷相比, ZrO_2 的逐渐引入使得平均晶粒尺寸显著减小, 表明 ZrO_2 颗粒可

能起到优化晶粒尺寸的作用^[26]。因此, 平均晶粒尺寸的减小是 E_b 值提升的影响因素之一。

2.5 禁带宽度分析

本征电响应贡献与 E_g 直接相关。图 6a 为 SBT-xZr 陶瓷的紫外-可见漫反射光谱。图 6b 为通过 Kubel Munk 公式^[27]从漫反射光谱转换而来的 SBT-xZr 陶瓷的光吸收光谱。带隙能量(E_g)可以通过式(4)计算:

$$(\alpha h\nu)^2 = A(h\nu - E_g) \quad (4)$$

其中: h 为 Planck 常数; ν 为频率; A 为常数; α 为吸收指数; E_g 为半导体禁带宽度。 E_g 从 SBT 陶瓷的 2.94 eV 增加到样品 SBT-5%Zr 的 3.02 eV。这可能

归因于部分 Zr^{4+} 融入 SBT 晶格而改变了晶体结构, 晶体结构的改变导致了能带结构的变化, 从而影响了带隙的大小^[21, 23, 26, 28]。较大的 E_g 意味着电子从价

带跳到导带需要更高的能量, 导致击穿的可能性较低, 获得的 E_b 值较高^[28]。因此, 引入 ZrO_2 后带隙能量的增加也是 E_b 增加的原因之一。

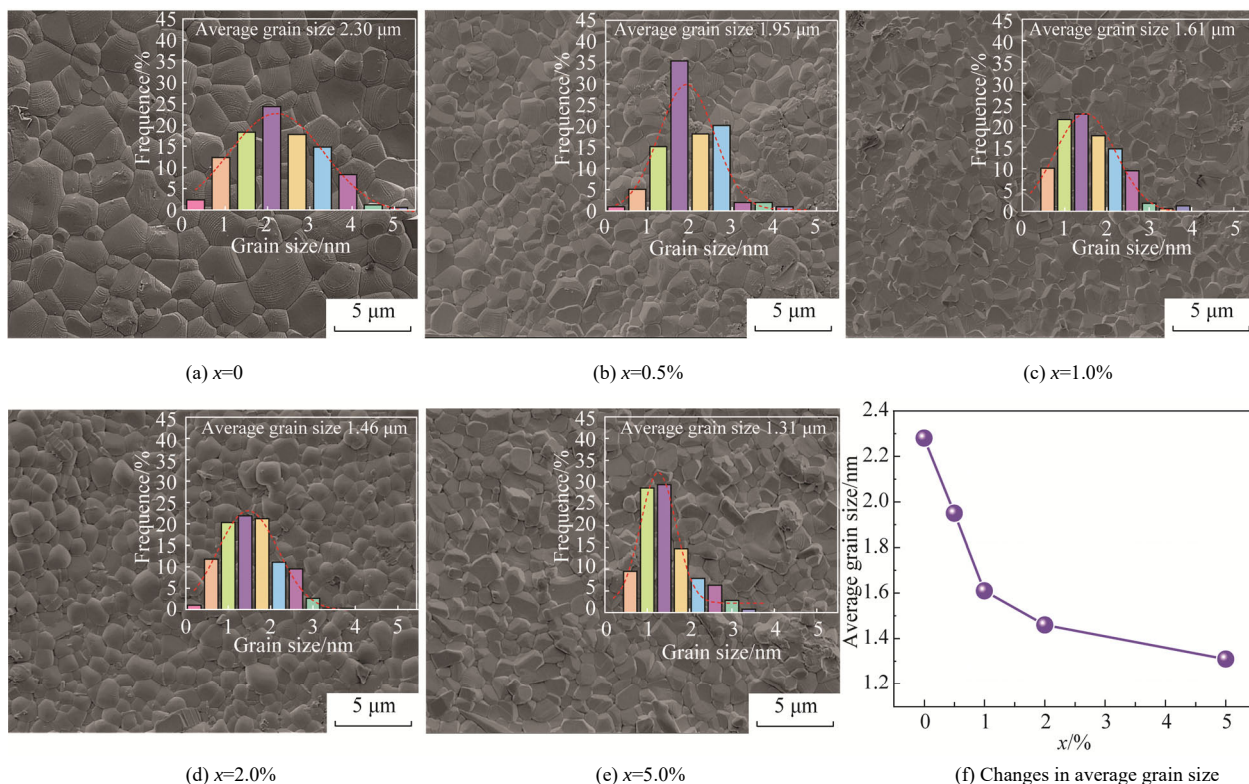
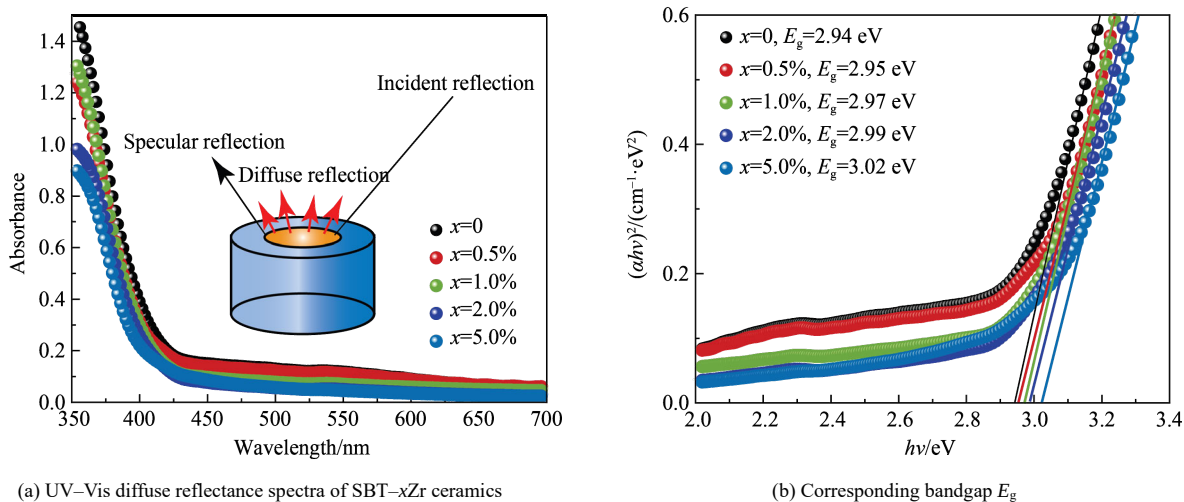


图 5 SBT- $x\text{Zr}$ 陶瓷的 SEM 显微结构照片和相应的晶粒尺寸分布及平均晶粒尺寸变化趋势

Fig. 5 SEM microstructure images and corresponding grain size distribution and average grain size variation trend of SBT- $x\text{Zr}$ ceramics



(a) UV-Vis diffuse reflectance spectra of SBT- $x\text{Zr}$ ceramics

(b) Corresponding bandgap E_g

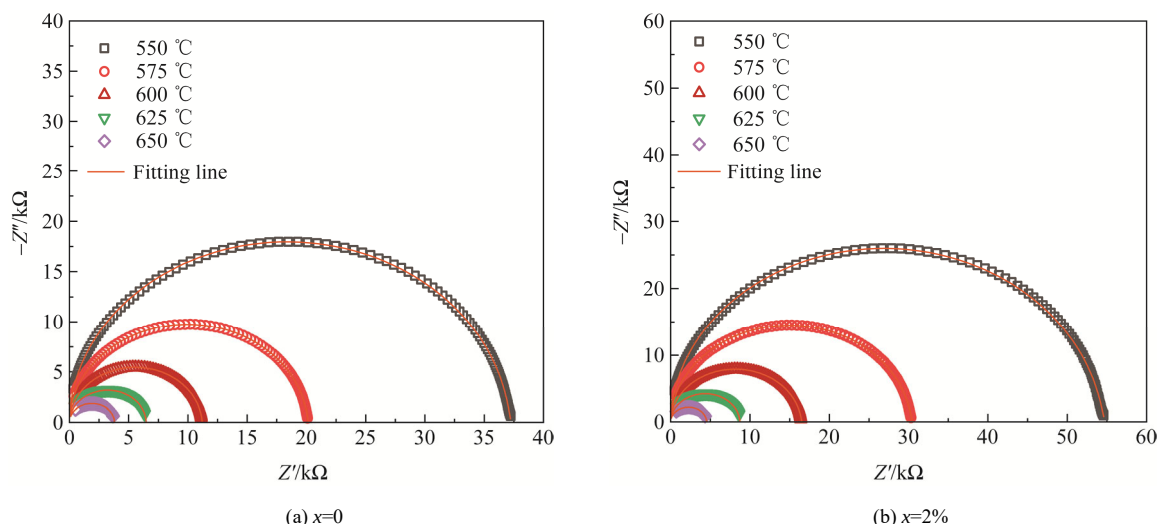
图 6 SBT- $x\text{Zr}$ 陶瓷的漫反射光谱, 转换得到的带隙能量(E_g)

Fig. 6 Diffuse reflection spectra of SBT- $x\text{Zr}$ ceramics, band gap energy (E_g) obtained by conversion

2.6 阻抗分析

阻抗谱可用于测量晶粒、晶界和电极扩散对介电陶瓷电性能的贡献^[29-30]。所有的复阻抗谱仅显示了 1 个在 550~650 °C 范围内的 Debye 半圆, 表明只有半圆的均匀电响应, 这主要由晶界决定^[17, 30-31]。

随着温度的升高, 所有组分的 Z'' 峰逐渐减小并向高频移动, 表明热激活弛豫的介电行为和弛豫时间正在减少^[32]。如图 7 所示, 样品 SBT-2%Zr 的半弧半径大于纯 SBT 陶瓷, 表明陶瓷的绝缘性能更好^[23]。

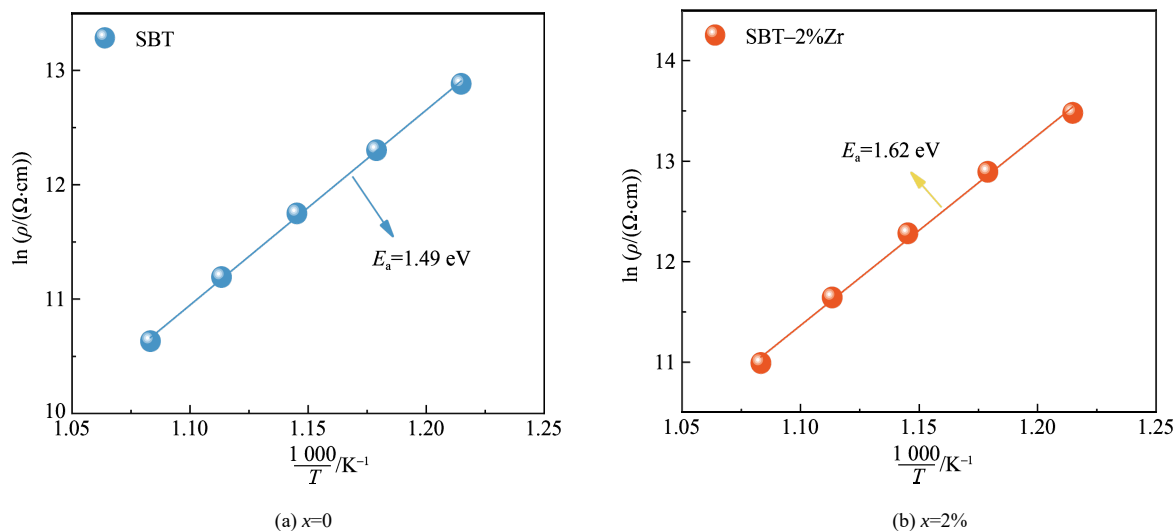
图7 SBT- x Zr 陶瓷的复阻抗图Fig. 7 Complex impedance diagrams of SBT- x Zr ceramics

弛豫过程的活化能(E_a)可以通过 Arrhenius 定律使用式(5)计算:

$$\rho = A \exp(E_a / kT) \quad (5)$$

其中: ρ 和 A 分别为电阻和指数前因子; k 为

Boltzmann 常数; T 为绝对温度^[27]。由图 8 可见, 电响应的 E_a 值从 1.49 eV 增加到 1.62 eV。高的 E_a 值可以阻碍缺陷空位的迁移和局部电子跳跃, 这有助于样品 SBT-2%Zr 获得高的 E_b ^[33]。

图8 SBT- x Zr 陶瓷的 Arrhenius 图Fig. 8 Arrhenius diagrams of SBT- x Zr ceramics

2.7 铁电稳定性分析

稳定性是电介质储能材料在实际应用中的一个重要指标^[34-35]。图 9a 为样品 SBT-2%Zr 在 350 kV/cm 下 1~1 000 Hz 频率范围内的 P - E 电滞回线。在测量的整个频率范围内, P - E 环路保持非常纤细。根据计算得出的 W_{rec} 和 η 随频率的增加而降低(见图 9b), 在整个频率范围内, 实现了良好的频率稳定性, 波动小于 13% (W_{rec} 的波动范围由 2.62 J/cm³ 至 3.00 J/cm³, η 的波动范围由 82.98% 至 86.95%)。此外, P - E 回

路的温度依赖性以及各种温度下相应计算的 W_{rec} 和 η 如图 9c 和图 9d 所示。当温度达到 100 °C 时, W_{rec} 从 2.95 J/cm³ 降至 2.72 J/cm³ (变化幅度小于 8%), η 从 89.99% 降至 82.66% (变化幅度约 8%)。显示出良好的热稳定性。此外, 图 9e 中给出了在 350 kV/cm 的测试电场下疲劳循环增加的 P - E 回路。 P - E 循环的形状在整个循环数中几乎保持不变。由图 9f 可见, 在 5×10^4 次循环后, W_{rec} 值从 3.00 J/cm³ 轻微下降到 2.97 J/cm³, 变化小于 1%, 表现出优异的疲劳性能。

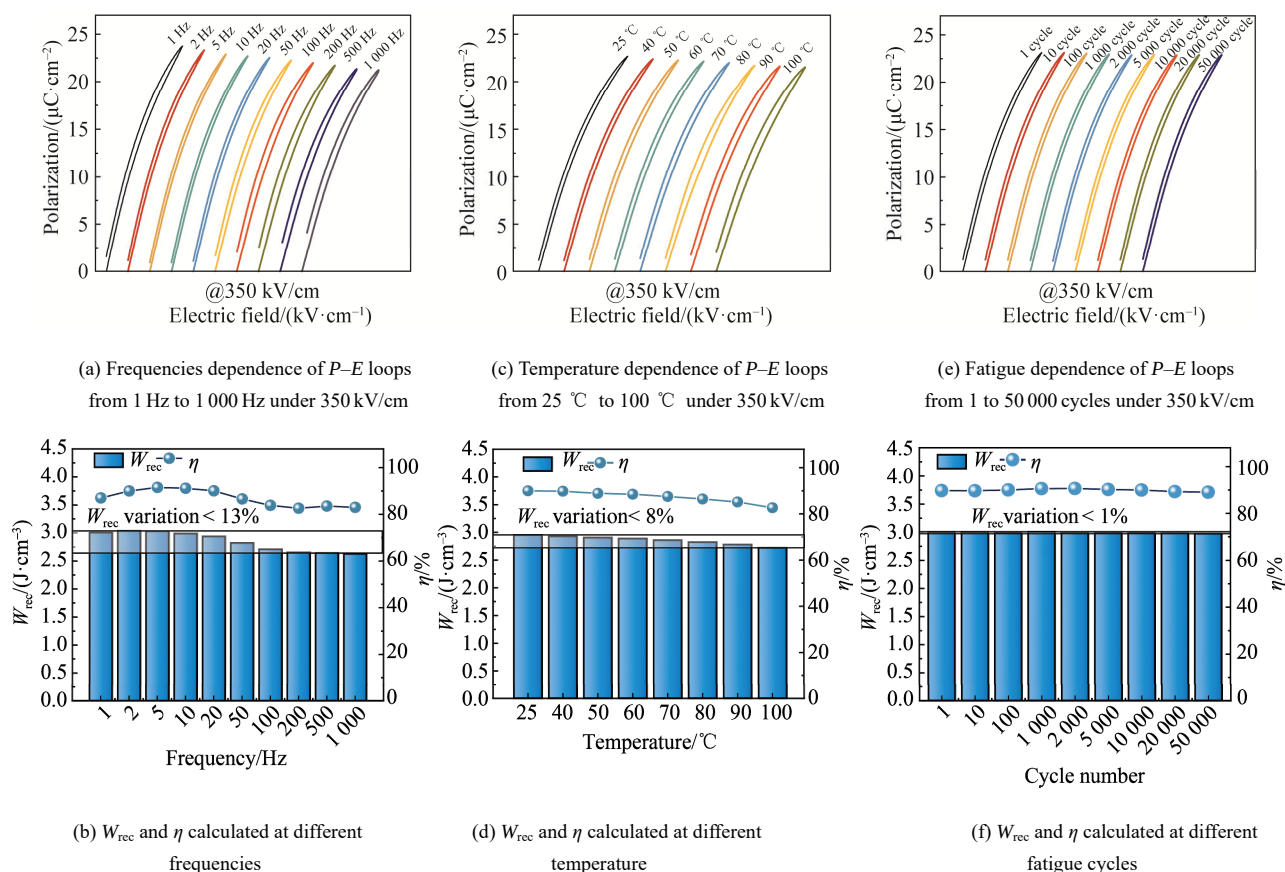


图 9 保持 350 kV/cm 下样品 SBT-2%Zr 在不同频率、温度、循环次数的单向 P - E 电滞回线和储能性能的变化
Fig. 9 Changes in unidirectional P - E hysteresis loop and energy storage performance of SBT-2%Zr sample at different frequencies, temperatures, and cycles at 350 kV/cm

2.8 充放电性能分析

测试了样品 SBT-2%Zr 的实际充放电性能,以评估材料在实际应用中的价值。图 10a 为在室温施加电场范围内的过阻尼脉冲放电电流曲线。由图 10a 可见,所有放电过程持续时间小于 $0.3 \mu\text{s}$ 。图 10b 为放电能量密度(W_d)曲线,随着电场的增加, W_d 从 0.04 J/cm^3 增加到 2.15 J/cm^3 。与电场相关的放电时间($t_{0.9}$)通常用于描述 W_d 下降 90% 所用的时间^[36]。 $t_{0.9}$ 在不同电场下保持小于 80 ns , 表现出优异的快速放电能力。样品 SBT-2Zr 在各种外加电场下的欠阻尼放电曲线如图 10c 所示。随着电场增加到 320 kV/cm , 电流的峰值从 4.667 A 逐渐上升到 33.300 A 。同时,相应的电流(I_{max})、电流密度($C_D = I_{\text{max}}/S$, S 为电极面积)和功率密度($P_D = E \cdot I_{\text{max}}/2S$)在图 10d 中给出, C_D 和 P_D 分别获得 1060.51 A/cm^2 和 169.68 MW/cm^3 的最大值。因此,样品 SBT-2%Zr 也展现出了良好的充放电性能。

3 结论

基于电介质电容器中的弛豫铁电陶瓷的优越的

稳定性和储能特性,通过高效稳定的固相反应法制备了一种新型的无铅 SBT 基弛豫铁电陶瓷。

1) 经过不同含量 ZrO_2 掺杂的陶瓷样品具有原有的晶体结构,部分 Zr^{4+} 融入了晶格,其余以第二相的形式存在于晶界和晶粒表面。

2) 击穿增强的物理机制:所有样品均获得了致密的微观表面且无气孔产生,平均晶粒尺寸从 $2.30 \mu\text{m}$ 降低至 $1.31 \mu\text{m}$,有利于获得更多高绝缘的晶界,陶瓷晶界处存在空间电荷耗尽层,这成为了载流子穿过晶界传输的屏障; E_g 从 SBT 陶瓷的 2.94 eV 增加到样品 SBT-5%Zr 的 3.02 eV ,这意味着电子需要更大的外加电场才能实现价带和导带的跃迁;阻抗圆的增大代表着材料的电阻率更高,而高的激活能可以抑制带电载流子的传输。

3) 样品 SBT-2%Zr 展现出最好的储能性能(能量密度 $W_{\text{rec}} = 5.57 \text{ J/cm}^3$, 能量效率 $\eta = 88.97\%$),优异的疲劳稳定性(循环 5×10^4 次, W_{rec} 变化幅度 $< 1\%$),良好的充放电性能($W_d = 2.15 \text{ J/cm}^3$, $C_D = 1060.51 \text{ A/cm}^2$ 和 $P_D = 169.68 \text{ MW/cm}^3$)。

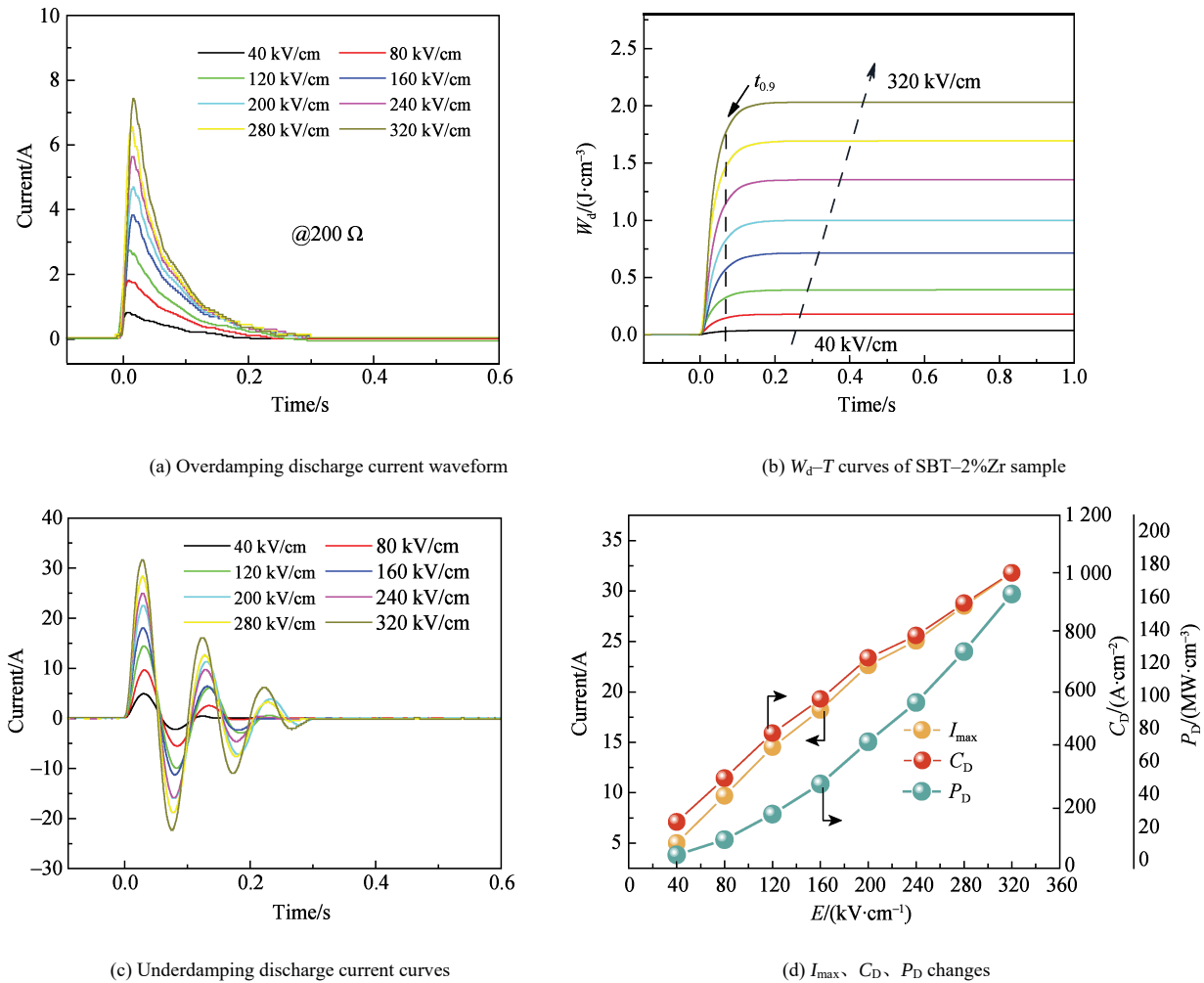


图 10 样品 SBT-2%Zr 的过阻尼放电电流波形、放电能量密度 W_d 、欠阻尼放电电流波形、以及最大电流($I_{\max}$)、电流密度(C_D)、功率密度(P_D)的变化

Fig. 10 Overdamped discharge current waveform, discharge energy density W_d , underdamped discharge current waveform, and the change of maximum current ($I_{\max}$), current density (C_D) and power density (P_D) of SBT-2%Zr sample

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Effect of Zr Doping on Energy Storage Performance of $\text{Sr}_{0.7}\text{Bi}_{0.2}\text{TiO}_3$ Ferroelectric Ceramics

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Extended Abstract

Introduction Dielectric ceramic capacitors are essential components in next-generation advanced pulse power systems due to their ultra-fast charging/discharging rates and remarkable power density. As a typical lead-free perovskite material, $\text{Sr}_{0.7}\text{Bi}_{0.2}\text{TiO}_3$ (SBT) has a larger permittivity rather than SrTiO_3 because Bi modification favors producing a high polarization due to the intense hybridization between the $6s^2$ orbitals of Bi^{3+} and O 2p orbitals. Moreover, it also has a superior ferroelectric relaxor behavior with a diffused maximum dielectric constant in a wide temperature range, benefiting from Bi^{3+} off centering and Sr site vacancies. However,

SBT ceramic still has a critical challenge for improving dielectric breakdown strength (E_b). Some previous studies indicate that adding some oxides can effectively inhibit grain growth and increase E_b . In this paper, the SBT ceramics were synthesized by a conventional solid-state sintering method with ZrO_2 as an additive. A part of Zr^{4+} was deposited on the grain boundary in the form of oxides to inhibit grain growth. The breakdown strength and the energy storage density of the ceramics with different ZrO_2 contents were analyzed.

Materials and method Bi_2O_3 (99.5%, in mass. The same below), $SrCO_3$ (99.5%), TiO_2 (99.8%), and ZrO_2 (99.9%) were used as raw materials. The raw materials were weighed according to the stoichiometric ratio. The materials were mixed with anhydrous ethanol and ground in a ball mill with zirconium balls for 12 h. The slurry was dried in an oven. After pre-firing at 850 °C for 5 h, the powder was further ground for 24 h according to the corresponding mass ratio $Sr_{0.7}Bi_{0.2}TiO_3+xZrO_2$ (SBT- x Zr, $x=0, 0.5\%, 1.0\%, 2.0\%, 5.0\%$, in mass fraction). The dried ground powder was pressed into sheets with a thickness of 0.8 mm and a diameter of 12 mm, and then sintered at a rate of 4 °C/min at 1 200–1 250 °C for 3 h, and then cooled down naturally.

Results and discussion Based on the XRD patterns and mapping energy spectra, element Zr partially dissolves in the SBT lattice in the form of Zr^{4+} , and the rest exists in the form of ZrO_2 on the grain boundary and surface, showing the formation of a 0–3 type composite structure. The dielectric constant of SBT–2%Zr ceramic consistently exhibits a high value, while the low dielectric loss mitigates excess waste heat, which is beneficial to the energy storage performance. The heightened energy storage density primarily stems from the increased E_b value. With the augmentation of ZrO_2 content, the E_b value of the SBT–2%Zr increases, reaching a peak of 580 kV/cm, which is 27.6% higher than that of pure SBT ceramic. Consequently, the recoverable energy storage density (W_{rec}) experiences an elevation from 4.07 J/cm³ for the ceramic without x to 5.57 J/cm³ for the ceramic with x of 2%, while energy efficiency (η) maintains 88.97%. However, for the ceramic with x of 5%, despite achieving a high E_b value, the introduction of excessive ZrO_2 leads to a notable reduction in maximum polarization (P_{max}), preventing the attainment of the maximum W_{rec} value. The average grain size decreases from 2.30 μm to 1.31 μm , facilitating the attainment of more highly insulated grain boundaries. Also, the band gap energy (E_g) increases from 2.94 eV for the SBT ceramic to 3.02 eV for the SBT–5%Zr ceramic. This signifies that electrons require a larger applied electric field to achieve the valence band and conduction band transition. The expansion of the impedance circle indicates a higher resistivity of the material, and the elevated activation energy (E_a) effectively restrains the transmission of charged carriers. These interrelated mechanisms are crucial factors contributing to the substantial enhancement of E_b . In addition, SBT–2%Zr ceramic also shows an excellent fatigue stability (*i.e.*, 5×10^4 cycles, W_{rec} change <1%) and a good charge–discharge performance (*i.e.*, discharge energy density $W_d=2.15$ J/cm³, current density $C_D=1\,060.51$ A/cm² and power density $P_D=169.68$ MW/cm³).

Conclusions A lead-free 0–3 type relaxation ferroelectric ceramic based on SBT was prepared by a stable solid-state reaction method. The ceramics doped with different concentrations of ZrO_2 exhibited an original crystal structure with some Zr^{4+} in the lattice. The remaining Zr^{4+} existed in the form of a second phase, predominantly appearing at the boundaries and surfaces of grains. The increase of energy storage density mainly depended on the increase of E_b , and the possible physical mechanisms (*i.e.*, grain size, band gap, impedance and activation energy) cooperated to promote the increase of E_b . SBT–2%Zr ceramic had the optimum energy storage performance, *i.e.*, recoverable energy storage density ($W_{rec}=5.57$ J/cm³) and energy efficiency ($\eta=88.97\%$). After 5×10^4 cycles, SBT–2%Zr ceramic with a good performance stability (*i.e.*, W_{rec} change amplitude <1%) could be used as a promising candidate material for pulse power energy storage capacitors.

Keywords strontium bismuth titanate based ceramics; energy storage; dielectric breakdown strength; physical mechanisms