

Sr_{0.7}Bi_{0.2}ZrO₃ 改性钛酸铋钠陶瓷的结构、介电及储能性能

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摘 要: 近年来随着电子元件产业的快速发展, 高能量密度以及快速充放电的电容器成为新的研究热点, 这对于脉冲功率电容器的储能密度及效率提出了更高的要求。通过引入 Sr_{0.7}Bi_{0.2}ZrO₃ (SBZ), 提高了 Na_{0.5}Bi_{0.5}TiO₃ (NBT) 陶瓷的储能密度和效率。SBZ 的加入将 T_m (最大介电常数温度) 从 309.03 °C 降到 240.15 °C, 同时还增强了弛豫性。在 265 kV·cm⁻¹ 的电场强度下, 样品 0.8NBT-0.2SBZ 陶瓷同步实现了较高的可回收能量密度 ($W_{rec}=3.15 \text{ J} \cdot \text{cm}^{-3}$) 和能量效率 ($\eta=76.05\%$)。此外, 在 150 kV·cm⁻¹ 的电场强度下, 实现了出色的温度稳定性 (20~120 °C) 和频率稳定性 (1~100 Hz), 以及在 120 kV·cm⁻¹ 下, 0.8NBT-0.2SBZ 陶瓷获得超大的功率密度 ($P_D=11.31 \text{ MW} \cdot \text{cm}^{-3}$), 超快的放电时间 ($t_{0.9}=52.6 \text{ ns}$)。结果表明, 0.8NBT-0.2SBZ 陶瓷有望应用于宽温, 宽频的大功率脉冲设备中。

关键词: 钛酸铋钠; 储能陶瓷; 弛豫铁电体; 充放电特性

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环境污染和能源短缺日益严重, 虽然太阳、风和潮汐等可再生资源发挥关键作用^[1-2]。由于可再生能源间歇性, 煤炭和天然气仍是能源发电关键。如何有效储存能量、减少能量损耗成为近年来研究热点^[3]。与超级电容器和电池相比, 电介质陶瓷电容器具有寿命长、充放电速率快、功率密度高、良好温度稳定等诸多优点。电介质陶瓷电容器储能效率低、能量损耗大, 限制进一步应用。高能量密度、高效率、良好的温度和频率稳定性是电介质陶瓷电容器未来发展方向^[4]。衡量电介质陶瓷电容器能量存储能力的可回收储能密度 (W_{rec}) 和效率 (η) 可根据式(1)~式(4)由电滞回线 (P - E) 计算得到^[5-6]:

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

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

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

$$W_{loss} = W - W_{rec} = W \times (1 - \eta) \quad (4)$$

其中: P_{max} 、 P_r 、 P 、 E 、 W 和 W_{loss} 为最大极化强度、剩余极化强度、极化强度、电场强度、总储能密度

和损耗的储能密度。要求材料具有高极化及高击穿场强(BDS)之外, 还要有低的 P_r , 尽可能获得大的 W_{rec} 和 η ^[7-8]。

Na_{0.5}Bi_{0.5}TiO₃ (NBT) 是 A 位复合 ABO₃ 钙钛矿结构铁电体。NBT 的 Curie 温度为 320 °C, 具有大 P_{max} (40~50 $\mu\text{C}/\text{cm}^2$), 宽烧结温度区间, 成为储能陶瓷研究热点体系之一^[9-10]。但 NBT 具有较高 P_r (~38 $\mu\text{C}/\text{cm}^2$), 因此 W_{rec} 和 η 较低。在 NBT 中引入低 P_r 组分形成固溶体可细化 P - E , 同时提高材料 BDS, 达到高 W_{rec} 要求^[11]。Ma 等^[12]采用 AgNbO₃ 改性 0.76Na_{0.5}Bi_{0.5}TiO₃-0.24SrTiO₃ (NBT-ST), 降低 P_r 同时保持较大 P_{max} , 获得 2.03 J/cm³ 的 W_{rec} , 和 82.1% 的 η 。Zhang 等^[13]采用 SnO₂ 对 0.4NBT-0.6ST 掺杂, 发现适量 SnO₂ 可改善介电性能, 影响 NBT-ST 基体弛豫行为, 有效降低 W_{loss} 优化储能性能, 获得 2.35 J/cm³ 的 W_{rec} 。Sr_{0.7}Bi_{0.2}TiO₃ (SBT) 是一种典型的弛豫铁电体, Qiao 等^[14]在 NBT 中引入 SBT, 随 SBT 含量增加, NBT-SBT 体系从典型铁电体过渡到弛豫铁电体, 0.6NBT-0.4SBT 陶瓷在 160 kV/cm 获得 2.2 J/cm³ 的 W_{rec} 。Liu 等^[15]合成

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0.7NBT-0.3SBT 弛豫铁电体陶瓷在 135 kV/cm 获得 2.04 J/cm^3 的 W_{rec} 。但 NBT-SBT 体系仅对 NBT 的 A 位进行改性, 本课题组尝试通过 Zr^{4+} 替换 SBT 中的 Ti^{4+} 。 $\text{Sr}_{0.7}\text{Bi}_{0.2}\text{ZrO}_3$ (SBZ) 的引入将分别增强 NBT 钙钛矿结构中 A 位和 B 位无序程度, 有效地打破铁电长程有序结构, 从而进一步增强 NBT 陶瓷的弛豫铁电性。选择 Zr^{4+} 代替 Ti^{4+} 是因为 Zr^{4+} 化学性质更稳定, 通过引入离子半径差和氧空位, 引起晶格畸变, 材料的性能会得到进一步改善。其次 ZrO_2 禁带宽度更大, 大带隙有利于提高 BDS, 实现高储能性能^[16]。另外, 目前尚未见到 NBT 基中引入 SBZ 的储能性能的研究报道。

本工作通过 SBZ 引入, 将 NBT 典型铁电 P - E 回线变瘦长, 达到改善传统 NBT 陶瓷 W_{rec} 小, η 低的问题。采用固相法制备 $(1-x)\text{NBT}-x\text{SBZ}$ 陶瓷, 系统研究晶体结构、微观形貌与介电、储能性能随成分变化关系, 研究宽温度及宽频率下, 陶瓷储能性能工作稳定性和充放电特性, 为开发新型储能材料开拓思路。

1 实验

1.1 样品制备

通过固相法合成 $(1-x)\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3-x\text{Sr}_{0.7}\text{Bi}_{0.2}\text{ZrO}_3$ (NBT-SBZ, $x=0.1, 0.2, 0.3, 0.4$) 陶瓷。原料为国药集团化学试剂有限公司生产的 Na_2CO_3 (99.8%, 质量分数, 下同), Bi_2O_3 (99.9%), ZrO_2 (99.0%), SrCO_3 (99.0%), 和 TiO_2 (98.0%)。Bi 和 Na 过量 2%, 在酒精中球磨 24 h。干燥后粉末在 850 °C 煅烧 4 h。陶瓷坯体直径为 12 mm, 在 200 MPa 压力下冷等静压 3 min。在 1 090~1 150 °C 空气环境中保温烧结 4 h。

1.2 样品表征

NBT-SBZ 陶瓷样品相结构由 X 射线衍射仪 (XRD, D8 Advance, Bruker, 德国) 在 $20^\circ\sim 80^\circ$ 表征。显微结构由扫描电子显微镜 (SEM, S4800, RIGAKU, 日本) 观察, 介电性能由精密 LCR (4980A, Agilent, 美国) 测试, 介电性能样品厚度为 0.6 mm, 在 850 °C 烧制银电极。用铁电分析仪 (Radiant, Premier II, 美国) 对样品进行 P - E 测试。 P - E 测试样品厚度为 0.1 mm, 溅射直径为 2 mm 金电极。充放电特性由充放电系统 (CFD-003, Gogo, 上海) 获得。样品厚度为 0.3 mm, 在 850 °C 烧制银电极。

2 结果与讨论

2.1 物相及显微结构

图 1a 为 NBT-SBZ 陶瓷 XRD 谱, 所有样品均呈现 NBT 钙钛矿结构, 随 SBZ 含量增加, 出现 ZrO_2 和 $\text{Bi}_2\text{Ti}_2\text{O}_7$ 杂相, 其中 (111) 峰和 (200) 峰为对称单峰, 未发生劈裂, 证明所有样品均呈现伪立方相^[17]。由图 1b 可见, 在 46.5° 附近 (200) 峰随 SBZ 含量增加向低角度移动, 说明陶瓷晶面间距增大。NBT 陶瓷 A、B 位平均离子半径分别为 95.5 pm 和 68.0 pm, SBZ 的 A、B 位平均离子半径分别为

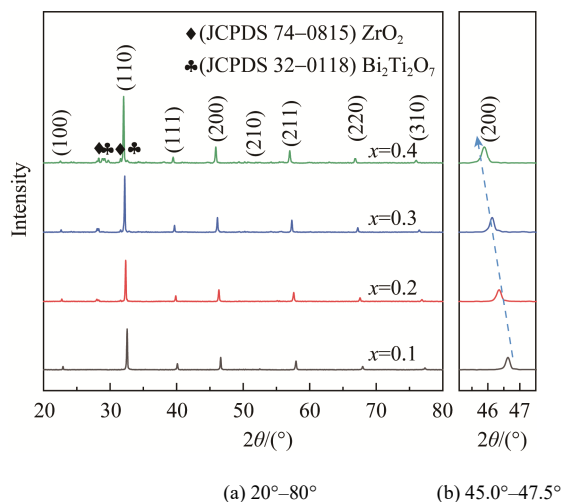


图 1 NBT-SBZ 陶瓷 XRD 衍射谱
Fig. 1 XRD diffraction patterns of NBT-SBZ ceramics

98.3 pm 和 79.0 pm。NBT-SBZ 陶瓷的晶面间距增大是由于离子半径大元素取代导致。NBT-SBZ 陶瓷晶胞参数和晶胞体积从 $3.97 \text{ \AA}$ 和 $62.6 \text{ \AA}^3$ ($x=0.1$) 增大至 $3.99 \text{ \AA}$ 和 $63.94 \text{ \AA}^3$ ($x=0.4$)。图 2a~图 2d 为样品的 SEM 照片。所有样品晶粒尺寸分布均匀且呈现正态分布, 具有明显晶界。样品平均晶粒尺寸随 SBZ 含量增加显著减小, 从 $1.57 \text{ \mu m}$ ($x=0.1$) 逐渐减小到 $1.06 \text{ \mu m}$ ($x=0.4$)。较大半径离子取代提高了晶格应变能并阻碍了晶界移动, 导致晶粒细化^[11]。晶粒细化和孔隙减少有利于获得更大 BDS。

2.2 介电性能

随 SBZ 含量增加, 介电和铁电性能发生显著变化。图 3a 为不同频率介电常数 (ϵ_r) 和损耗 ($\tan\delta$)。所有样品 ϵ_r 随频率增加逐渐减小, 从 870.5 ($x=0.1$) 降低到 668.5 ($x=0.4$), 是由于极化机制减少造成。随 SBZ 含量增加, 1 kHz 的 $\tan\delta$ 从 0.041 ($x=0.1$) 逐渐降低到 0.029 ($x=0.4$)。 $\tan\delta$ 降低有助于提高 η ^[11,18]。图 3b~图 3e 为室温~400 °C 介电温谱。所有样品显示明显弛豫铁电体特征。与 XRD 室温表现伪立方体相

一致。随 SBZ 含量增加, 介电双峰融合并不断向低温方向移动。NBT 基陶瓷介电双峰主要存在铁电性较强状态, 当 $x=0.1$ 时材料铁电性相对较强, 还存在 2 个介电峰。随 SBZ 含量增加, SBZ 引入增加位点无序性和电荷波动, 削弱 $[\text{TiO}_6]$ 八面体耦合效应^[4], 从而导致 Curie 温度下降。极化失配增强, 降低材料稳定性, 从而导致介电峰逐渐融合并往低温区移动^[19]。图 3f 为最大介电常数(ϵ_m), ϵ_m 对应温度

(T_m)和弛豫因子(γ), γ 由式(5)计算获得:

$$\frac{1}{\epsilon} - \frac{1}{\epsilon_m} = \frac{(T - T_m)^\gamma}{C} \quad (5)$$

其中: ϵ 、 C 为温度 T 下的 ϵ_r 和 Curie 常数。图 3f 中 γ 在 1.73~1.84, 表明所有 NBT-SBZ 样品都具有弛豫铁电特性。 ϵ_m 和 T_m 随 SBZ 含量增大分别从 1 842.6 和 309.03 °C ($x=0.1$)逐渐降低到 926.6 和 240.15 °C ($x=0.4$)。

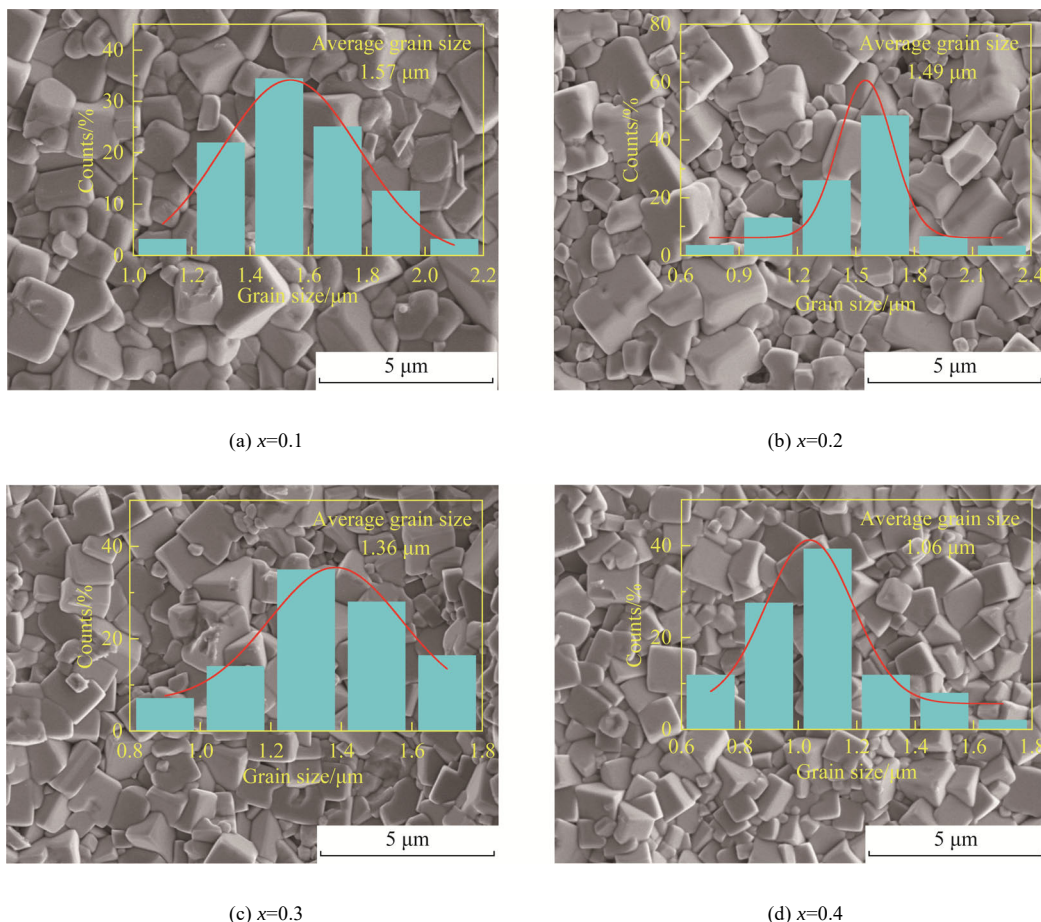


图 2 NBT-SBZ 陶瓷 SEM 照片和平均晶粒尺寸(插图)

Fig. 2 SEM images of NBT-SBZ ceramics, illustrated with average grain size

2.3 储能性能

图 4 为室温 10 Hz 的 NBT-SBZ 陶瓷铁电性能。图 4a 和图 4b 分别表示 100 kV·cm⁻¹ 所有样品双轴 P - E 和双轴 I - E 曲线。 $P_{\max}$ 、 P_r 和 ΔP ($\Delta P = P_{\max} - P_r$) 随 SBZ 含量增加发生显著变化, $P_{\max}$ 、 P_r 和 ΔP 从 ($x=0.1$) 27.33、8.71 $\mu\text{C}\cdot\text{cm}^{-2}$ 和 18.62 $\mu\text{C}\cdot\text{cm}^{-2}$ 降低至 ($x=0.4$) 7.07、0.96 $\mu\text{C}\cdot\text{cm}^{-2}$ 和 6.11 $\mu\text{C}\cdot\text{cm}^{-2}$ 。电滞回线也从典型铁电体形状变成弛豫铁电体瘦长形状, 电流密度(J)- E 电流峰逐渐趋向于矩形, 说明随着 SBZ 加入导致 NBT-SBZ 陶瓷弛豫铁电性逐渐增强。

图 4c 为 NBT-SBZ 陶瓷漏电流密度和电场强度关系, 样品漏电密度随着 SBZ 含量增大逐渐减小。

图 4d 中 Weibull 分布拟合 β 值都在 10 以上, 说明样品良好的击穿稳定性。BDS 从 189.7 kV/cm ($x=0.1$)增加到 298.1 kV/cm ($x=0.4$), 与平均晶粒尺寸减小和漏电流密度降低相吻合, 说明小晶粒尺寸和致密显微结构是取得高 BDS 重要原因^[20-21]。图 4e 为不同 SBZ 含量 BDS 下单轴 P - E 回线, 图 4f 为相应 W_{rec} 和 η , 样品 0.8NBT-0.2SBZ ($x=0.2$)在 265 kV·cm⁻¹ 获得 3.15 J/cm³ 的 W_{rec} 和 76.05% 的 η 。NBT-SBZ 陶瓷

η 随 SBZ 含量增加从 62.39% ($x=0.1$) 增加到 85.2% ($x=0.4$)。为了使储能陶瓷能够胜任实际的复杂工况, 研究频率和温度对陶瓷储能性能的影响非常重要。SBZ 的引入使得铁电体 NBT 转化为弛豫铁电体, 增强了极化无序并诱导了多态的极性纳米微区

(PNRs), 动态 PNRs 对外加电场的快速响应有助于实现 $P-E$ 回线良好的温度和频率稳定性^[22]。图 5a 和图 5b 为样品 0.8NBT-0.2SBZ 室温 150 kV/cm 下 1~100 Hz 不同频率对储能性能的影响和相应的性能参数。随着频率的增加, $P-E$ 回线变化较小,

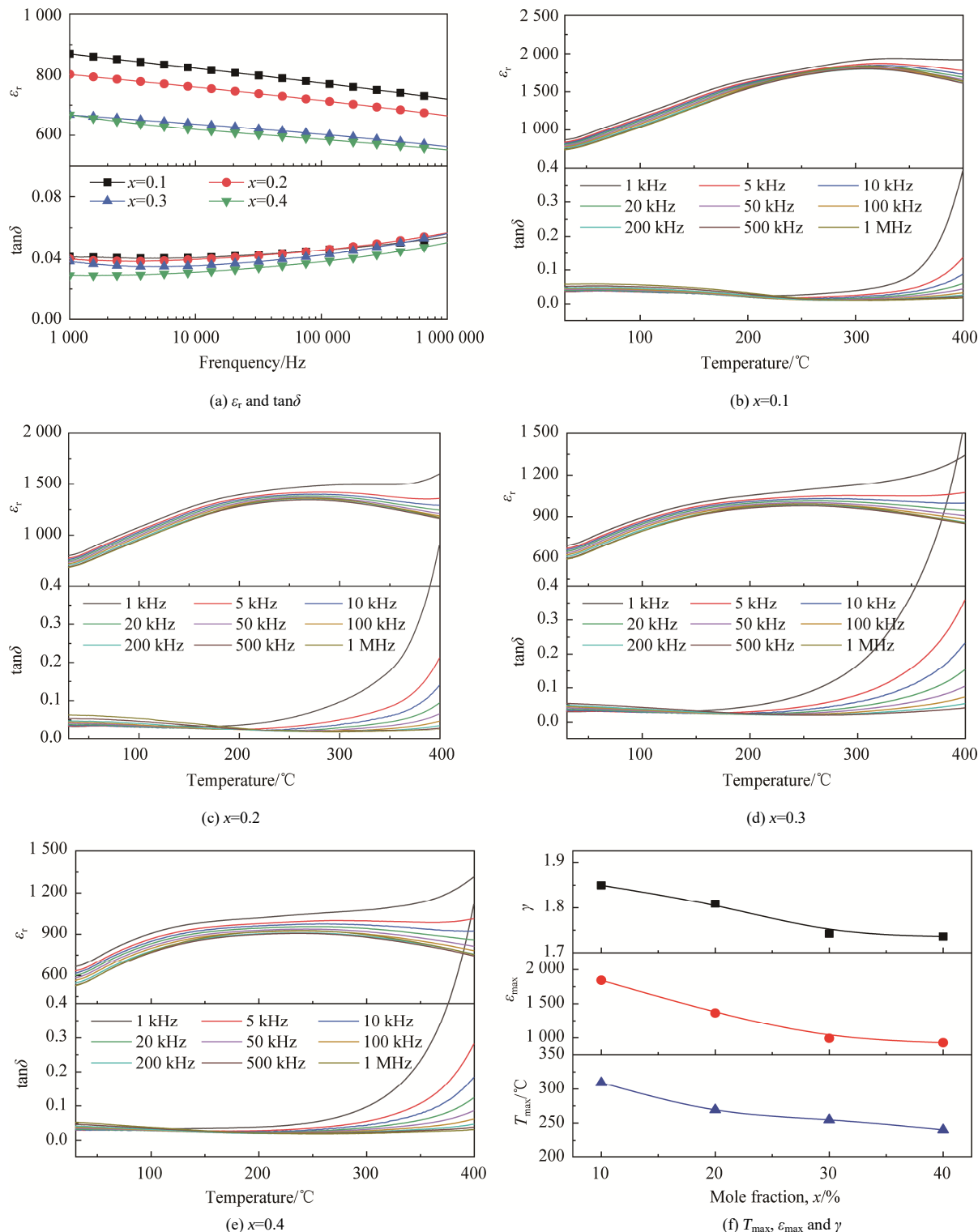
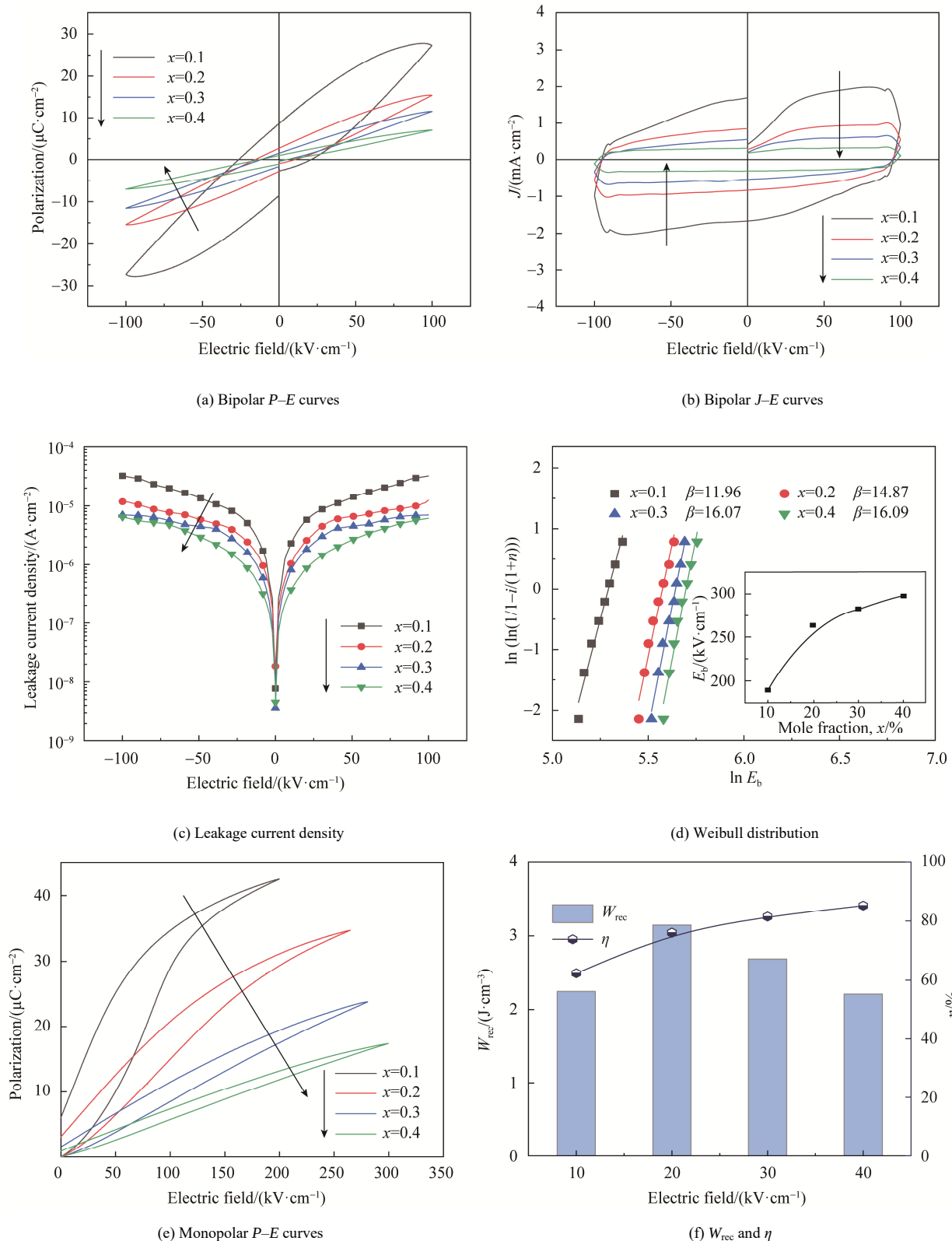


图 3 NBT-SBZ 陶瓷介电频谱, 介电温谱, 1 MHz 下 ϵ_m , T_m 和 γ

Fig. 3 Frequency dependence of dielectric constant (ϵ_r) and dielectric loss ($\tan\delta$), temperature dependence of ϵ_r and $\tan\delta$, maximum dielectric constant (ϵ_m), maximum dielectric constant temperature (T_m) and relaxor diffuseness factor (γ) at 1 MHz for NBT-SBZ ceramics



J is current density; W_{rec} is recoverable energy density; η is energy storage efficiency; E_b is breakdown strength.

图4 NBT-SBZ 陶瓷在室温 10 Hz 下铁电性能和储能性能

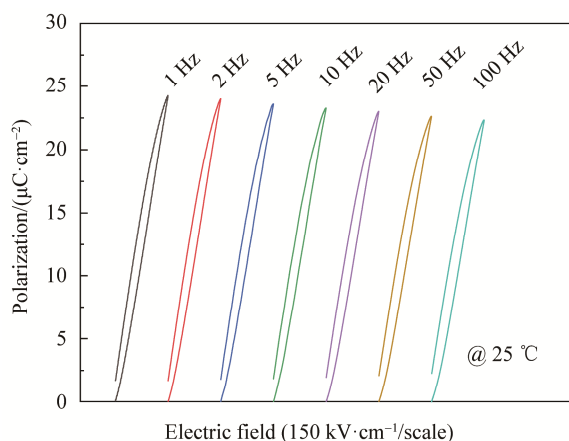
Fig. 4 Ferroelectric properties and energy storage properties of NBT-SBZ ceramics at room temperature and 10 Hz

P_{max} 略有下降。不同频率下 W_{rec} 和 η 的波动范围分别小于 12.64% 和 6.11%，表明陶瓷具有出色的储能

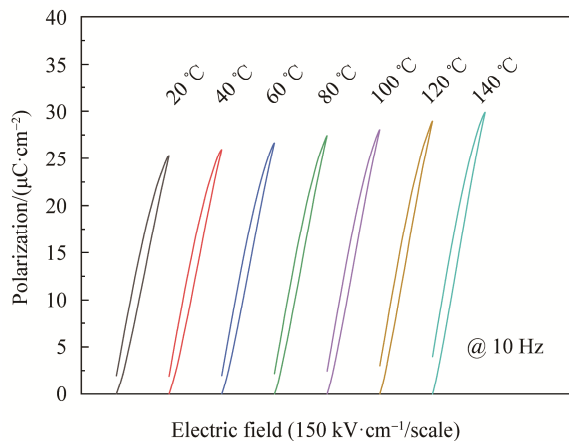
性能频率稳定性。图 5c 和图 5d 为 10 Hz 和 150 kV/cm 下 20~140 °C 不同温度对储能性能的影响和相应的

性能参数。结果表明,在测试温度范围内, P - E 回线变化较小, $P_{\max}$ 随温度升高略有上升, W_{rec} 和 η

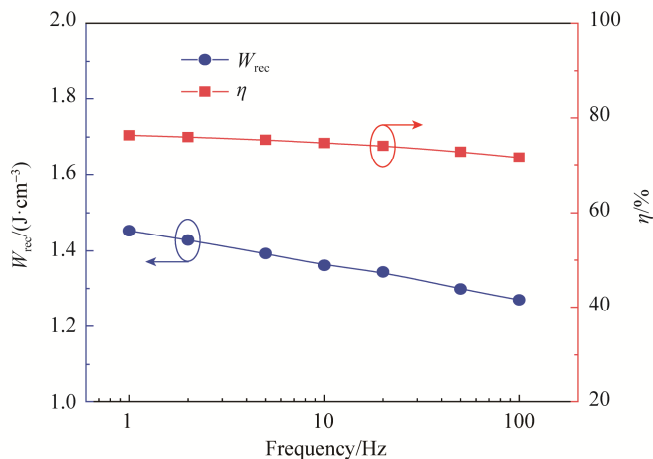
的波动范围分别小于 8.0%和 3.51%,表明该陶瓷具有优秀的储能性能温度稳定性。



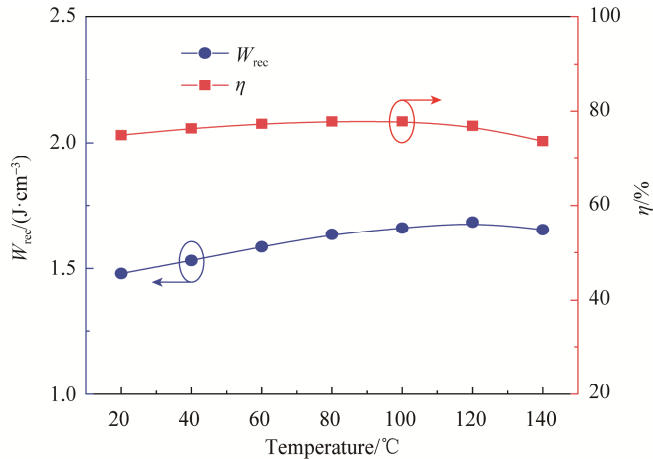
(a) Frequency dependence of P - E loops



(c) Temperature dependence of P - E loops



(b) Frequency dependence of W_{rec} and η



(d) Temperature dependence of W_{rec} and η

图 5 样品 0.8NBT-0.2SBZ 在不同频率和不同温度的单轴 P - E 回线和储能性能

Fig. 5 Monopolar P - E loop and energy storage properties of 0.8NBT-0.2SBZ sample at different frequencies and temperatures

2.4 充放电性能

为了更好地模拟陶瓷在实际应用中充放电情况,测试样品 0.8NBT-0.2SBZ 室温和变温条件下充放电性能。放电能量密度(W_{dis})可用式(6)计算:

$$W_{\text{dis}} = R \int \frac{I(t)^2 dt}{V} \quad (6)$$

其中: R , I , t 和 V 分别为负载电阻, 电流, 时间和样品体积。

电流密度(C_D)和功率密度(P_D)用式(7)和式(8)描述:

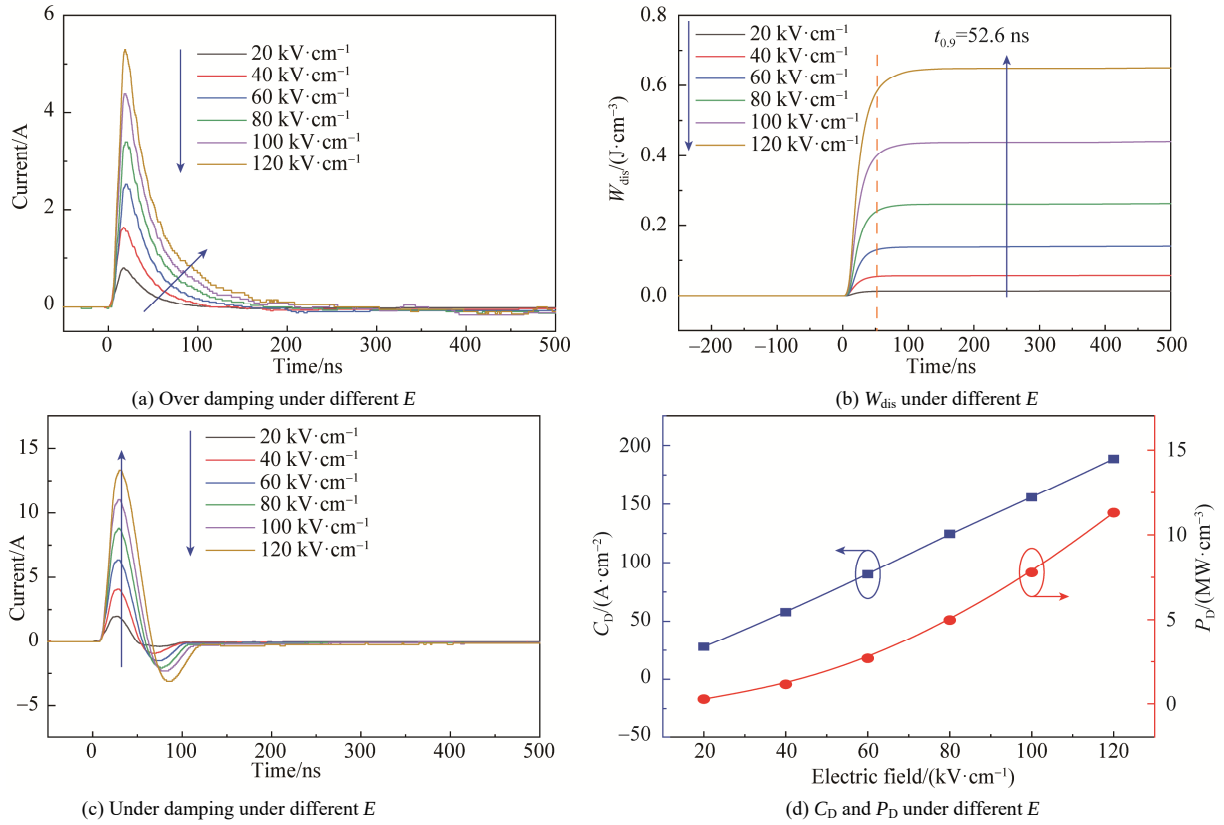
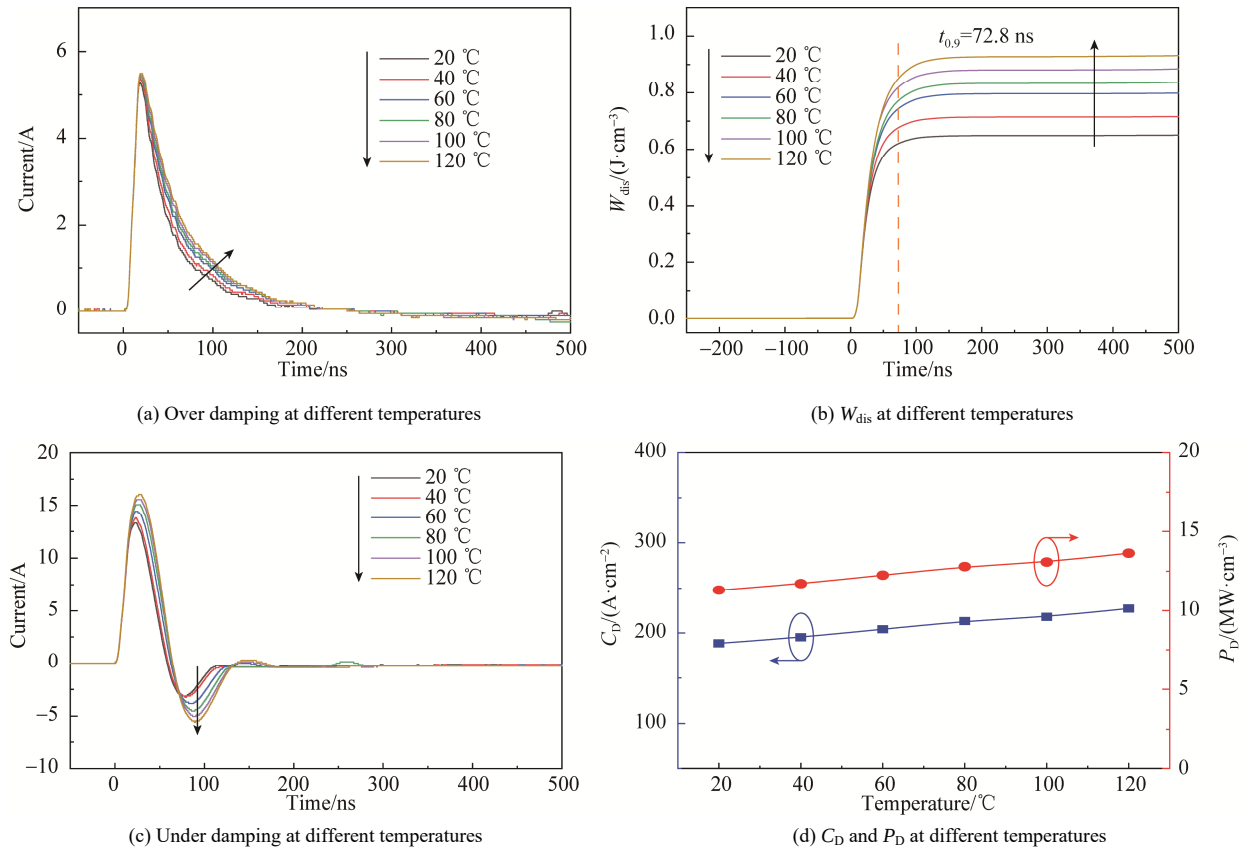
$$C_D = \frac{I_{\max}}{S} \quad (7)$$

$$P_D = \frac{I_{\max} E}{2S} \quad (8)$$

其中: $I_{\max}$ 、 S 、和 R 分别为正向电流峰值、电极面积、和负载电阻^[23-24]。图 6a 和图 6b 为样品 0.8NBT-0.2SBZ 室温过阻尼充放电性能。 W_{dis} 从 0.013 J/cm³ (20 kV/cm)增加到 0.66 J/cm³ (120 kV/cm)。图 6b 给

出了释放 90%最大能量的 $t_{0.9}$, 在 120 kV/cm 获得极快的 52.6 ns 的 $t_{0.9}$ 。表明样品 0.8NBT-0.2SBZ 具有用于脉冲功率器件的潜力。

图 6c 和图 6d 为室温欠阻尼充放电曲线。图 6c 中电流呈现周期性的变化, $I_{\max}$ 与外加电场成正比, 120 kV/cm 的最大电流为 13.32 A。图 6d 为欠阻尼测试对应的电流密度(C_D)和功率密度(P_D), 在 120 kV/cm 下分别为 188.54 A/cm² 和 11.31 MW/cm³。陶瓷充放电性能的温度稳定性十分重要, 图 7a 和图 7b 为样品 0.8NBT-0.2SBZ 从 20 °C 到 120 °C 过阻尼充放电性能, W_{dis} 有小幅增加, 从 0.66 J/cm³ 增加到 0.95 J/cm³, 120 °C 时 72.8 ns 的 $t_{0.9}$ 与室温接近。从图 7c 和图 7d 中可以发现 $I_{\max}$ 、 C_D 和 P_D 受到温度影响也都略微增加, 与变温电滞回线的变化相吻合。样品 0.8NBT-0.2SBZ 具有出色的充放电性能的温度稳定性, 是一种有潜力用于脉冲系统的材料。

图6 在不同电场下的过阻尼和欠阻尼充放电曲线, W_{dis} 曲线, C_D 和 P_D Fig. 6 Over damping charging and discharging curves, discharge energy density (W_{dis}), current density (C_D) and power density (P_D) under different electric fields图7 在不同温度下的过阻尼和欠阻尼充放电曲线, W_{dis} 曲线, C_D 和 P_D Fig. 7 Over damping charging and discharging curves, W_{dis} , C_D and P_D at different temperature

3 结论

通过引入 SBZ, 制备了 NBT-SBZ 弛豫铁电体陶瓷, 提高了 NBT 陶瓷的弛豫铁电性和储能性能。在 265 kV/cm 下, 样品 0.8NBT-0.2SBZ 实现了最佳储能特性($W_{\text{rec}}=3.15 \text{ J/cm}^3$, $\eta=76.05\%$), 同时在宽频率范围($1\sim 100 \text{ Hz}$)和宽温度范围($20\sim 140 \text{ }^\circ\text{C}$)内具有优秀的储能性能稳定性, 对电子设备极端条件下的运行具有重要意义。样品 0.8NBT-0.2SBZ 的 C_D 和 P_D 在 120 kV/cm 分别为 188.54 A/cm^2 和 11.31 MW/cm^3 , 以及极快的 $t_{0.9}$ (52.6 ns)。由此可见样品 0.8NBT-0.2SBZ 具有出色的温度、频率稳定性, 超大的功率密度及极快的放电时间, 在脉冲电源设备中具有巨大的应用潜力。

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Structure, Dielectric and Energy Storage Properties of $\text{Sr}_{0.7}\text{Bi}_{0.2}\text{ZrO}_3$ Modified Bismuth Sodium Titanate Ceramics

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Extended Abstract

Introduction Environmental pollution and energy shortage become more serious. How to effectively store energy and reduce energy loss is a recent challenge. Dielectric ceramic capacitors have some advantages such as long lifespan, fast charging and discharging speed, high power density, and good temperature stability. $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ (NBT) is a ferroelectric material with an A-site composite ABO_3 perovskite structure. The Curie temperature of NBT is 320 °C, with a large maximum polarization (P_{max}) (40–50 $\mu\text{C}/\text{cm}^2$) and a wide sintering temperature range. NBT is one of the hot research topics in energy storage ceramics. However, a high remanent polarization (P_r) (~38 $\mu\text{C}/\text{cm}^2$) results in low recyclable energy storage density (W_{rec}) and efficiency (η) for NBT. Introducing a low P_r component into NBT to form a solid solution can refine the polarization–electric field (P – E), and improve the material breakdown strength (BDS) to achieve a high W_{rec} . In this paper, Ti^{4+} was replaced in $\text{Sr}_{0.7}\text{Bi}_{0.2}\text{TiO}_3$ by Zr^{4+} . The introduction of $\text{Sr}_{0.7}\text{Bi}_{0.2}\text{ZrO}_3$ (SBZ) could enhance the degree of disorder in the A-site and B-site in the NBT, respectively. The ferroelectric long-range ordered structure was effectively break, further enhancing the relaxor ferroelectricity of NBT ceramics. Zr^{4+} was chosen instead of Ti^{4+} because Zr^{4+} was more stable chemically, and the properties of the material were further improved via introducing ionic radius difference and oxygen vacancies, leading to the lattice distortion. Also, ZrO_2 with a larger band gap was conducive to improving BDS and achieving a high energy storage performance.

Methods The $(1-x)\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3-x\text{Sr}_{0.7}\text{Bi}_{0.2}\text{ZrO}_3$ (NBT–SBZ, $x=0.1, 0.2, 0.3, 0.4$) ceramics were synthesized by a solid-phase method. Na_2CO_3 (99.8%, in mass fraction, the same below), Bi_2O_3 (99.9%), ZrO_2 (99.0%), SrCO_3 (99.0%), and TiO_2 (98.0%) (National Pharmaceutical Group Chemical Reagent Co., China) were used as raw materials. The raw materials were mixed with alcohol and ground in a ball mill for 24 h. After drying, the powder was calcined at 850 °C for 4 h. The green body with a diameter of 12 mm was pressed by cold isostatic pressing at 200 MPa for 3 min. The green body was sintered in air at 1 090–1 150 °C for 4 h.

The phase structure of NBT–SBZ ceramic samples was characterized by a model D8 Advance X-ray diffractometer (XRD, Bruker Co., Germany) at 20°–80°. The microstructure was determined by a model S4800 scanning electron microscope (SEM, RIGAKU Co., Japan). The dielectric properties were measured by a model 4980A precision LCR (Agilent Co., USA). The thickness of the dielectric properties sample was 0.6 mm, and a silver electrode was fired at 850 °C. The P – E loops were tested by a model Premier II ferroelectric analyzer (Radiant Co., USA). The P – E test sample thickness was 0.1 mm and a diameter of 2.0 mm for a gold electrode. The charging and discharging characteristics were determined from a model CFD-003 charging/discharging system (Gogo Co., China). The sample thickness was 0.3 mm, and a silver electrode was fired at 850 °C.

Results and discussion The XRD pattern of NBT–SBZ ceramics indicates that all the samples exhibit a NBT pseudocubic perovskite structure. ZrO_2 and $\text{Bi}_2\text{Ti}_2\text{O}_7$ second phase appear as the SBZ content increases. A peak at 46.5° (200) shifts towards a lower angle as the SBZ content increases, indicating an increase in the spacing between ceramic crystal planes. The SEM images indicate that the grain size distribution of all the samples is uniform and presents a normal distribution. The average grain size decreases from 1.57 μm for the sample with x of 0.10 μm to 1.06 μm for the sample with x of 0.4 with the increase of SBZ content. The substitution of larger radius ions increases the lattice strain energy and hinders the grain boundary movement, leading to a grain refinement. The grain refinement and reduction of pores are beneficial to obtaining a larger BDS. The dielectric constant (ϵ_r) decreases from 870.5 for the sample with x of 0.1 to 668.5 for the sample with x of 0.4 with increasing the frequency due to a decrease in polarization mechanism. As the SBZ content increases, the dielectric loss ($\tan\delta$) at 1 kHz decreases from 0.041 for the sample with x of 0.100 to 0.029 for the sample with x of 0.4. All the samples exhibit obvious relaxor ferroelectric characteristics. The P – E loops also change from a typical ferroelectric shape to a thin and elongated shape of a relaxor ferroelectric, and the current density (J)– E current peak becomes rectangular, indicating that the relaxor ferroelectricity of NBT–SBZ ceramics increases with the addition of SBZ. BDS increases from 189.7 kV/cm for the sample with x of 0.1 to 298.1 kV/cm for the sample with x of 0.4, which is consistent with the decrease in average grain size and leakage current density, indicating that small grain size and dense microstructure are important reasons for achieving a high BDS. 0.8NBT–0.2SBZ ceramic with x of 0.2 at 265 kV/cm obtains W_{rec} of 3.15 J/cm³ and η of 76.05%. 0.8NBT–0.2SBZ ceramics exhibit a superior frequency/temperature stability in energy storage performance. C_D and P_D of 0.8NBT–0.2SBZ ceramics are 188.54 A/cm² and 11.31 MW/cm³ at 120 kV/cm, with an extremely fast $t_{0.9}$ of 52.6 ns.

Conclusions NBT–SBZ relaxor ferroelectric ceramics were prepared via introducing SBZ to improve the relaxor ferroelectricity and energy storage properties of NBT ceramics. 0.8NBT–0.2SBZ ceramic achieved the optimum energy storage properties (i.e., $W_{\text{rec}}=3.15$ J/cm³, $\eta=76.05\%$) at 265 kV/cm, as well as a superior stability of the energy storage performance at 1–100 Hz) and 20–140 °C. The C_D and P_D of 0.8NBT–0.2SBZ ceramic were 188.54 A/cm² and 11.31 MW/cm³ at 120 kV/cm, respectively, with a fast $t_{0.9}$ of 52.6 ns. The 0.8NBT–0.2SBZ ceramic had a superior temperature/frequency stability, a super high power density, and extremely fast discharge time, having a great potential for application in pulse power supply equipment.

Keywords sodium bismuth titanate; energy storage ceramics; relaxor ferroelectrics; charge–discharge properties