

通过弛豫性调控 BaTiO₃ 基陶瓷的储能性能

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摘 要: BaTiO₃(BT)作为一种典型的无铅铁电陶瓷被广泛的研究,然而大的剩余极化以及施加电场后的极化翻转损耗限制其进一步应用。通过在 BT 陶瓷中引入 Bi_{0.5}Na_{0.5}TiO₃-Sr_{0.7}La_{0.2}TiO₃ (BNT-SLT)组元调控弛豫性,从而实现高的储能性能。研究结果表明,随着 BNT-SLT 含量的增加,BT 陶瓷的弛豫性明显提高。因此,0.55BT-0.45 (BNT-SLT)陶瓷在低电场 280 kV/cm 时实现了高的储能密度: W_{rec} 约为 3.12 J/cm³ 和效率 η 约为 93.3%。同时,该陶瓷具有优异的频率稳定性、温度稳定性及疲劳特性。以上结果表明,经过弛豫性调控的 BT 基铁电陶瓷在储能领域有着巨大的应用潜力。

关键词: 钛酸钡陶瓷; 弛豫性; 储能密度; 效率

中图分类号: TQ174 文献标志码: A 文章编号: 0454-5648(2024)04-1384-08

网络出版时间: 2024-03-11



储能设备在现代电气装置和电子工业中发挥着至关重要的作用^[1-3]。目前,被广泛使用的储能器件包括电池、电化学电容器和电介质电容器等^[4-6]。其中电介质陶瓷电容器由于具有超高的功率密度、快速的充放电速率、优良的热稳定性和机械强度被应用于混合动力汽车、医疗器件、航天航空、先进电子脉冲装置等领域^[7-8]。电介质电容器的储能密度是决定其电学性能最关键的电学参数之一,通常可由式(1)~式(3)来量化铁电电容器的储能密度:

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

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

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

其中: W 、 W_{rec} 、 P_r 、 P_{max} 及 E 分别为电容器的总储能密度、放电储能密度、剩余极化强度、最大极化强度和外加电场强度^[9-10]。式(1)~式(3)表明:通过增加 P_{max} 和 P_r 的差值(ΔP)可有效提升放电储能密度和效率。

铁电陶瓷通常被分为线性电介质(LE)、铁电体(FE)、弛豫性铁电体(RFE)以及反铁电体(AFE) 4 种^[11-13]。其中线性介质虽然拥有大的击穿场强以

及低的 P_r ,但受限于低的 P_{max} ,很难有优秀的储能表现^[14]。AFE 由于具有较高的 ΔP ,确实可以成为高功率储能器件的候选材料。然而,反铁电-铁电相变带来的相变损耗往往会造成 η 值的大幅降低^[15]。近年来,RFE 陶瓷被认为是具有极大应用潜力的储能材料,出色的弛豫特性对提高陶瓷的储能性能有着显著优势^[16]。BaTiO₃(BT)作为一种典型的无铅铁电陶瓷具有巨大的介电常数和长程有序的自发极化,在介电电容器材料中得到了广泛的研究和应用^[17-18]。然而纯的 BT 材料通常存在大的剩余极化,以及在施加电场后会发生巨大的极化翻转的能量损耗,这限制了 BT 材料在储能领域的进一步发展^[17, 19]。为了优化原始 BT 陶瓷的储能性能,提出了成分调制和离子掺杂等有效的方法。目的是打破其原有的长程有序的铁电畴结构,产生纳米级的极性纳米畴结构,这可以加快极化响应速率,增强铁电体的弛豫性^[20-22]。

近年来,由于 Bi³⁺的 6s 和 O 的 2p 的轨道强杂化可以导致高的饱和极化强度,含有 Bi 基的铁电陶瓷在储能领域中得到了广泛的研究^[23],例如 Bi_{0.5}Na_{0.5}TiO₃(BNT)、K_{0.5}Bi_{0.5}TiO₃(KBT)和 Sr_{0.7}Bi_{0.2}TiO₃(SBT)等^[24]。研究报道发现 Bi 基陶瓷和

收稿日期: 2023-11-07。 修订日期: 2024-01-18。

基金项目: 国家自然科学基金(51902167)。

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Received date: 2023-11-07. Revised date: 2024-01-18.

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BT 材料的掺杂耦合可以显著地改进 BT 材料的低 ΔP , 离子掺杂带来的价态涨落和尺寸差异让 BT 材料产生了极性纳米畴, 极大地增强了弛豫性^[25]。受以上研究内容启发, 设计了系列 $(1-x)\text{BaTiO}_3-x(0.6\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3-0.4\text{Sr}_{0.7}\text{La}_{0.2}\text{TiO}_3)$ ($x=0.20, 0.30, 0.40, 0.45, 0.50$) ($(1-x)\text{BT}-x(\text{BNT}-\text{SLT})$) 储能陶瓷来改进 BT 铁电陶瓷的储能性能。利用 BNT 材料的强轨道杂化来增强体系的饱和极化强度; SLT 的加入为了进一步加大离子尺寸差异, 提高弛豫行为。此外, 体系中还引入了部分空位设计, 这通常会在陶瓷中形成缺陷偶极子。缺陷偶极子在外电场作用下难以改变极化方向, 保持初始极化状态, 抑制了极化反转, 并使矫顽场 E_c 增大。同时, 去除外电场后, 产生的反作用力能将极化方向恢复至最初状态, 导致材料的剩余极化降低甚至趋于零, 进而提高了储能密度^[26]。

通过固态反应法制备了一系列 BT-BNT-SLT 陶瓷。随着 BNT-SLT 含量的增加, 体系在同电场下的弛豫特性有了显著增强, 同时还伴随着放电储能密度的提高。尤其是, $0.55\text{BT}-0.45(\text{BNT}-\text{SLT})$ 陶瓷获得最优的储能性能, 其储能密度约为 3.12 J/cm^3 和效率约为 93.3%。

1 实验

通过固态反应法制备了一系列 $(1-x)\text{BT}-x(\text{BNT}-\text{SLT})$ 陶瓷, 将纯度(质量分数)分别为 99.500% 的 Na_2CO_3 (麦克林)、99.000% 的 BaCO_3 (罗恩)、99.975% 的 Bi_2O_3 (赛默飞世尔)、99.000% 的 SrCO_3 (沪试)、99.000% 的 TiO_2 (麦克林)、99.000% 的 La_2O_3 (麦克林) 烘干后按照化学计量比配料。将称得原料混合

于球磨罐中, 并加入一定比例的无水乙醇和二氧化锆球 [$m(\text{原料}):m(\text{无水乙醇}):m(\text{二氧化锆球})=1.0:2.5:4.0$] 球磨 12 h。球磨结束后, 将球磨浆料在 100°C 干燥 12 h。之后, 利用玛瑙研钵充分研磨所获得的干燥原料达 0.5 h 以上。最后, 将研磨后的原料倒入氧化铝的坩埚中压实, 放入实验箱式炉中进行第 1 次预烧结。预烧结温度为 850°C , 保温 2 h, 自然冷却到室温。之后依照上述操作进行二次球磨和二次烧结。将二次预烧结后所得的粉末, 研磨处理后称取 2~4 g 的粉料, 置于玛瑙研钵中, 加入质量分数为 8% 的聚乙烯醇(PVA)粘结剂, 通过研磨使其与粉料均与混合。利用手动压片机, 称取约 0.2 g 的粉末倒入圆柱形的金属模具中, 施加 10 MPa 的压力, 保压 5 min, 压制成直径 10 mm、厚度 0.5 mm 的小圆片。然后在 $1130\sim 1220^\circ\text{C}$ 烧结 2 h 得到 BT-BNT-SLT 陶瓷样品。之后将烧制后的样品打磨、抛光至 $100 \mu\text{m}$ 后涂覆直径为 2 mm 的金电极进行铁电测试。

采用荷兰 PANalytical 公司 PANalytical Empyrean 型 X 射线衍射仪(XRD)对陶瓷进行物相分析。采用日本日立公司 Regulus 8230 型扫描电子显微镜(SEM)对样品进行表面形貌表征。采用常州同惠公司 TH2838A 型介电性能测试分析系统对样品进行介电常数和介电损耗的表征。采用美国 Polyk 公司 TF Analyzer 2000 型铁电测试仪来测试样品的铁电性能。采用上海同果公司 TLRS-003 型高低温冷热系统来控制测试温度。

2 结果与讨论

图 1a 为 $(1-x)\text{BT}-x(\text{BNT}-\text{SLT})$ 陶瓷的 XRD 谱, 所有组分的衍射峰位置都属于标准的钙钛矿结构。

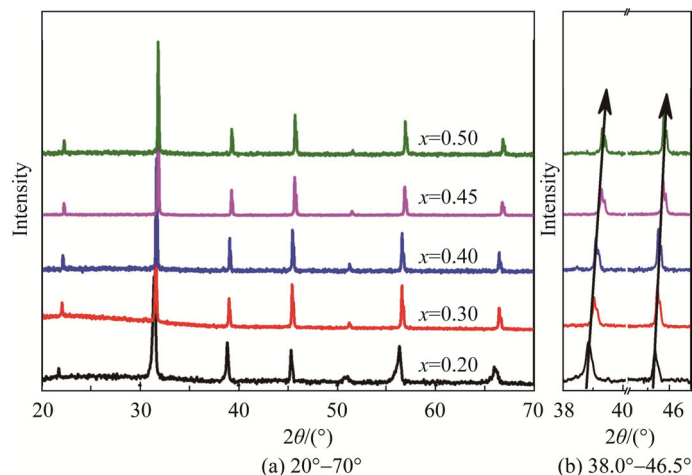


图 1 $(1-x)\text{BT}-x(\text{BNT}-\text{SLT})$ 陶瓷的 X 射线衍射谱和特征峰放大谱
Fig. 1 X-ray diffraction patterns and enlarged peaks of $(1-x)\text{BT}-x(\text{BNT}-\text{SLT})$ ceramics

由图 1a 可见, 所有成分均达到完全固溶, 没有生成其他二次相。2 θ 角度在 38°~47° 的放大峰如图 1b 所示。由图 1b 可见, 随着 x 的增加, 衍射峰发生向大角度偏移。根据 Bragg 定律, 这表明晶格参数的减小, 由于小尺寸离子掺杂带来的晶格参数的减小^[27], A 位掺杂的 Bi³⁺, Na⁺, Sr²⁺, La³⁺ 相对于 Ba²⁺ 均存在离子半径减小。此外, 由图 1b 中可见, XRD 峰型存在由单峰向双峰的演变, 这可能是由于离子

掺杂引起的 Curie 相变点逐渐移动到室温, 使得四方铁电相和立方顺电相在室温同时存在。

图 2 为 (1- x)BT- x (BNT-SLT), $x=0.30$ 、0.40、0.45、0.50 的 SEM 照片。由图 2 可见, 所有样品的表面形貌均为清晰明显的晶粒、晶界分明, 并且粒度分布均匀, 排列紧密、陶瓷致密性好、成瓷性高。在 SEM 照片中并没有观察到其它形态的杂质相, 这与 XRD 谱表征结果一致。

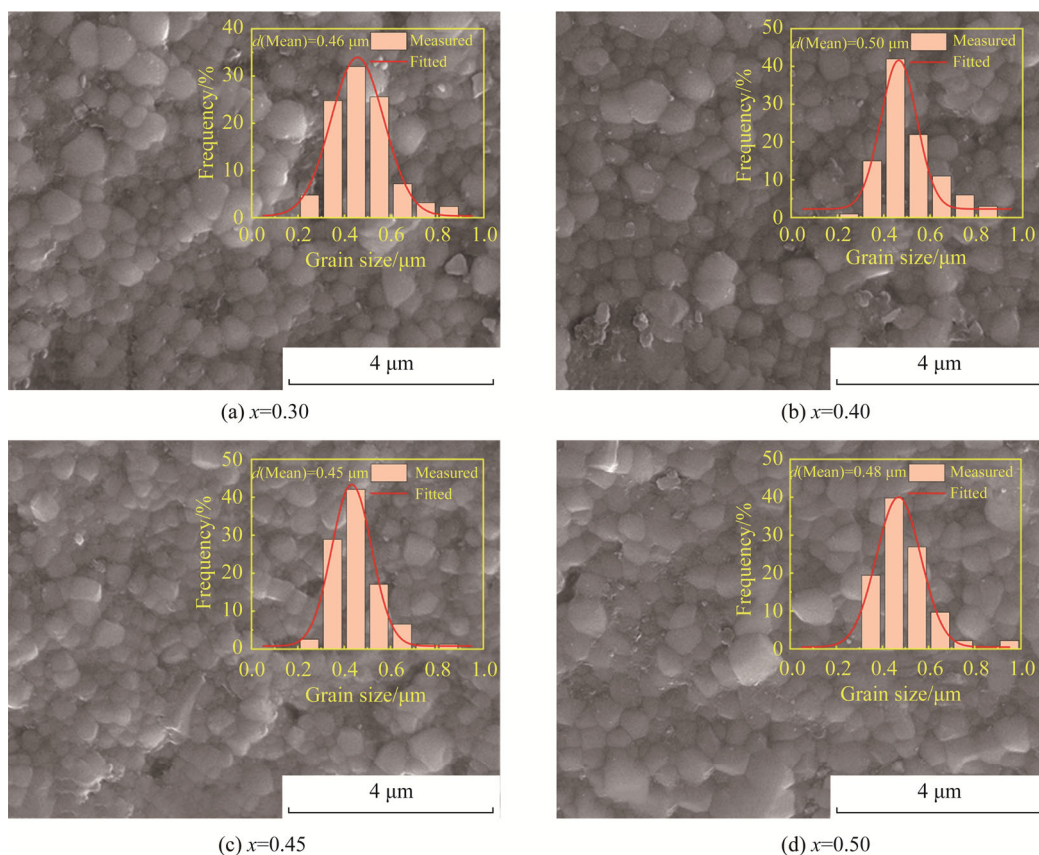


图 2 (1- x)BT- x (BNT-SLT)陶瓷的 SEM 照片
Fig. 2 SEM images of (1- x)BT- x (BNT-SLT) ceramics

图 3a~图 3e 为 (1- x)BT- x (BNT-SLT)陶瓷的介电温谱测试, 所有介电温谱测试中都存在 1 个明显的介电异常峰(T_m), 这是铁电陶瓷达到了 Curie 相变温度所致。随着 BNT-SLT 含量的增加, 介电异常峰发生明显的宽化, 这是弛豫特性的重要表现^[7]; 并逐渐伴随出现弛豫行为导致的频率色散^[16]。随着 x 值的增加, 最大介电异常峰逐渐向低温移动, 表明随着 BNT-SLT 的掺杂, 相结构在室温逐渐从铁电相转变到顺电相。此外, 随着掺杂含量增加, 介电常数逐渐减小, 这是因为极性纳米畴的出现大幅度减小了畴壁尺寸, 限制了部分电偶极子的翻转, 是弛豫特性增强的一种表现^[9]。同时, 体系发生的铁电相到顺电相的相变也不可避免的会导致介电常数的减

小^[18]。在测试温度中, 各组分在所有温度范围中的介电损耗都小于 0.2, 这表明(1- x)BT- x (BNT-SLT)陶瓷具有优异的效率和温度稳定性。在铁电陶瓷中, 改进的 Curie-Weiss 定律常被用来证明陶瓷的弛豫性, 扩散度 γ 可由 Curie-Weiss 公式拟合, 如式(4)所示:

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

其中: ϵ_m 为介电异常峰 T_m 处的介电常数; ϵ_r 为各温度下对应的介电常数; C 为 Curie-Weiss 常数; γ 代表体系扩散度。一般来说, $\gamma=1$ 表示典型的铁电体, $\gamma=2$ 代表理想的弛豫性铁电体。如图 3f 所示, 随着 x 值的增加, γ 值从 1.60 逐渐增加到 1.77, 表明体系弛豫特性的增强。

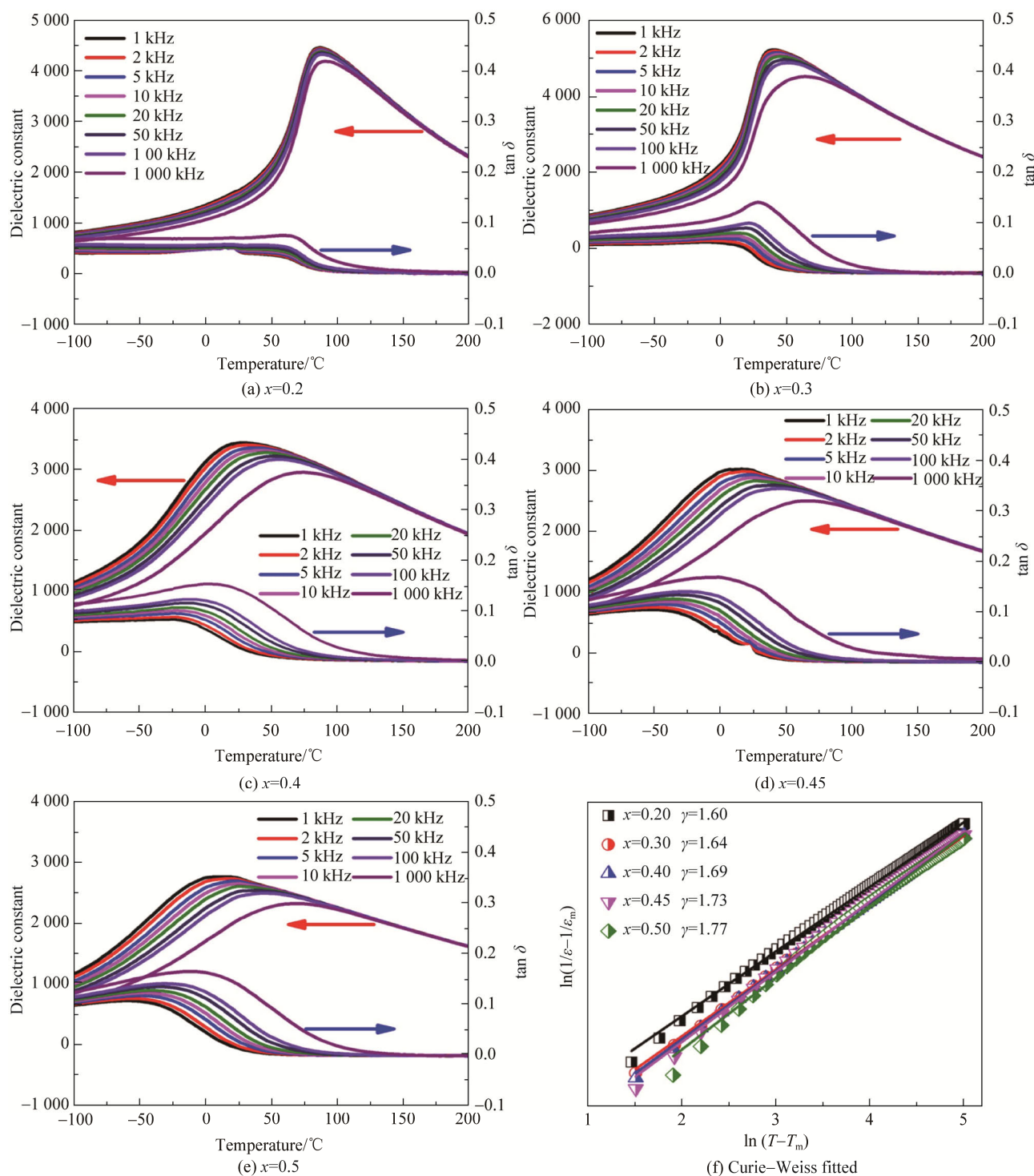


图 3 样品的介电常数和介电损耗对温度的依赖性和 Curie-Weiss 拟合

Fig. 3 Temperature dependence of dielectric constant & dielectric loss and Curie-Weiss fitting of samples

图 4a 为 $(1-x)\text{BT}-x(\text{BNT}-\text{SLT})$ 陶瓷在 200 kV/cm 的 $P-E$ 曲线。随着 x 组分的增加, 曲线逐渐变得细长。效率 η 从 $x=0.2$ 时的 75.7% 增加到 $x=0.5$ 时的 94.5% , 这是由于增强的弛豫行为导致的快速的极化响应速率, 减小了极化损耗。随着 Bi 基组分的增

加, 最大极化明显升高, $P_{\max}$ 从 $x=0.2$ 组分的逐渐增加, 到 $x=0.4$ 时达到了最大值 $25.32 \mu\text{C/cm}^2$ 。然而极性纳米畴的产生必然会阻碍部分电偶极子的翻转, 导致最大极化强度下降的主要原因^[2]。在 $x=0.5$ 时最大极化降低到了 $19.52 \mu\text{C/cm}^2$ 。图 4b 为在相同

电场 200 kV/cm 下所得到的 $(1-x)\text{BT}-x(\text{BNT-SLT})$ 陶瓷的储能性能,放电储能密度从 $x=0.2$ 时的 1.0 J/cm^3 逐渐提升,在 $x=0.45$ 时达到了最大值 $W_{\text{rec}} \sim 1.96 \text{ J/cm}^3$ 。而在 $x=0.5$ 时陶瓷的储能性能出现了明显的下降,因为室温的相结构变为立方顺电相,其极化强度相对于铁电相明显降低。在图 4c 中,对 0.55BT-0.45

(BNT-SLT)陶瓷做了完整的铁电性能测试,最终在 280 kV/cm 的临界击穿场强下获得了大的 W_{rec} (约为 3.12 J/cm^3)及高的 η (约为 93.3%)。图 4d 对比了 0.55BT-0.45(BNT-SLT)陶瓷与其他 BT 基陶瓷储能性能,显然所制备陶瓷的 W_{rec} 和 η 都保持在一个相对较高的水平。

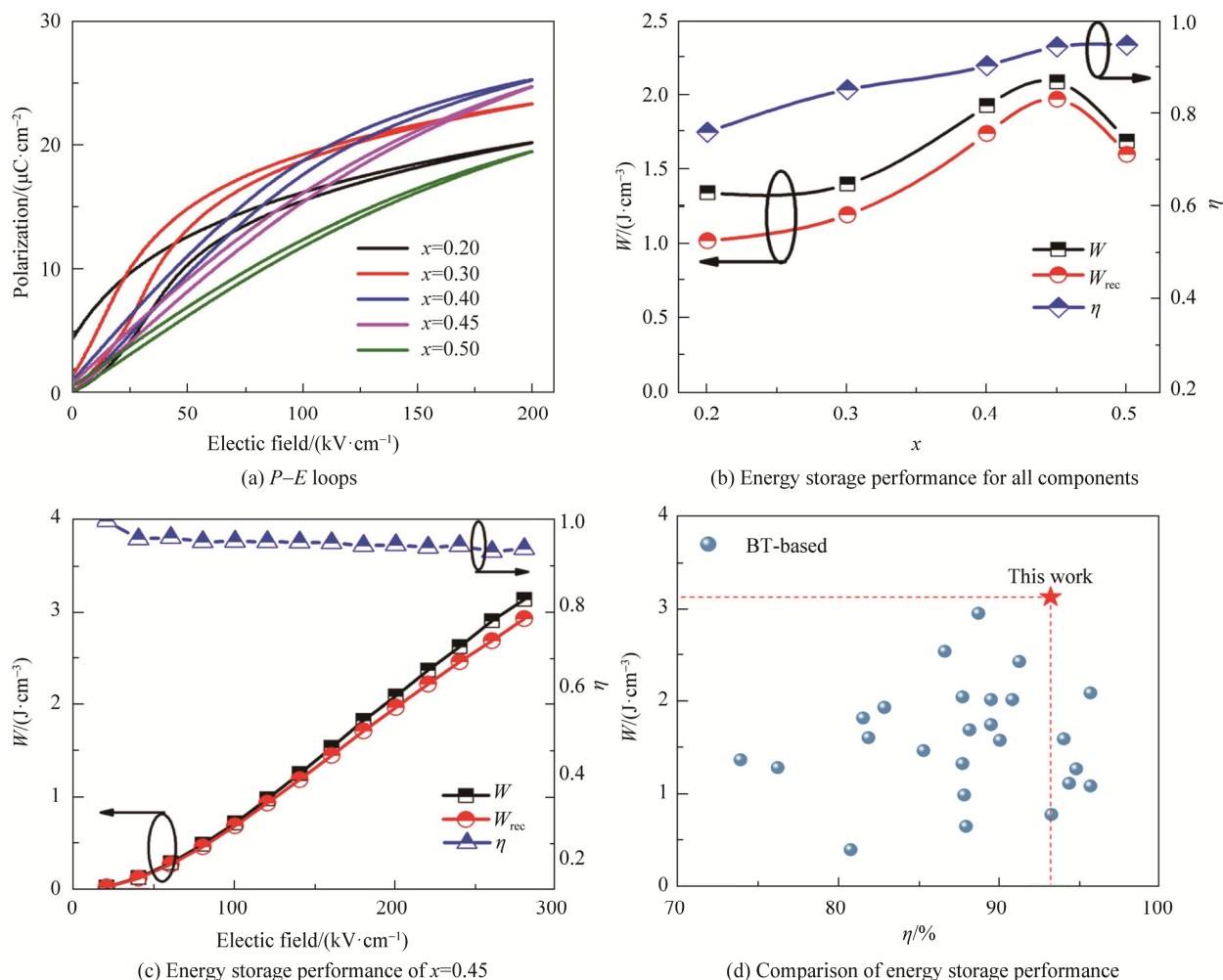


图 4 $(1-x)\text{BT}-x(\text{BNT-SLT})$ 陶瓷在 200 kV/cm 的 $P-E$ 曲线, 储能密度和效率, 以及 0.55BT-0.45(BNT-SLT)陶瓷的储能密度和效率和 0.55BT-0.45(BNT-SLT)陶瓷的储能性能与其他 BT 陶瓷对比

Fig. 4 $P-E$ loops and energy density and efficiency of $(1-x)\text{BT}-x(\text{BNT-SLT})$ ceramics under 200 kV/cm; energy density and efficiency of 0.55BT-0.45(BNT-SLT) ceramic; energy storage performance of 0.55BT-0.45(BNT-SLT) ceramics to compare other BT ceramics

在实际应用中,性能稳定性的表现是至关重要的参数。对 0.55BT-0.45(BNT-SLT)陶瓷进行了各项性能稳定性测试。测试条件为在室温施加场强为 200 kV/cm, 频率为 100 Hz 的测试电场。如图 5 所示,在 10^5 的循环稳定性测试中,0.55BT-0.45(BNT-SLT)陶瓷的效率变化小于 1%,放电储能性能变化小于 2%,这表明 0.55BT-0.45(BNT-SLT)陶瓷具有出色的抗疲劳性能。之后改变外加电场的频率

为从 1~5 000 Hz,陶瓷的效率变化小于 2%,放电储能性能变化小于 3% (图 6),证明 0.55BT-0.45(BNT-SLT)陶瓷有优异的频率稳定性。且在频率稳定性测试中 $P-E$ 曲线保持稳定的细长形状,即使在 5 000 Hz 的高频下效率变化也小于 2%,证明产生的极性纳米畴对电场有快速的响应速率,反映出体系有出色的弛豫性。将温度从室温升高到 160 $^{\circ}\text{C}$, 0.55BT-0.45(BNT-SLT)陶瓷的效率变化 <5%, W_{rec}

变化小于 10% (图 7), 这符合欧盟关于电子设备稳定性的要求^[2]。此外, 与近年来报道的其他 BT 基

陶瓷相比, 本工作具有较好的稳定性和更高的储能性能。

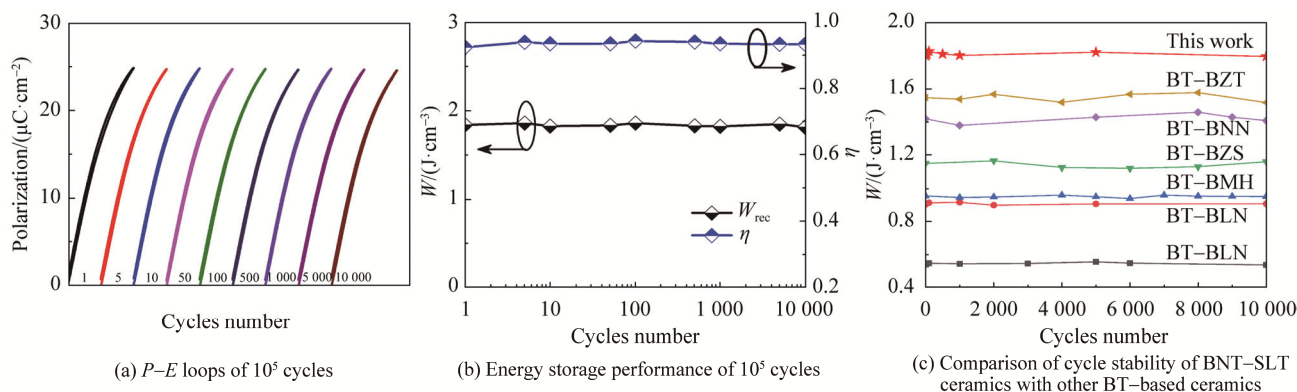


图 5 0.55BT-0.45(BNT-SLT)陶瓷的循环稳定性

Fig. 5 Cycle stability of 0.55BT-0.45(BNT-SLT) ceramics

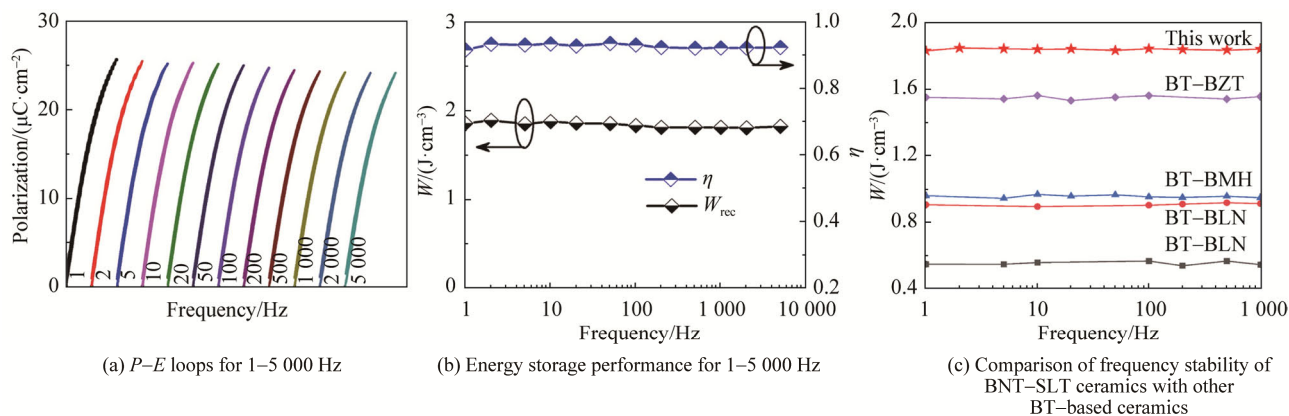


图 6 0.55BT-0.45(BNT-SLT)陶瓷的频率稳定性

Fig. 6 Frequency stability of 0.55BT-0.45(BNT-SLT) ceramics

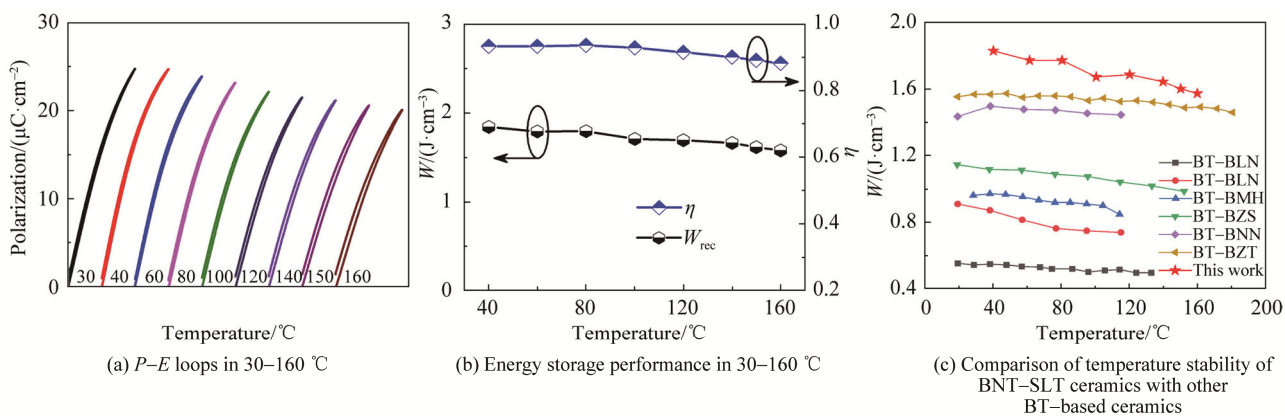


图 7 0.55BT-0.45(BNT-SLT)陶瓷的温度稳定性

Fig. 7 Temperature stability of 0.55BT-0.45(BNT-SLT) ceramics

3 结论

通过固相反应法制备了一系列 $(1-x)\text{BT}-x(\text{BNT-SLT})$ 陶瓷。SEM 照片表明陶瓷颗粒清晰, 具有良好的致密性。介电温谱表明离子掺杂对于调控

BT 基陶瓷的弛豫性有显著效果。铁电测试结果表明经过弛豫性调控的 BaTiO₃ 基陶瓷在储能性能上有着巨大改进, 尤其是样品 0.55BT-0.45 (BNT-SLT) 在低电场 280 kV/cm 下获得最佳储能性能, 其中 W_{rec} 约为 $3.12 \text{ J}/\text{cm}^3$ 及 η 约为 93.3%。同时, 该陶瓷具有

优异的频率稳定性、温度稳定性及疲劳特性。综合以上数据和稳定性测试证明弛豫性调控后的 BT 基铁电陶瓷在储能应用中有着巨大潜力。

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Enhancing Energy Storage Performance of BaTiO_3 -Based Ceramics through Relaxor Regulation

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Extended Abstract

Introduction In recent years, relaxor ferroelectrics (RFE) ceramics are recognized as materials with a tremendous potential for

energy storage applications. Their relaxor characteristics significantly contribute to enhancing the energy storage performance of ceramics. BaTiO₃ (BT) as a typical lead-free ferroelectric ceramic is popular due to its immense dielectric constant and long-range ordered spontaneous polarization. This ceramic is extensively investigated and applied in dielectric capacitor materials. However, pure BT materials often exhibit a large residual polarization and a considerable energy loss due to polarization reversal upon the application of an electric field, affecting the further development of BT materials in energy storage. To optimize the energy storage performance of the original BT ceramics, effective methods such as compositional modulation and ionic doping are proposed. The objective of this paper was to disrupt an original long-range ordered ferroelectric domain structure, creating nano-sized polar nanodomains. This could accelerate the polarization response speed and enhance the relaxor behavior of ferroelectrics.

Methods (1- x)BT- x (BNT-SLT) ceramics were synthesized by a solid-state reaction method. Na₂CO₃ (purity: 99.500%, in mass fraction, the same below), BaCO₃ (purity: 99.000%), Bi₂O₃ (purity: 99.975%), SrCO₃ (purity: 99.000%), TiO₂ (purity: 99.000%) and La₂O₃ (purity: 99.000%) were used as raw materials. These materials were dried and mixed in stoichiometric proportions. The mixture was then ground with anhydrous ethanol in a grinding mill with zirconium dioxide balls in a mass ratio of 1.0:2.5:4.0 for 12 h. After grinding, the slurry was dried at 100 °C for 12 h. The dried materials were subsequently ground using an agate mortar for over half an hour. The ground materials were firstly transferred and compacted in an alumina crucible, pre-sintered in a box furnace at 850 °C for 2 h, and then cooled naturally to room temperature. The powder obtained from the second pre-sintering was further ground and mixed with a polyvinyl alcohol (PVA) as a binder at a mass fraction of 8%. The mixture was manually pressed into small discs with 10 mm in diameter and 0.5 mm in thickness under 10 MPa for 5 min. These discs were sintered at 1 130–1 220 °C for 2 h to produce BT-BNT-SLT ceramic samples. After post-sintering, the ceramic samples were polished and coated with 2 mm diameter gold electrodes for ferroelectric testing.

The phase composition of the ceramics was analyzed by a model PANalytical Empyrean X-ray diffractometer (XRD), while the surface morphology was characterized by a model Regulus 8230 scanning electron microscope (SEM). The dielectric properties, such as dielectric constant and loss, were assessed by a model TH2838A dielectric performance analysis system. The ferroelectric properties were evaluated by a model Polyk TF Analyzer 2000, and the temperature in testing was controlled by a model TLRS-003 high-low temperature thermal system.

Results and discussion The energy storage ceramics of (1- x)BaTiO₃- x (0.6Bi_{0.5}Na_{0.5}TiO₃-0.4Sr_{0.7}La_{0.2}TiO₃)(x =0.20, 0.30, 0.40, 0.45, 0.50) ((1- x)BT- x (BNT-SLT)) with different compositions (*i.e.*, x of 0.20, 0.30, 0.40, 0.45, and 0.50) were prepared to enhance the energy storage performance of BT ferroelectric ceramics. The incorporation of BNT material can strengthen the system saturation polarization through an enhanced orbital hybridization. Also, the inclusion of SLT can further increase an ionic size disparity, thereby enhancing a relaxor behavior. The system integrates a partial vacancy design, typically resulting in the formation of defect dipoles within the ceramics. These defect dipoles in an external electric field are less likely to alter their polarization direction, preserving the initial state of polarization. This mechanism inhibits a polarization reversal and increases the coercive field (E_c). Furthermore, in the absence of the external field, a generated reaction force can revert the polarization direction back to its initial state, leading to a reduction or even a nullification of the residual polarization, consequently enhancing the energy storage density.

Conclusions (1- x)BT- x (BNT-SLT) ceramics were fabricated by a solid-state reaction method. The SEM images revealed that the ceramics had clear grains and great density. The dielectric spectroscopy indicated that ion doping regulated the relaxor behavior of BT-based ceramics. The results by ferroelectric tests demonstrated substantial improvements in energy storage performance of the relaxor-modulated BaTiO₃-based ceramics, particularly for the 0.55BT-0.45(BNT-SLT) ceramic, obtaining an optimal energy storage performance at 280 kV/cm with a recoverable energy density (W_{rec}) of approximately 3.12 J/cm³ and an efficiency (η) of 93.3%. In addition, these ceramics also exhibited superior frequency stability, temperature stability, and fatigue properties. The amalgamation of these data and stability tests indicated that the relaxor-modulated BT-based ferroelectric ceramics could have a promising potential for energy storage applications.

Keywords barium titanate ceramics; relaxor; energy storage density; efficiency