

文章编号 1672-6634(2024)04-0070-07

DOI 10.19728/j.issn1672-6634.2023100007

BaTiO₃-x Bi(Mg_{2/3}Sb_{1/3})O₃ 陶瓷的储能特性研究

詹圣晖,任 香,张立华,李 朋,郝继功,李 伟

(聊城大学 材料科学与工程学院,山东省教育厅敏感材料与器件实验室,山东 聊城 252059)

摘 要 采用固相法制备了(1-x)BaTiO₃-x Bi(Mg_{2/3}Sb_{1/3})O₃ (x=0, 0.08, 0.12, 0.16) (BT-xBMS)陶瓷。系统研究了不同含量的 BMS 对 BT 基陶瓷的微观形貌、结构、介电和铁电性能的影响。结果表明:BT-xBMS 陶瓷为单一的钙钛矿结构。随着 BMS 含量的增加,BT-xBMS 陶瓷呈现出细化的晶粒尺寸,同时从正常铁电体逐渐转变为弛豫型铁电体。此外,BT-xBMS 陶瓷的剩余极化显著降低,有助于获得优异的储能性能。当 x=0.12 时,在 460 kV·cm⁻¹ 的电场下获得最优的可回收储能密度(W_{rec}=3.06 J·cm⁻³)和储能效率(η=94.02%)。结果表明 BT-xBMS 陶瓷在介电电容器领域具有巨大的应用前景。

关键词 无铅压电;储能;铁电体;掺杂改性;BaTiO₃

中图分类号 TQ174.75

文献标志码 A

开放科学(资源服务)标识码(OSID)



Research on Energy Storage Characteristics of BaTiO₃-x Bi(Mg_{2/3}Sb_{1/3})O₃ Ceramics

ZHAN Shenghui, REN Xiang, ZHANG Lihua,
LI Peng, HAO Jigong, LI Wei

(School of Materials Science and Engineering, Laboratory of Sensitive Materials and Devices Shandong
Department of Education, Liaocheng University, Liaocheng 252059, China)

Abstract (1-x)BaTiO₃-x Bi(Mg_{2/3}Sb_{1/3})O₃ (x=0, 0.08, 0.12, 0.16) (BT-xBMS) ceramics were prepared by solid phase method. The effects of BMS content on the microstructure, structure, dielectric and ferroelectric properties of BT-based ceramics were systematically investigated. The results indicate that BT-xBMS ceramics have a single perovskite structure. With the increase of BMS content, the BT-xBMS ceramics exhibit a refined grain size and transform from normal ferroelectrics to relaxor ferroelectrics. In addition, the residual polarization of BT-xBMS ceramics is significantly reduced, which contributes to obtaining excellent energy storage performance. When x=0.12, high recyclable energy storage density (W_{rec}=3.06 J·cm⁻³) and energy storage efficiency (η=94.02%) can be obtained at 460 kV·cm⁻¹, which

收稿日期:2023-10-18

基金项目:国家自然科学基金项目(52102132);山东省自然科学基金项目(ZR2020ME031; ZR2020ME033);聊城大学大学生
创新计划项目(CXCX2023025)资助

通信作者:李伟,男,汉族,博士,教授,电介质储能材料与器件,E-mail:liwei@lccu.edu.cn。

indicates that the BT-xBMS ceramics have great development potential in the field of dielectric capacitors.

Key words lead-free piezoelectric; energy storage; ferroelectric; doping modification; BaTiO₃

0 引言

随着储能电子器件的快速发展,具有高功率密度和快速充放电能力的介电储能陶瓷受到广泛关注^[1]。其中,具有优异储能性能的铅基介电储能陶瓷材料在国防工业、航空航天、微电子技术、医疗设备、家用电器等领域具有广阔的应用^[2,3]。然而,这种材料中铅的毒性与挥发性会造成严重的资源破坏与生态污染等问题。因此,具有绿色高效、高温稳定性、高储能密度的无铅介电储能陶瓷材料的研究与开发迫在眉睫^[4]。BaTiO₃(BT)陶瓷作为典型的铁电体,其优异的铁电特性吸引了国内外众多学者,但较高的剩余极化强度导致了较低的储能密度,使得 BT 陶瓷在储能领域的发展备受限制^[5]。

近年来,许多学者通过掺杂改性的方式诱导铁电体向弛豫铁电体转变,从而获得了一系列具有优异储能性能的 BT 基储能陶瓷。Zhao 等人^[6]通过固相法在 BT 中引入 Bi(Ni_{2/3}Ta_{1/3})O₃ 进行掺杂改性,通过降低场致应变来提高击穿场强,从而获得了较高的储能性能($W_{\text{rec}}=0.55 \text{ J} \cdot \text{cm}^{-3}$, $\eta=87.15\%$)。Zhang 等人^[7]通过固相法在 BT 中引入 Li⁺ 进行掺杂改性,采用 B 位缺陷偶极子工程降低其剩余极化,并提高其介电击穿强度,从而实现了陶瓷储能性能的优化($W_{\text{rec}}=1.11 \text{ J} \cdot \text{cm}^{-3}$, $\eta=60\%$)。Huang 等人^[8]通过固相法在 BT 中引入 Bi(Ni_{1/2}Ti_{1/2})O₃ 进行掺杂改性,使得 0.85BT-0.15BNT 陶瓷在低电场($170 \text{ kV} \cdot \text{cm}^{-1}$)下获得了优异的储能性能($W_{\text{rec}}=1.46 \text{ J} \cdot \text{cm}^{-3}$, $\eta=94.3\%$)。Liu 等人^[9]通过固相法在 BT 中引入 Bi(Mg_{3/4}W_{1/4})O₃ 进行掺杂改性,使陶瓷晶粒得到细化,从而获得了优异的储能性能($W_{\text{rec}}=1.71 \text{ J} \cdot \text{cm}^{-3}$, $\eta=91.97\%$)。因此,可以通过组元掺杂的方式在 BT 中引入第二组元,诱导其由铁电态向弛豫态的转变,从而获得具有优异储能性能的弛豫铁电体^[10-12]。

基于以上所述,本文通过固相法制备了 (1-x)BaTiO₃-xBi(Mg_{2/3}Sb_{1/3})O₃ 陶瓷,系统研究了 BMS 掺杂对 BT 基陶瓷的微观形貌、结构、铁电、介电与储能性能的影响,通过调整显微结构和相结构获得具有优异储能特性的 BT 基介电储能陶瓷,为新型储能材料的开发拓展思路^[13]。

1 实验

1.1 样品制备

采用固相法制备 (1-x)BaTiO₃-xBi(Mg_{2/3}Sb_{1/3})O₃ (BT-xBMS) 陶瓷,以 BaTiO₃ (99.95%)、TiO₂ (99.9%)、Bi₂O₃ (99.9%)、MgO (99.99%) 和 Sb₂O₅ (99.95%) 为原料,根据样品化学计量比进行配料称量,将粉料置于球磨罐中加入无水乙醇,置于行星式球磨机中球磨 20 h。将浆料烘干后压制成片,于 1 050 °C 预烧 4 h。将预烧粉料二次球磨 20 h。将浆料烘干后造粒,在 1.5 MPa 下将粉末压制成直径 10 mm,厚度约 1 mm 的圆片生坯,于 1 180 ~ 1 310 °C 烧结 2 h 得到陶瓷样品。将处理后的样品进行喷金制备电极(直径 2 mm),进行性能测试。

1.2 样品表征

采用 X 射线衍射仪(XRD, SmartLab, Japan)测定陶瓷样品的相组成。采用场发射扫描电子显微镜(FE-SEM, Merlin Compact, Germany)观察陶瓷样品的微观形貌。利用 Nano Measure 软件计算陶瓷样品的晶粒尺寸。采用高低温介电性能测试系统(HCT1821, Tongguo Technology, China)测定陶瓷样品的介电性能。采用铁电分析仪(TF Analyzer 3000, Germany)测定陶瓷样品的铁电性能。采用高压充放电测量仪(CFD-003 plus, Tongguo Technology, China)测定陶瓷样品的充放电性能。

2 结果与讨论

2.1 陶瓷的物相结构

图 1 是 BT- x BMS 陶瓷的室温 XRD 图谱。BT- x BMS 陶瓷为单一的钙钛矿结构,没有检测到其他物相,这表明 BMS 完全扩散到钙钛矿结构的主体晶格中,形成了稳定的固溶体^[14]。当 $x=0$ 时,在 45° 附近观察到分裂峰(002)和(200),这表明 BT 陶瓷的晶体结构主要由四方相组成^[15]。随着 BMS 含量的增加,(002)和(200)衍射峰合并为单峰(200),这表明此时的晶体结构由四方相转变为了具有弛豫特性的伪立方相。

此外,(200)衍射峰略微向低角度偏移,说明随着 BMS 含量的增加晶面间距增大,晶胞体积增大。陶瓷样品的晶胞参数如表 1 所示。可以观察到,当 $x=0$ 时陶瓷的晶胞体积为 $6.440\ 6\times10^{-2}\text{ nm}^3$,当 $x=0.16$ 时陶瓷的晶胞体积增大到 $6.476\ 6\times10^{-2}\text{ nm}^3$ 。这主要是由于 A 位和 B 位离子的取代,如 Ba^{2+} ($r=0.161\text{ nm}$)被 Bi^{3+} ($r=0.136\text{ nm}$)部分取代, Ti^{4+} ($r=0.060\ 5\text{ nm}$)被 Mg^{2+} ($r=0.072\text{ nm}$)与 Sb^{5+} ($r=0.060\text{ nm}$)部分取代,而结果表明晶面间距增大的主要因素是 B 位的取代^[16]。

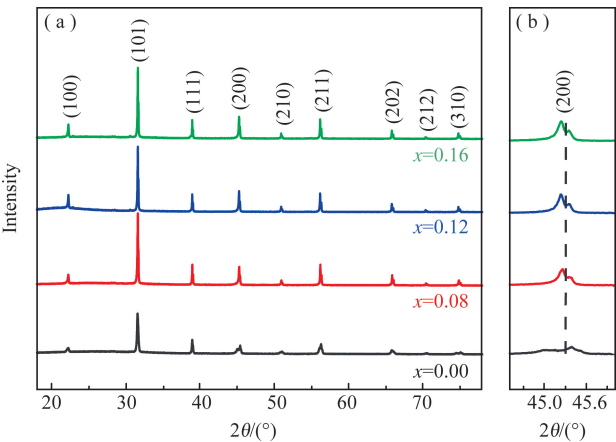


图 1 BT- x BMS 陶瓷的 XRD 图谱:(a) $2\theta=20^\circ\sim70^\circ$, (b) $2\theta=45^\circ\sim45.6^\circ$

Fig. 1 XRD patterns of BT- x BMS ceramics: (a) $2\theta=20^\circ\sim70^\circ$, (b) $2\theta=45^\circ\sim45.6^\circ$

表 1 BT- x BMS 陶瓷的晶胞参数

Table 1 Cell parameters for BT- x BMS ceramics

Samples	a/nm	b/nm	c/nm	$\alpha=\beta=\gamma/(\text{^\circ})$	Cell volume/ nm^3
BT	0.399 7	0.399 7	0.403 1	90	$6.440\ 6\times10^{-2}$
0.92BT-0.08BMS	0.400 7	0.400 7	0.401 7	90	$6.448\ 1\times10^{-2}$
0.88BT-0.12BMS	0.401 2	0.401 2	0.401 2	90	$6.457\ 3\times10^{-2}$
0.84BT-0.16BMs	0.401 6	0.401 6	0.401 6	90	$6.476\ 6\times10^{-2}$

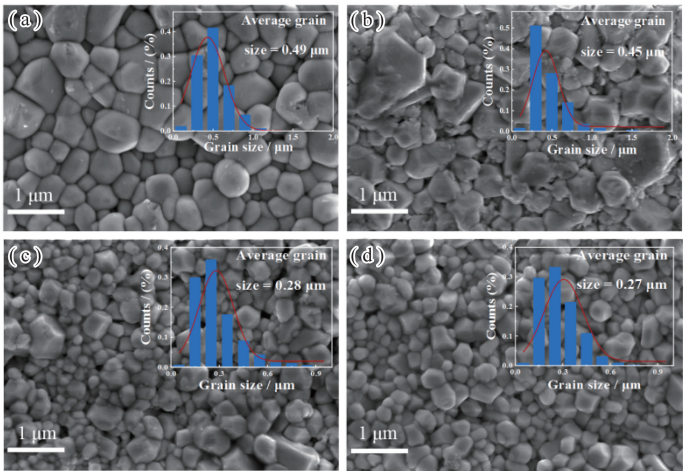


图 2 BT- x BMS 陶瓷的表面微观形貌和晶粒尺寸分布图:(a) $x=0$; (b) $x=0.08$; (c) $x=0.12$; (d) $x=0.16$

Fig. 2 Surface microstructures and grain size distributions of BT- x BMS ceramics: (a) $x=0$; (b) $x=0.08$; (c) $x=0.12$; (d) $x=0.16$

2.2 陶瓷的微观形貌

图2为BT-*x*BMS陶瓷的SEM图。可以看到BT-*x*BMS陶瓷具有相对致密的表面微观形貌,并且随着BMS含量的增加晶粒尺寸显著减小。通过Nano Measure软件分析了样品的平均晶粒尺寸(AGS),其结果如图2插图所示。可以看到,在 $x=0$ 时AGS为 $0.49\text{ }\mu\text{m}$,随着BMS含量的增加AGS呈现减小的趋势,在 $x=0.16$ 时AGS达到最小为 $0.27\text{ }\mu\text{m}$,这说明BMS的添加可以有效抑制晶粒的生长。通常陶瓷的晶粒尺寸越小,晶界越多^[17]。在极化的过程中,电子需要获得更多的能量来跨越晶界,而这有助于提高陶瓷的击穿场强,从而提高陶瓷的储能密度^[18,19]。

为进一步研究BT-*x*BMS陶瓷的致密性,采用阿基米德法测定了陶瓷样品的密度和相对密度。图3为BT-*x*BMS陶瓷在烧结后的密度与相对密度随 x 变化的关系。可以观察到,BT-*x*BMS陶瓷样品的相对密度与组分密切相关^[20]。随着BMS含量的增加,BT-*x*BMS陶瓷的相对密度呈现出先增大后减小的趋势,在 $x=0.12$ 时,相对密度达到最佳为97.18%。这一结果表明BMS的添加可以改善BT陶瓷的致密性。此外,在 $x=0.16$ 时,相对密度减小到88.97%,这可能与过量Bi³⁺的挥发导致样品中出现的气孔有关^[21]。

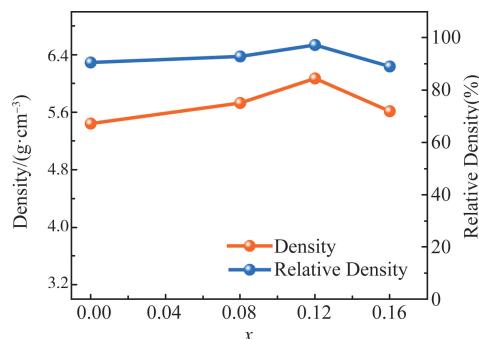


图3 BT-*x*BMS陶瓷的密度和相对密度随 x 变化的关系

Fig. 3 Density and relative density of BT-*x*BMS ceramics as a function of x value

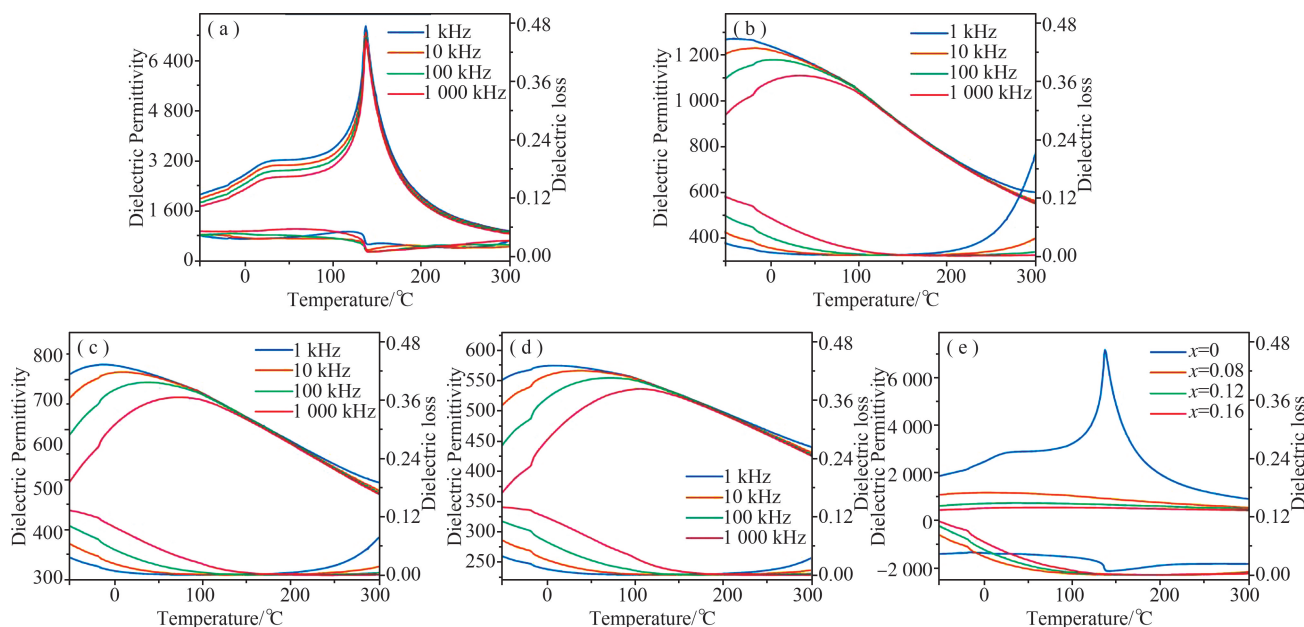


图4 BT-*x*BMS陶瓷的介电常数与介电损耗随温度变化的关系:(a) $x=0$; (b) $x=0.08$; (c) $x=0.12$; (d) $x=0.16$; (e) 100 kHz时BT-*x*BMS陶瓷的介电常数与介电损耗随温度变化

Fig. 4 Temperature-dependent permittivity and loss of BT-*x*BMS ceramics as a function of temperature: (a) $x=0$; (b) $x=0.08$; (c) $x=0.12$; (d) $x=0.16$; (e) temperature-dependent permittivity and loss of BT-*x*BMS ceramics as a function of temperature at 100 kHz

2.3 陶瓷的介电性能

图4给出了在1、10、100、和1 000 kHz条件下测量的BT-*x*BMS陶瓷的介电常数与介电损耗随温度变化的关系。如图4(a)所示,未掺杂BMS的陶瓷样品,分别在20℃和130℃附近观察到介电峰,在130℃附近观察到没有频散现象的尖峰,符合正常铁电体的特征。从图4(a~d)可以看出,随着BMS含量的增加,低温峰开始消失,BT-*x*BMS陶瓷逐渐表现出明显的扩散相变和频率色散行为,这表明陶瓷从典型的铁电体逐

渐转变为弛豫铁电体^[22,23]。而扩散相变的出现可能与弛豫铁电体中的晶格畸变和极性纳米微区(PNRs)有关^[24]。从图 4(e)中可以观察到,随着 BMS 含量的增加,介电常数明显下降。而适中的介电常数和较低的介电损耗能够使 BT-*x*BMS 陶瓷在工作过程中承受较高的电场^[25]。通常采用修正的 Curie-Weiss 定律来描述陶瓷的弛豫行为,计算公式为^[26]

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

式中 ϵ 为温度(T)下的介电常数, T_m 为介电常数最大(ϵ_m)时的温度, C 为居里常数, γ 为弛豫系数。一般而言,当 $\gamma=1$ 时陶瓷为正常铁电体, $\gamma=2$ 时陶瓷为理想的弛豫铁电体^[27]。根据式(1)计算得到的 $\ln(1/\epsilon - 1/\epsilon_m)$ 随 $\ln(T - T_m)$ 变化的关系,如图 5 所示。可以观察到,当 $x=0.08$ 时其弛豫系数最大(1.871 4),这可能是由于 BMS 的掺杂破坏了长程铁电有序,导致 PNRs 的形成,从而提高了弛豫系数^[28]。然而,当 $x \geq 0.12$ 时弛豫系数略有减小。

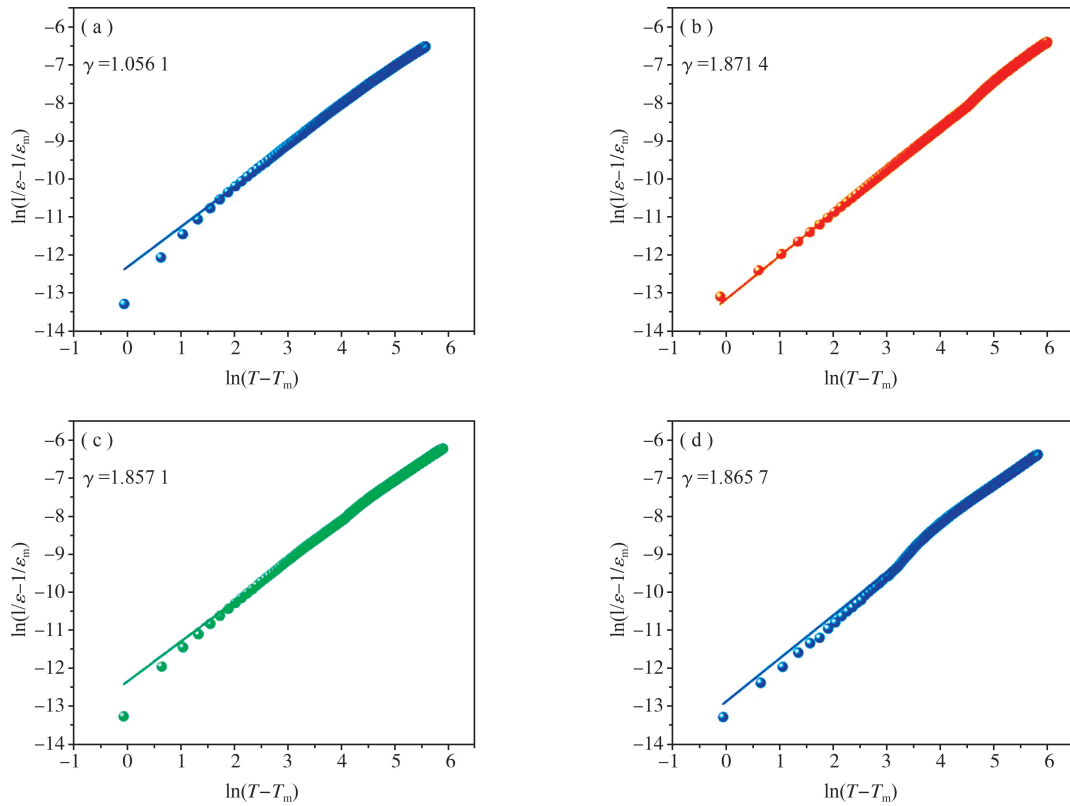


图 5 BT-*x*BMS 陶瓷的 $\ln(1/\epsilon - 1/\epsilon_m)$ 随 $\ln(T - T_m)$ 变化的关系 (a) $x=0$;

(b) $x=0.08$; (c) $x=0.12$; (d) $x=0.16$

Fig. 5 The plots of $\ln(1/\epsilon - 1/\epsilon_m)$ versus $\ln(T - T_m)$ of BT-*x*BMS ceramics

(a) $x=0$; (b) $x=0.08$; (c) $x=0.12$; (d) $x=0.16$

2.4 陶瓷的铁电性能

图 6(a)为 BT-*x*BMS 陶瓷的单极 P - E 曲线。随着 BMS 含量的增加,单极 P - E 曲线从“饱和”铁电转变为“细长”弛豫铁电,这有助于提高 BT 基陶瓷的储能能效^[29]。通过对 P - E 曲线进行数学积分,可以得到与储能特性相关的参数,如可回收储能密度(W_{rec})、总能量密度(W)和转化效率(η),其计算公式为^[30]

$$W = \int_0^{P_{\text{max}}} E dP, \quad (2)$$

$$W_{\text{rec}} = \int_{P_r}^{P_{\text{max}}} E dP, \quad (3)$$

$$\eta = \frac{W_{\text{rec}}}{W} \times 100\%, \quad (4)$$

式中 P_{max} 、 P_r 和 E 分别为最大极化、剩余极化和相应的外加电场。由式(2~4)可知,高 P_{max} 、低 P_r 和大的击穿强度(E_b)是制备具有优异储能性能的 BT 基陶瓷的关键。

图 6(b)为 BT- x BMS 陶瓷的 P_m 、 P_r 、 E 随 x 变化的关系。BMS 的加入使得 BT 陶瓷的 P_{max} 、 P_r 总体减小,这是由于 Mg^{3+} 和 Sb^{5+} 的加入打破了铁电体的长程有序结构,从而提高了陶瓷的弛豫特性^[31]。然而,过量的 BMS 会使 E_b 减小,不利于储能密度的提高。图 6(c)为 BT- x BMS 陶瓷的 W 、 W_{rec} 、 η 随 x 变化的关系。在未掺杂 BMS 的情况下,BT 陶瓷的剩余极化高达 $4.58 \mu\text{C} \cdot \text{cm}^{-2}$,进而导致 W_{rec} 和 η 值较小,分别为 $1.12 \text{ J} \cdot \text{cm}^{-3}$ 和 83.07% 。然而,BMS 的掺杂大幅度地提高了 BT 陶瓷的 W_{rec} 和 η 。当 $x = 0.12$ 时,BT- x BMS 陶瓷获得了最优的储能性能($W_{\text{rec}} = 3.06 \text{ J} \cdot \text{cm}^{-3}$ 和 $\eta = 94.02\%$)。

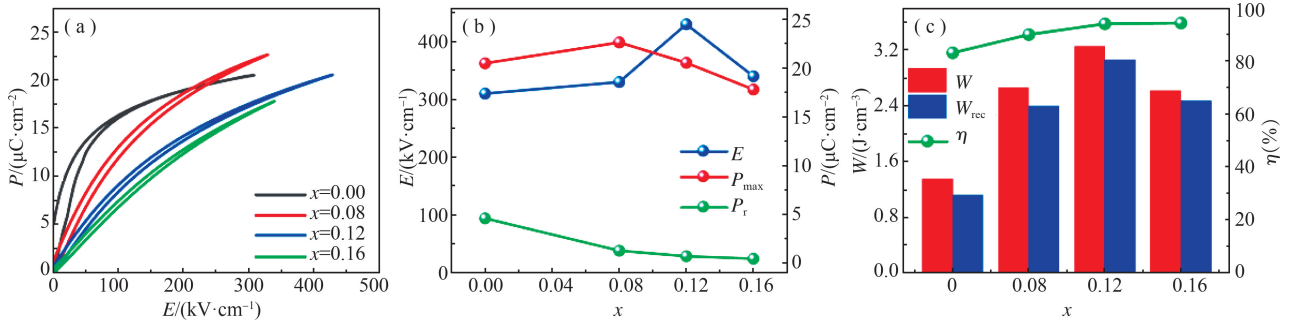


图 6 BT- x BMS 陶瓷的 (a) P - E 曲线; (b) P_{max} 、 P_r 、 E 和 (c) η 、 W 、 W_{rec} 随 x 的变化关系

Fig. 6 (a) The P - E curves and the variation relations of (b) P_{max} , P_r and E and (c) η , W and W_{rec} with x of BT- x BMS ceramics

2.5 陶瓷的充放电性能

为进一步研究 BT- x BMS 陶瓷作为脉冲电力系统储能器件的适用性,测试了室温下 BT- x BMS 陶瓷样品在欠阻尼和过阻尼的条件下的充放电性能,结果如图 7 所示。通常充放电时间越短,越适合脉冲电源^[32]。图 7(a)为不同电场作用下的欠阻尼放电电流曲线。BT- x BMS 陶瓷的电流密度(C_D)和功率密度(P_D)的计算公式为^[33]

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

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

式中 I_{max} 和 S 分别为最大电流和电极面积。根据式(5)和(6)的计算结果如图 7(b)所示,在 $320 \text{ kV} \cdot \text{cm}^{-1}$ 的击穿电场下, I_{max} 、 C_D 和 P_D 可分别达到 28.05 A 、 $892.89 \text{ A} \cdot \text{cm}^{-2}$ 和 $285.72 \text{ MW} \cdot \text{cm}^{-3}$ 。BT- x BMS 陶瓷的放电能量密度(W_D)的计算公式为^[34,35]

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

式中 V 为样品的有效体积, R 为总负载电阻(187Ω)。图 7(c)为不同电场作用下的过阻尼放电电流曲线。根据式(7)计算可得到不同电场下的 W_D ,如图 7(d)所示。可以观察到,随着电场强度的增加, W_D 大幅度增加。当电场为 $340 \text{ kV} \cdot \text{cm}^{-1}$ 时,BT- x BMS 陶瓷的 W_D 可达到 $2.25 \text{ J} \cdot \text{cm}^{-3}$ 。此外,BT- x BMS 陶瓷具有超快的充放电速度,放电时间 $t_{0.9}$ (释放 90% 的 W_D 所需的时间,通常用于评估介电电容器存储装置的放电速度)仅为 62.4 ns 。以上分析表明,BT- x BMS 陶瓷作为未来大功率和脉冲功率储能电容器具有极大的应用潜力。

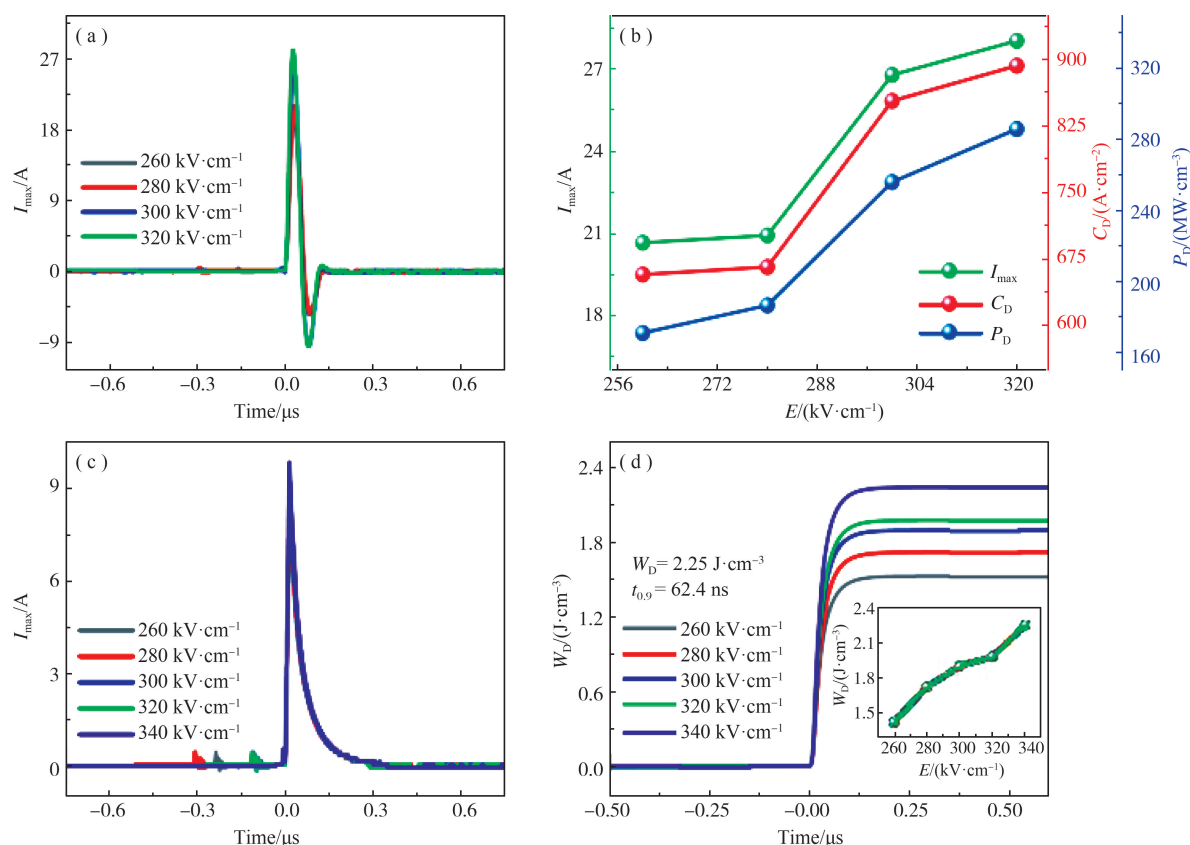


图7 BT-xBMS 陶瓷的(a) 欠阻尼条件下的放电曲线;(b) $I_{\max}$ 、 C_D 和 P_D 随电场的变化曲线;(c) 过阻尼条件下的放电曲线;(d) W_D 随时间的变化曲线,插图对应其 W_D 随电场的变化曲线

Fig. 7 (a) Curve of underdamped discharge; (b) the variation curve of $I_{\max}$, C_D and P_D with E ; (c) curve of over-damped discharge; (d) the variation curve of W_D with time (the inset shows the variation curve of W_D with E) of BT-xBMS ceramics

3 结论

采用固相法制备了 BT-xBMS 无铅弛豫铁电陶瓷。BMS 的掺杂使得 BT-xBMS 陶瓷从四方相转变为伪立方相。同时,平均晶粒尺寸得到细化,从而使得击穿场强增加。随着 BMS 含量的增加,介电常数显著降低,由正常铁电体转变为弛豫铁电体, $P-E$ 曲线逐渐变细,陶瓷的 E_b 从 310 $kV \cdot cm^{-1}$ 增加到 430 $kV \cdot cm^{-1}$ 。在 0.88BT-0.12BMS 陶瓷中获得了最佳的储能特性($W_{rec} = 3.06 J \cdot cm^{-3}$ 和 $\eta = 92.02\%$)。此外,0.88BT-0.12BMS 陶瓷具有极高的电流密度($892.89 A \cdot cm^{-2}$)和功率密度($285.72 MW \cdot cm^{-3}$),以及超快的充放电速度($t_{0.9} = 62.4 ns$)和放电能量密度($W_D = 2.25 J \cdot cm^{-3}$)。结果表明,BT-xBMS 陶瓷同时实现了较高的 W_{rec} 和 η 以及优异的充放电性能,对 BT 基陶瓷在储能领域的应用起到了积极推动作用。

参 考 文 献

- [1] LI D X, ZENG X J, LI Z P, et al. Progress and perspectives in dielectric energy storage ceramics[J]. Journal of Advanced Ceramics, 2021, 10(4): 675-703.
- [2] WANG J. High-performance dielectric ceramic for energy storage capacitors[J]. Coatings, 2022, 12(7): 889.
- [3] SHI X H, LI K, SHEN Z Y, et al. $BS_{0.5}BNT$ -based relaxor ferroelectric ceramic/glass-ceramic composites for energy storage[J]. Journal of Advanced Ceramics, 2023, 12(4): 695-710.
- [4] ADEDIJI Y B, ADEYINKA A M, YAHYA D I, et al. A review of energy storage applications of lead-free $BaTiO_3$ -based dielectric ce-

- ramic capacitors[J]. *Energy, Ecology and Environment*, 2023, 8: 401-419.
- [5] DAI Z H, XIE J L, LIU W G, et al. Effective strategy to achieve excellent energy storage properties in lead-free BaTiO₃-based bulk ceramics[J]. *ACS Applied Materials & Interfaces*, 2020, 12(27): 30289-30296.
- [6] ZHAO H Y, YANG X M, PANG D F, et al. Enhanced energy storage efficiency by modulating field-induced strain in BaTiO₃-Bi(Ni_{2/3}Ta_{1/3})O₃ lead-free ceramics[J]. *Ceramics International*, 2021, 47(16): 22734-22740.
- [7] ZHANG Y, LI G A, ZHANG R, et al. Optimization of energy storage properties in lead-free barium titanate-based ceramics via B-site defect dipole engineering[J]. *ACS Sustainable Chemistry & Engineering*, 2022, 10(9): 2930-2937.
- [8] HUANG X C, LI S, WANG C C, et al. Structural, dielectric, and ferroelectric properties of BaTiO₃-Bi(Ni_{1/2}Ti_{1/2})O₃ lead-free ceramics with remarkable energy storage performance under low electric fields[J]. *Journal of Materials Science: Materials in Electronics*, 2022, 33: 10042-10056.
- [9] LIU Q, FENG H P, LI T Y, et al. BaTiO₃-Bi(Mg_{3/4}W_{1/4})O₃ lead-free relaxor ferroelectric ceramics with improved energy storage properties[J]. *Journal of Materials Science: Materials in Electronics*, 2023, 34: 1569-1579.
- [10] 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 Communications*, 2023, 362: 115100.
- [11] JAN A, LIU H X, HAO H, et al. Lead-free relaxor-ferroelectric ceramics for high-energy-storage applications[J]. *Journal of Materials Chemistry C*, 2020, 8: 8962-8970.
- [12] XIA X Y, SUN X Y, WANG J, et al. Improved strain and low hysteresis in (0.9-x)BaTiO₃-xCaTiO₃-0.1Ba(Zr_{0.7}Sn_{0.3})O₃ lead-free relaxor ferroelectrics[J]. *Ceramics International*, 2020, 46(15): 24231-24237.
- [13] YANG X M, ZHOU F P, WANG C X, et al. High energy storage density and ultrafast discharge in lead lutetium niobate based ceramics[J]. *Journal of Materials Chemistry A*, 2019, 7: 8414-8422.
- [14] REHMAN M U, MANAN A, KHAN M A, et al. Improved energy storage performance of Bi(Mg_{0.5}Ti_{0.5})O₃ modified Ba_{0.55}Sr_{0.45}TiO₃ lead-free ceramics for pulsed power capacitors[J]. *Journal of the European Ceramic Society*, 2023, 43(6): 2426-2441.
- [15] LIU Z G, LI M D, TANG Z H, et al. Enhanced excellent energy storage density and efficiency in lead-free Bi(Mg_{1/2}Hf_{1/2})O₃ modified BaTiO₃ ceramics[J]. *Chemical Engineering Journal*, 2021, 418(15): 129379.
- [16] ZHU W, SHEN Z Y, DENG W, et al. A review: (Bi, Na)TiO₃(BNT)-based energy storage ceramics[J]. *Journal of Materials*, 2023, DOI: 10.1016/j.jmat.2023.05.002.
- [17] YAN G W, LIU Q Q, FANG B J, et al. Correlation between phase structure and polarization of Mg doped (Ba_{0.98}Li_{0.02})TiO₃ energy storage ceramics[J]. *Journal of Materials Science: Materials in Electronics*, 2022, 33: 20981-20991.
- [18] YAN K, CHEN X L, WANG F F, et al. Large piezoelectricity and high transparency in fine-grained BaTiO₃ ceramics[J]. *Applied Physics Letters*, 2020, 116(8): 082902.
- [19] DONG X Y, LI X, CHEN X L, et al. Simultaneous enhancement of polarization and breakdown strength in lead-free BaTiO₃-based ceramics[J]. *Chemical Engineering Journal*, 2021, 409: 128231.
- [20] WANG D, LI L X, DU M K. Ultra-low dielectric loss lithium-based, temperature stable microwave dielectric ceramics[J]. *Ceramics International*, 2022, 48(1): 1394-1401.
- [21] CHENG S, ZHANG B P, WANG L J, et al. Enhanced piezoelectric and ferroelectric properties of tetragonal BiFeO₃-BaTiO₃ ceramics via tailoring sintering temperature and dwell time[J]. *Journal of Materials Science: Materials in Electronics*, 2021, 32: 24496-24506.
- [22] REN J J, ZHOU D, LI W B, et al. Improved energy storage density performance of the (1-x)[0.88BaTiO₃-0.12Bi(Li_{0.5}Nb_{0.5})O₃]-x(0.8BaTiO₃-0.2SrTiO₃) lead-free ceramics[J]. *Materials Research Bulletin*, 2023, 161: 112157.
- [23] SI F, TANG B, FANG Z X, et al. Enhanced energy storage and fast charge-discharge properties of (1-x)BaTiO₃-xBi(Ni_{1/2}Sn_{1/2})O₃ relaxor ferroelectric ceramics[J]. *Ceramics International*, 2019, 45(14): 17580-17590.
- [24] LI T Y, CHEN P F, LI F, et al. Energy storage performance of Na_{0.5}Bi_{0.5}TiO₃-SrTiO₃ lead-free relaxors modified by AgNb_{0.85}Ta_{0.15}O₃ [J]. *Chemical Engineering Journal*, 2021, 406: 127151.
- [25] LUO L C, LI J L, WANG M W, et al. High dielectric permittivity and ultralow dielectric loss in Nb-doped SrTiO₃ ceramics[J]. *Ceramics International*, 2022, 48(19): 28438-28443.
- [26] ZENG D F, NONG P, XU M Z, et al. Relaxor ferroelectric ceramics with excellent energy storage density obtained from BT-based ceramics[J]. *Journal of Power Sources*, 2023, 580: 233454.

- [57] STERGIOU A D, SYMES M D. High yield and selective electrocatalytic reduction of nitroarenes to anilines using redox mediators[J]. *Cell Reports Physical Science*, 2022, 3(7): 100914.
- [58] ZHEN N, DONG J, LIN Z G, et al. $\{V_6\}$ ring sandwiched polyoxoniobate as molecular electrocatalyst for oxidant-free synthesis of sulfoxides[J]. *Chemistry-A European Journal*, 2023, 29(23): e202203903.
- [59] LIU G, CHEN Y F, CHEN Y L, et al. Indirect electrocatalysis S-N/S-S bond construction by robust polyoxometalate based foams[J]. *Advanced Materials*, 2023, 35(40): 2304716.
- [60] YANG H Z, YANG D R, ZHOU Y, et al. Polyoxometalate interlayered zinc-metallophthalocyanine molecular layer sandwich as photo-coupled electrocatalytic CO_2 reduction catalyst[J]. *Journal of the American Chemical Society*, 2021, 143(34): 13721-13730.
- [61] PENG M T, CHEN C, ZHANG Y, et al. Exploring the role of sandwich-type polyoxometalates in $\{K_{10}(PW_9O_{34})_2M_4(H_2O)_2\}@PCN-222$ ($M=Mn, Ni, Zn$) for electroreduction of CO_2 to CO[J]. *Dalton Transactions*, 2023, 52: 10737-10743.
- [62] SUN W C, YAO D, TAI Y H, et al. Efficient electrocatalytic CO_2 reduction to ethanol through the proton coupled electron transfer process of $PV_nMo_{(12-n)}$ ($n=1, 2, 3$) over indium electrode[J]. *Journal of Colloid and Interface Science*, 2023, 650: 121-131.
- [63] WANG M, ZHONG W, ZHANG S S, et al. An overall water-splitting polyoxometalate catalyst for the electromicrobial conversion of CO_2 in neutral water[J]. *Journal of Materials Chemistry A*, 2018, 6: 9915-9921.

(责任编辑:蒲锡鹏)

(上接第 77 页)

- [27] YIN M, BAI G J, LI P, et al. Achieving ultrahigh energy storage properties with superior stability in novel $(Ba_{(1-x)}Bi_x)(Ti_{(1-x)}Zn_{0.5x}Sn_{0.5x})O_3$ relaxor ferroelectric ceramics via chemical modification[J]. *Chemical Engineering Journal*, 2023, 460: 141724.
- [28] CHEN F K, ZHAO K, JIANG X T, et al. Improved dielectric energy storage performance of $Na_{0.5}Bi_{0.5}TiO_3$ -based lead-free relaxation ferroelectric ceramics achieved by domain structural regulation and enhanced densification[J]. *Ceramics International*, 49(19): 31152-31162.
- [29] LIU Z G, TANG Z H, HU S C, et al. Excellent energy storage density and efficiency in lead-free Sm-doped $BaTiO_3$ - $Bi(Mg_{0.5}Ti_{0.5})O_3$ ceramics[J]. *Journal of Materials Chemistry C*, 2020, 8: 13405-13414.
- [30] TANG X Y, HU Z M, KOVAL V, et al. Energy storage properties of samarium-doped bismuth sodium titanate-based lead-free ceramics[J]. *Chemical Engineering Journal*, 2023, 473: 145363-145476.
- [31] SHI J, DONG R Z, HE J Y, et al. Regulating ferroelectric polarization and dielectric properties of BT-based lead-free ceramics[J]. *Journal of Alloys and Compounds*, 2023, 933(5): 167746-167754.
- [32] YAN Y, ZENG X Y, TANG M Y, et al. Enhancement in energy storage performance of La-modified bismuth-ferrite-based relaxor ferroelectric ceramics by defect compensation and process optimization[J]. *Ceramics International*, 2022, 48(22): 33553-33562.
- [33] GE P Z, LIU Z G, HUANG X X, et al. Excellent energy storage properties realized in novel $BaTiO_3$ -based lead-free ceramics by regulating relaxation behavior[J]. *Journal of Materiomics*, 2023, 9(5): 910-919.
- [34] WAN Y H, HOU N J, REN P R, et al. High temperature energy storage properties of $Bi_{0.5}Na_{0.5}TiO_3$ based ceramics modified by $NaNbO_3$ [J]. *Journal of Alloys and Compounds*, 2021, 888: 161591.
- [35] WANG C Y, LIANG C, CAO W J, et al. Boosting energy-storage efficiency and thermal stability via defect dipoles in $BaTiO_3$ -based lead-free ceramics[J]. *Ceramics International*, 2023, 49(9): 13330-13338.

(责任编辑:蒲锡鹏)