

Sr_{0.7}Bi_{0.2}TiO₃ 改性 Bi_{0.5}Na_{0.5}TiO₃ 基薄膜电储能特性的优化

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摘 要: 无铅(Bi_{0.5}Na_{0.5})TiO₃ (BNT)基弛豫铁电薄膜以其高 Curie 温度和大极化在介质储能中受到广泛关注, 然而较低的击穿电场限制了它们的应用。选择 Sr_{0.7}Bi_{0.2}TiO₃ (SBT)作为固溶组元, 通过组分调控提高薄膜击穿强度, 优化储能性能。结果表明: BNT-xSBT 薄膜均为单一钙钛矿结构, 没有明显的第二相。随 SBT 含量增加, 晶胞参数先增大后降低, 介电常数略微下降, 介电损耗保持稳定, 击穿强度先上升后降低。最终, 在最优组分样品 BNT-0.40SBT 中获得了 3 622.25 kV/cm 的高击穿强度和 85.99 J/cm³ 的高储能密度。这种优异的能量存储密度和出色的稳定性, 表明样品 BNT-0.40SBT 是脉冲功率和电力电子应用电容器的有前途的候选者。

关键词: 电介质电容器; 薄膜; 击穿强度; 储能性能

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为满足当前对于能源(尤其是电能)的迫切需求, 开发新材料或新技术进行能量的存储与转换变得尤为重要^[1-2]。电介质电容器, 相比于锂电池或燃料电池, 具有高功率密度、快速充放电能力、长循环寿命以及良好热稳定性等优势, 因而在固体脉冲功率器件领域存在广泛应用前景^[3-4]。但是, 高工作电压和低能量密度问题限制其在电子器件小型化、轻量化以及集成化方面的发展。

对于电介质材料来说, 其总能量储存密度(W_{tot})、可恢复储能密度(W_{rec})、能量转换效率(η)可通过极化-电场(P - E)曲线积分计算, 如式(1)~式(3)所示^[5-6]:

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

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

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

其中: P_{max} , P_r 为电介质材料在外电场 E 下的最

大极化强度与剩余极化强度。电介质材料可容忍最大外电场为其击穿电场 E_b 。可见, 电介质材料实现高能量密度的关键在于高 P_{max} , 低 P_r 以及高 E_b ^[7]。根据电介质材料在外电场不同极化行为, 其大致可以分为线性电介质、铁电体、弛豫铁电体和反铁电体^[8-9], 其中, 弛豫铁电体材料具有较大的介电常数和饱和极化, 表现出具有低 P_r 的纤细 P - E 曲线, 在储能领域受到了越来越多的关注。相较于块体陶瓷材料, 弛豫铁电体薄膜材料因其具有高 E_b 而受到广泛的关注, 但高电场将使得薄膜的能量效率明显下降, 因此如何优化薄膜材料的使用电场与极化强度来提升储能密度变得十分重要^[9-10]。

钛酸铋钠[(Bi_{0.5}Na_{0.5})TiO₃, BNT]是典型的弛豫铁电体材料, 具有高 Curie 温度和大极化强度而受到广泛关注, 但较低的 E_b 限制了其在介电储能领域的潜在应用^[11-12]。Zhang 等^[12-13]引入化学价态稳定的钛酸锶 SrTiO₃(STO)来减少 A 位 Bi/Na 的挥发, 减低薄膜氧空位等缺陷浓度和漏电流密度, 从而在

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3 134.3 kV/cm 电场下获得 W_{rec} 为 33.58 J/cm^3 。然而, STO 室温为顺电体, 它的引入将使得 BNT 基薄膜在相同电场下的极化强度下降, 因而能量密度的提升有限^[13-14]。相比之下, $\text{Sr}_{0.7}\text{Bi}_{0.2}\text{TiO}_3$ (SBT) 具有较高的介电常数, 这主要源于 Bi^{3+} 供体取代 Sr^{2+} 引起的局部电荷不平衡, 导致极性纳米区 (PNRs) 的偶极波动, 因此 SBT 的引入将增强 BNT 基薄膜的化学无序和结构畸变, 在改善薄膜 E_b 的基础上能够保持较高的极化强度^[15-16]。Qiao 等^[16-17] 在 $(1-x)\text{BNT}-x\text{SBT}$ 二元固溶体系陶瓷中发现, 随着 SBT 含量的增加, 长程铁电畴被破坏, 偶极子重新定向, 并把这种现象归因于钙钛矿 A 位离子的半径和价态差异, 产生局域电荷不平衡和局域结构畸变并引起了局域电场和局域弹性场, 从而导致击穿强度的增加和储能性能的改善。BNT 陶瓷的 E_b 从 120 kV/cm 提高到 0.6BNT-0.4SBT 的 160 kV/cm, 并获得了 2.20 J/cm^3 的大 W_{rec} 。但是目前尚缺乏 BNT-SBT 薄膜电学性质和储能性质的变化。基于上述原因, 本工作选择 SBT 作为第二组分来优化 BNT 基薄膜的极化行为, 同时对比分析了 SBT 含量对 BNT 基薄膜的相结构、微观结构、介电和储能性能的影响。

1 实验

1.1 样品制备

通过溶胶-凝胶法制备 $(1-x)(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3-x\text{Sr}_{0.7}\text{Bi}_{0.2}\text{TiO}_3$ (BNT- $x\text{SBT}$, $x=0.30, 0.35, 0.40, 0.45$ 和 0.50) 薄膜的前驱体溶液。以钛酸四丁酯 $[\text{C}_{16}\text{H}_{36}\text{O}_4\text{Ti}]$, 99% (质量分数, 国药集团, 下同)、五水硝酸铋 $(\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O})$, 99%、乙酸钠 $(\text{C}_2\text{H}_3\text{O}_2\text{Na})$, 99% 和乙酸锶 $(\text{C}_4\text{H}_6\text{O}_4\text{Sr})$, 99% 为原料, 乙二醇甲醚 $(\text{C}_3\text{H}_8\text{O}_2)$, 99.5% 和冰乙酸 $(\text{C}_2\text{H}_4\text{O}_2)$, 99.5% 为溶剂, 乙酰丙酮 $(\text{C}_5\text{H}_8\text{O}_2)$, 99.5% 为螯合剂。将原料按照化学计量比称量配制 100 mL 浓度为 0.15 mol/L 的前驱体溶液。为了进一步提高薄膜的储能性能, 添加 2% (摩尔分数) 的四水乙酸锰 $(\text{MnC}_4\text{H}_6\text{O}_4 \cdot 4\text{H}_2\text{O})$, 99%。将配制好的前驱体溶液在干燥环境下避光静置老化 24 h, 使溶液中化学反应充分进行后备用。

使用旋涂法在 Pt(111)/Ti/SiO₂/Si(100) 衬底上制备 BNT- $x\text{SBT}$ 薄膜, 先以 600 r/min 速率旋涂 10 s, 后以 4 500 r/min 速率旋涂 30 s。然后在加热板上进行干燥 (250 °C, 5 min) 和热处理 (450 °C, 5 min)。最后在 630 °C 快速退火 2 min, 重复此过程 8 次获得一定厚度的薄膜。采用磁控溅射法在样品表面沉积直

径为 0.2 mm 的铂电极, 用于电性能测量。

1.2 样品表征

利用荷兰 PANalytical X 'Pert PRO 型 X 射线衍射仪 (XRD) 分析薄膜的晶体结构。用德国蔡司 Ultra Plus 型扫描电子显微镜 (SEM) 观察样品表面和横截面的显微形貌。使用美国 Keithley 6517A 型静电/高阻计获得薄膜的漏电流密度。选用美国 PolyK CPE1801 型铁电工作站测试样品的铁电性能。采用美国 Agilent 4294A 型精密阻抗分析仪研究样品的介电性能。

2 结果与讨论

2.1 物相分析

图 1 为 BNT- $x\text{SBT}$ 薄膜的 XRD 谱。由图 1 可见, BNT- $x\text{SBT}$ 薄膜均为单一的赝立方相结构, 特征衍射峰没有明显的分裂, 同时没有发现明显的第二相。当 SBT 含量从 0.30 逐渐增加至 0.40 时, 特征衍射峰 (110) 向低角度偏移, 晶胞体积增大, 这可以归因于 Sr^{2+} (1.44 Å) 半径大于 Na^+ (1.39 Å) 和 Bi^{3+} (1.38 Å), Sr^{2+} 占据钙钛矿 A 位导致晶胞体积的增大^[18-19]。然而, 随着 SBT 含量进一步增加, (110) 峰转而向高角度偏移, 晶胞体积减小。这是由于 A 位空位的增多破坏局部对称, 产生局部电荷失配导致晶格畸变增强, 使得其它位置的元素向 A 位空位处的位移趋势增加, 进而导致晶胞的坍塌^[20]。晶胞尺寸受 A 位 Sr^{2+} 和空位的共同作用, 因此不是单向变化。

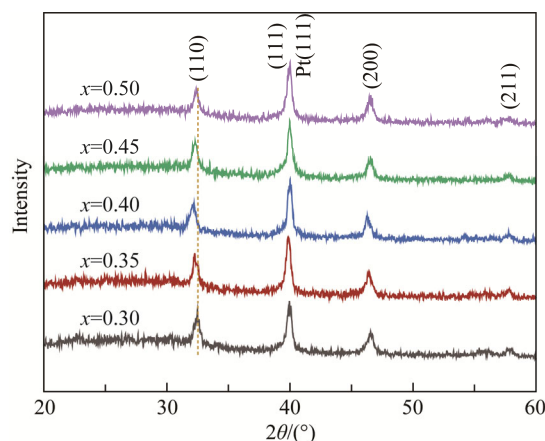


图 1 BNT- $x\text{SBT}$ 薄膜的 XRD 谱

Fig. 1 XRD patterns of $(1-x)(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3-x\text{Sr}_{0.7}\text{Bi}_{0.2}\text{TiO}_3$ (BNT- $x\text{SBT}$) thin films

2.2 显微结构分析

图 2 为 BNT- $x\text{SBT}$ 薄膜的表面 SEM 照片。所有样品表面均没有明显裂纹, 表面平整光滑, 晶界清晰, 晶粒尺寸在 20~40 nm, 较小的晶粒尺寸有

助于薄膜获得更高的击穿强度(BDS)^[20–21]。随 SBT 含量增加, 薄膜表面孔洞减少, 样品致密度增加, 说明添加 SBT 改善了 BNT 薄膜的烧结特性。此外,

样品 BNT–0.40SBT 的断面形貌如图 2f 所示。由图 2f 可见, 薄膜与 Pt 底电极的界面清晰, 说明薄膜与衬底结合良好, 没有明显的扩散, 薄膜厚度约为 140 nm。

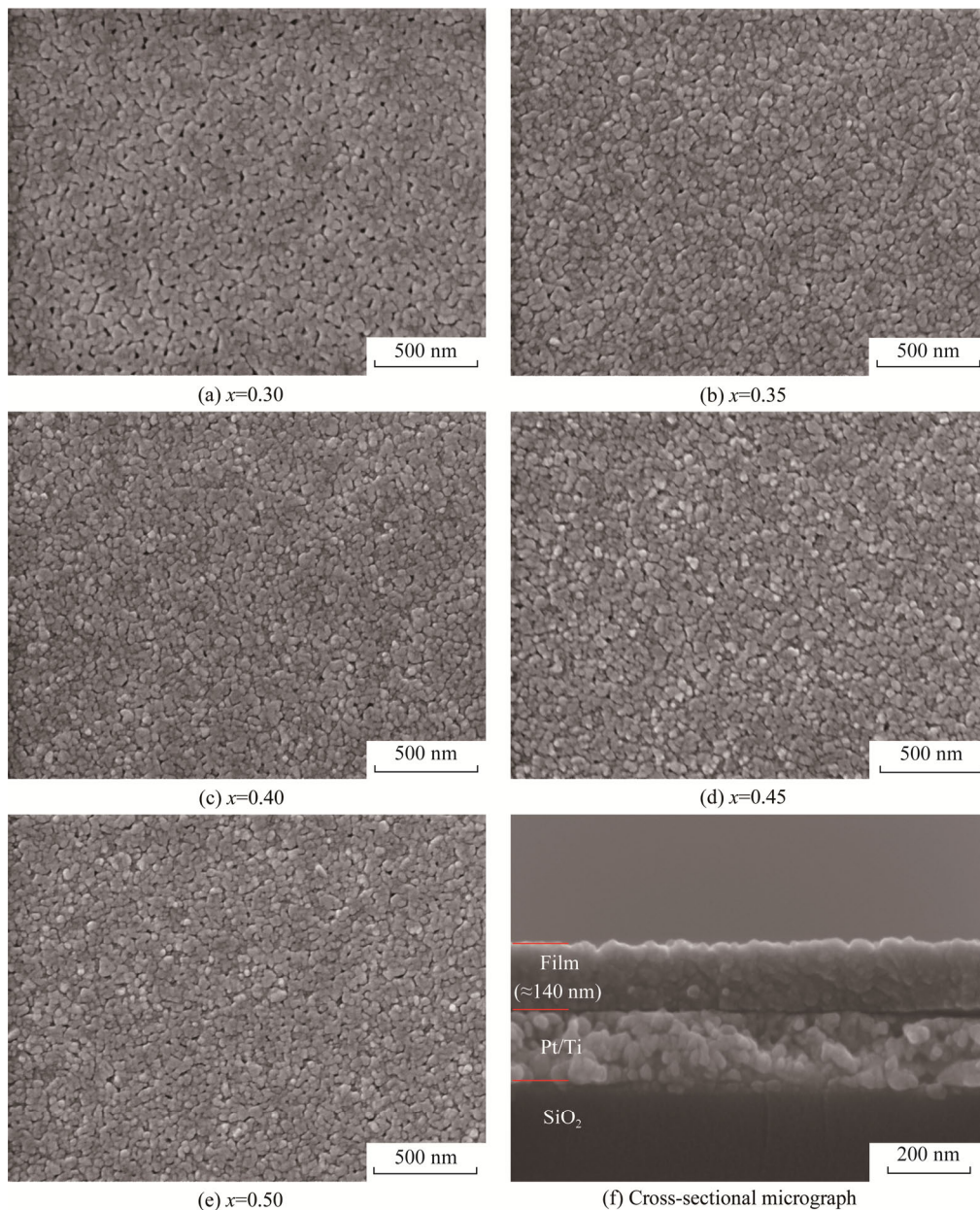


图 2 BNT– x SBT 薄膜的表面形貌和样品 BNT–0.40SBT 的断面形貌

Fig. 2 SEM surface morphology of BNT– x SBT films and cross-sectional micrograph of BNT–0.40SBT sample

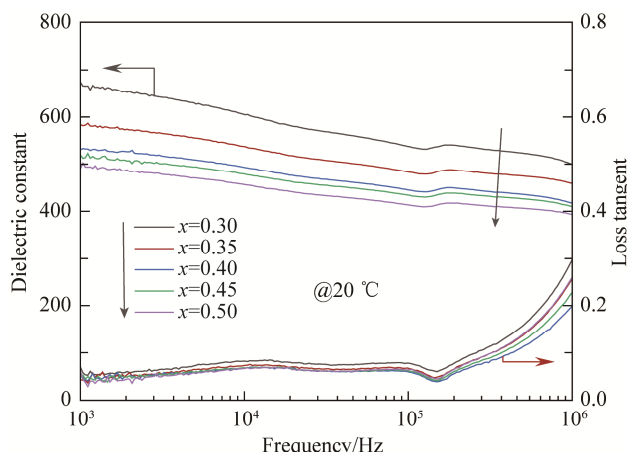
2.3 介电性能分析

图 3a 为室温 BNT– x SBT 薄膜介电性能和介电损耗随频率的变化曲线。随着 SBT 含量的增加, 薄膜的介电常数逐渐降低, 可以归因于 SBT 的介电常数略低于 BNT 基体。而 SBT 含量升高, 介电常数下降速率减缓, 这是因为 A 位 Sr 空位的引入会增强晶格畸变, 导致离子的相对位移增加, 这对介电常数的贡献不可忽视^[22]。同时随着测试频率的增加, BNT– x SBT 薄膜的介电常数降低, 这是由于高

频下电偶极子转向无法跟随电场方向切换及时响应造成的^[23]。但是, 高 SBT 含量样品随电场频率的增加下降更少, 具有更佳频率稳定性, 这可以归因于化学无序的增加和长程铁电有序的降低^[24]。在 $10^3 \sim 10^5$ Hz 频率范围内, 所有薄膜的介电损耗值接近, 均在 0.1 以下。随着 SBT 的引入, 长程铁电有序的降低导致介电损耗的降低。

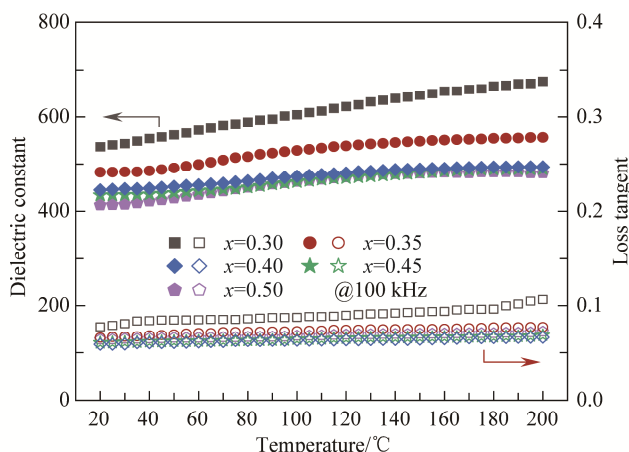
在 20~200 °C 的测试范围内, BNT– x SBT 薄膜介电常数和介电损耗的变化情况如图 3b 所示。随着温

度的上升, 所有薄膜样品的介电常数和介电损耗均增加, 这归因于高温下空位和离子的热运动加剧^[25]。



(a) Dielectric properties with frequency

BNT-0.40SBT 薄膜的介电常数相对比较稳定, 说明引入适量的 SBT 有利于提高薄膜的温度稳定性。



(b) Dielectric property with temperature

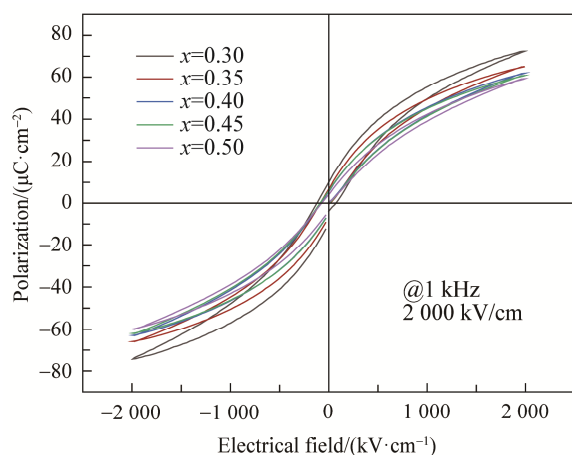
图 3 BNT- x SBT 薄膜的介电性能随频率和温度的变化关系

Fig. 3 Dielectric properties of the BNT- x SBT thin films as a function with frequency and temperature

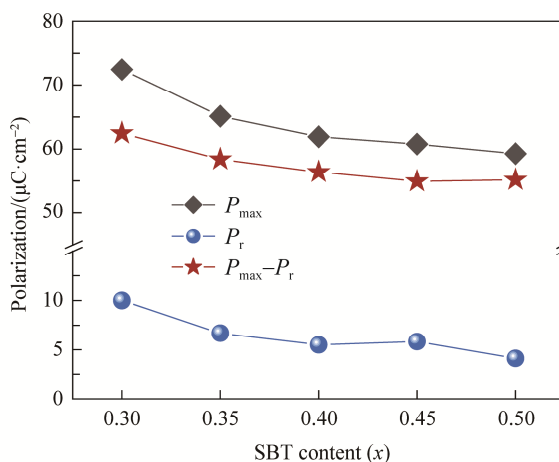
2.4 储能性能分析

图 4a 为 BNT- x SBT 薄膜在 2 000 kV/cm 电场强度下的 P - E 曲线。结果表明, 所有样品的 P - E 曲线均呈现纤细的形状, 具有明显的弛豫铁电特征。纤细的 P - E 曲线得益于薄膜钙钛矿结构中 A 位多元素占据带来的高化学无序性^[26]。同时, 由于离子取代而产生的电荷不平衡形成了弱耦合的极性结构, 从而诱导弛豫铁电态转变^[27]。随着 SBT 含量的增加,

薄膜的 $P_{\max}$ 从样品 BNT-0.30SBT 的 $72.45 \mu\text{C}/\text{cm}^2$ 降至样品 BNT-0.55SBT 的 $57.83 \mu\text{C}/\text{cm}^2$, 如图 4b 所示。 Sr^{2+} 的最外层电子排布属于惰性气体结构, 不容易在电场作用下被极化, 这与样品的介电性能相一致。相对应的, P_r 也从 $10 \mu\text{C}/\text{cm}^2$ 降至 $3.10 \mu\text{C}/\text{cm}^2$ 。SBT 中 Sr^{2+} 和 A 位空位的引入会导致局部电荷不平衡和失配应变, 有助于短程有序极性基团或 PNRs 的生成^[28]。



(a) P - E loops



(b) Polarization characteristics

图 4 BNT- x SBT 薄膜在 2 000 kV/cm 的 P - E 曲线和极化特性

Fig. 4 Polarization-electric field (P - E) loops and polarization characteristics of BNT- x SBT films at 2 000 kV/cm

BNT- x SBT 薄膜在 0~520 kV/cm 的外加电场范围内的漏电流密度如图 5a 所示。随着电场的增加, 薄膜的漏电流密度略微增加。在测试电场范围内, 薄膜可以维持较低的漏电流密度, 这表明样品具有良好的绝缘特性, 对提高材料的 E_b 和储能密度有利。随着 SBT

含量的增加, 薄膜的漏电流密度先下降后增加。 E_b 是决定介电材料的能量密度和工作电场的关键参数。根据 Weibull 分布统计参数 X_i 和 Y_i 之间线性关系确定了 BNT- x SBT 薄膜的平均 E_b , 如图 5b 所示。

$$X_i = \ln E_i \quad (4)$$

$$Y_i = \ln\{-\ln[1 - i / (n + 1)]\} \quad (5)$$

式中： n 为样品总数； i 为样品按照实际击穿电场从小到大的排序； E_i 为第 i 个样品的击穿电场。不同 SBT 含量样品拟合直线的斜率分别为 11.58, 13.91, 14.87, 15.48, 12.86 和 11.23。通常认为, Weibull 分布拟合线斜率越大, 拟合结果越能反应薄膜实际的 E_b [29]。随着 SBT 含量的增加, 薄膜的 E_b 先增加后降低, 样品 BNT-0.40SBT 获得了最大的 E_b 为 3 622.25 kV/cm, 这说明适量 SBT 的引入可以在很大程度上提高薄膜的 E_b 。但是, 当 SBT 含量进一步增加时, 薄膜的 E_b 反而下降, 这可能是 A 位引入了大量的 Sr^{2+} 空位导致的。 Sr^{2+} 空位等缺陷浓度的增加使薄膜中缺陷能级降低, 进而导致薄膜的漏电流密度增大, E_b 降低 [30]。

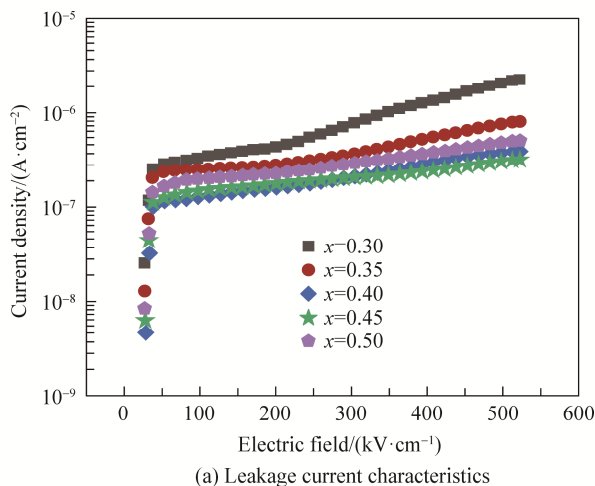


图 6 为室温 BNT- x SBT 薄膜在 E_b 下的 P - E 曲线。所有样品均呈现出瘦长的 P - E 曲线形状, 具有明显的弛豫铁电特征。在 E_b 下, 样品 BNT-0.30SBT 获得了最大的最大极化强度 ($87.51 \mu\text{C}/\text{cm}^2$) 和剩余极化强度 ($11.10 \mu\text{C}/\text{cm}^2$), 这归因于较大的介电常数。BNT- x SBT 薄膜在各自 E_b 下的储能性能如图 6f 所示。随着 SBT 含量的增加, 薄膜的 W_{tot} 和 W_{rec} 先上升后下降, η 相近。由于 $x=0.40$ 薄膜具有高达 3 622.25 kV/cm 的最大 E_b , 所以获得了最高的充放电储能密度 ($W_{\text{tot}}=116.20 \text{ J}/\text{cm}^3$, $W_{\text{rec}}=85.99 \text{ J}/\text{cm}^3$) 和 74% 的 η 。如表 1 所示, 与近 2 年报道的储能薄膜相比, 样品 BNT-0.40SBT 在储能密度和储能效率上显示出一定的优势, 在介电电容器方面具有很大的应用潜力 [25, 31–39]。

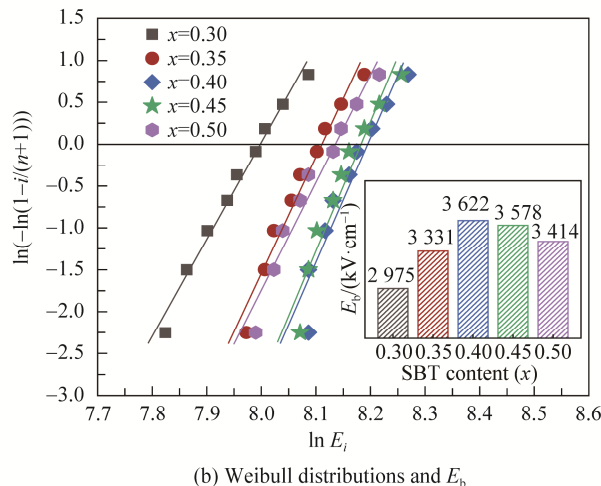


图 5 BNT- x SBT 薄膜的电流特征和 Weibull 分布和 E_b

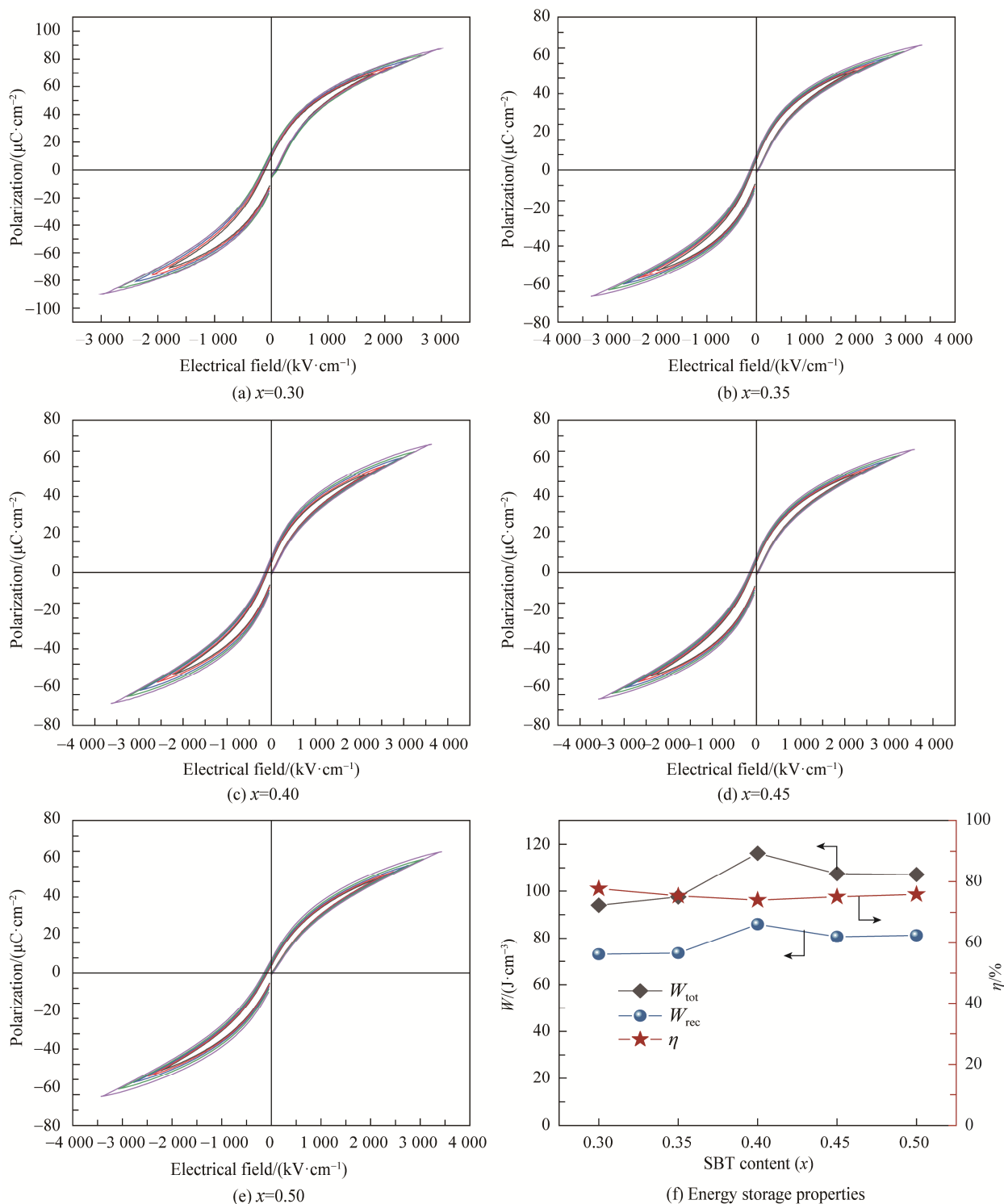
Fig. 5 Leakage current characteristics and Weibull distributions and E_b of BNT- x SBT thin films

表 1 样品 BNT-0.4SBT 与一些代表性介质薄膜的储能性能比较

Table 1 Comparisons of the energy storage performances of the BNT-0.4SBT sample and some reported representative dielectric films

Material	$E_b/(\text{kV}\cdot\text{cm}^{-1})$	$W_{\text{rec}}/(\text{J}\cdot\text{cm}^{-3})$	$\eta/\%$	Reference
BNT-0.4SBT	3 622.25	85.99	74.00	This work
BTO-BiScO ₃	3 600.00	40.50	85.00	[25]
0.94BNT-0.06BTO-6%(in mole) Mn	2 550.00	54.00	59.00	[31]
$\text{Na}_{0.5}\text{Bi}_{0.5}(\text{Fe}_{0.03}\text{Ti}_{0.97})\text{O}_3/\text{Na}_{0.5}\text{Bi}_{0.5}(\text{Zr}_{0.02}\text{Ti}_{0.98})\text{O}_3$	1 730.00	71.70	74.10	[32]
$\text{BaZr}_{0.25}\text{Ti}_{0.75}\text{O}_3$	5 219.00	60.80	68.00	[33]
$\text{AlO}_3/\text{BFO}/\text{AlO}_3/\text{BFO}$	3 775.00	54.20	51.40	[34]
0.7SBT-0.3BFO-2%(in mole) Mn	4 571.00	47.60	65.68	[35]
$\text{Pb}_{0.5}\text{Sr}_{0.5}\text{HfO}_3$	5 100.00	77.00	97.00	[36]
$\text{Pb}_{0.925}\text{La}_{0.05}\text{Zr}_{0.85}\text{Ti}_{0.15}\text{O}_3$	3 294.00	49.70	54.00	[37]
$\text{Bi}_2\text{Zn}_{2/3}\text{Nb}_{4/3}\text{O}_7$	3 782.00	63.47	61.00	[38]
$\text{CaBi}_2\text{Nb}_2\text{O}_9$	3 550.00	69.00	82.40	[39]

BNT: $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$; SBT: $\text{Sr}_{0.7}\text{Bi}_{0.2}\text{TiO}_3$; BFO: BiFeO_3 ; BTO: BaTiO_3 ; E_b is breakdown electric field; W_{rec} is recoverable energy storage density; η is energy conversion efficiency.



W_{tot} is total energy storage density.

图 6 BNT-xSBT 薄膜在 E_b 下的 P - E 曲线和储能性能

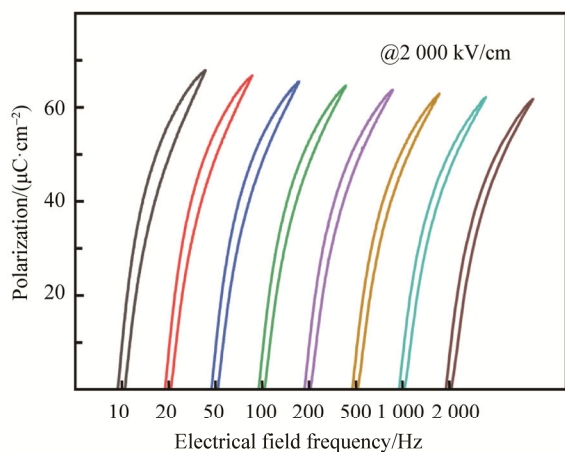
Fig. 6 P - E hysteresis loops and the energy storage properties of BNT-xSBT thin films at respective E_b

对于脉冲功率介质电容器器件的应用, 优异的高频稳定性、耐热性和抗疲劳性也是不可或缺的要求^[40]。图 7a 为 $2000\text{ kV}/\text{cm}$ 下不同频率的样品 BNT-0.40SBT 的单极 P - E 曲线。随着频率从 10 Hz 增加到 2000 Hz , P - E 曲线没有出现明显的变形, P_{max}

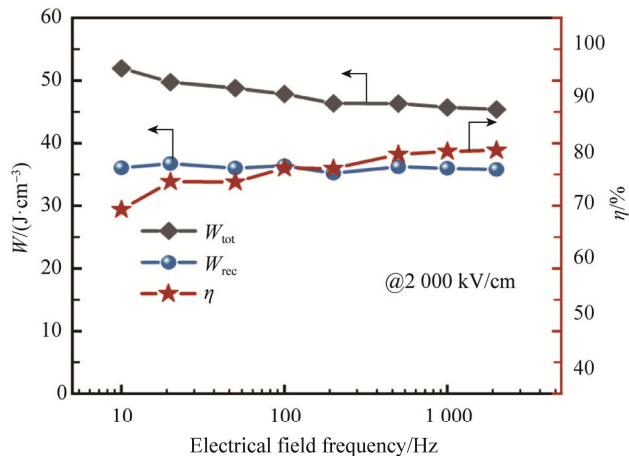
和 W_{tot} 略微降低, W_{rec} 保持稳定, η 逐渐上升(图 7a 和图 7b)。在宽频范围内, 样品 BNT-0.40SBT 储能性能表现出良好的频率稳定性。图 7c 为样品 BNT-0.40SBT 在 $20\sim 200\text{ }^{\circ}\text{C}$ 的 P - E 曲线。随着测试温度的升高, P_{max} 和 P_r 均呈现上升趋势, P_{max} 变化

率小于 2.5%，而 P_r 从 5.18 上升至 9.14，说明其极化行为受温度影响波动较小。薄膜的 W_{tot} 上升， W_{rec} 下降，但变化幅度均小于 10%。在 200 °C 的高温下，样品 BNT-0.40SBT 的 η 仍高于 70%，这意味着薄膜可以在较宽的温度范围内正常工作(图 7d)。图 7e

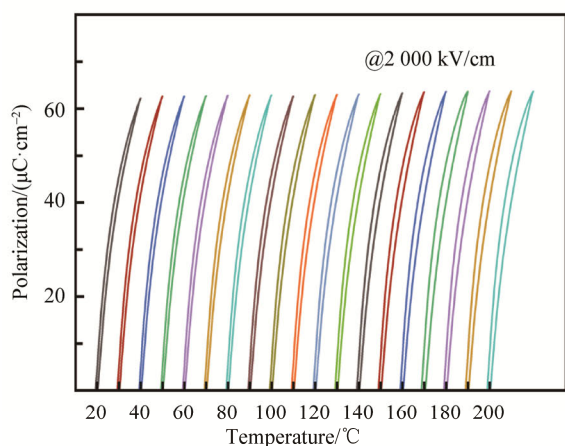
和图 7f 为样品 BNT-0.40SBT 在室温的疲劳特性。在 10^5 次循环下，薄膜的 $P-E$ 曲线和储能密度基本没有变化，保持了稳定的储能性能。因此，样品 BNT-0.40SBT 在频率、温度和疲劳方面实现了良好的稳定性，满足了先进脉冲功率器件的要求。



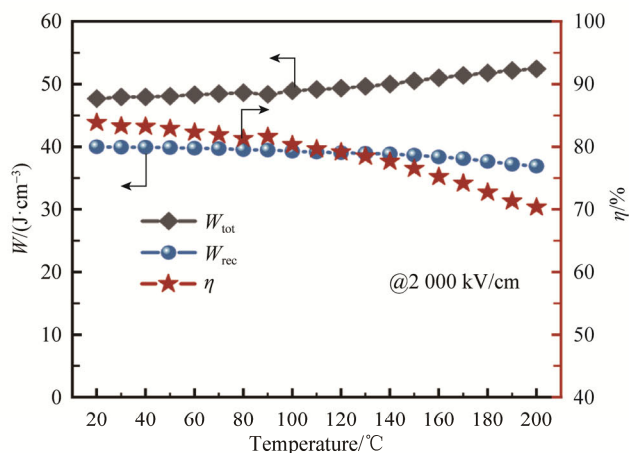
(a) $P-E$ loops with frequency



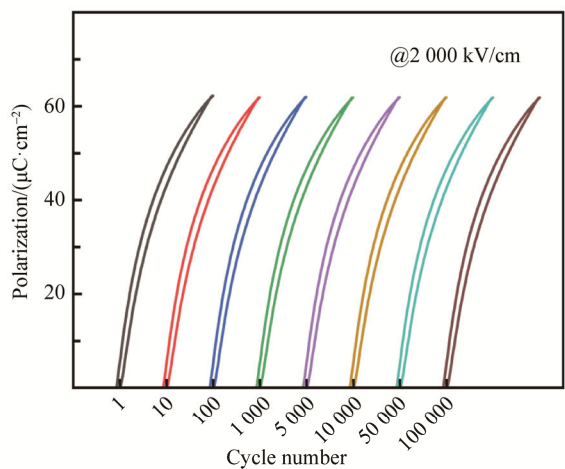
(b) Energy storage properties with frequency



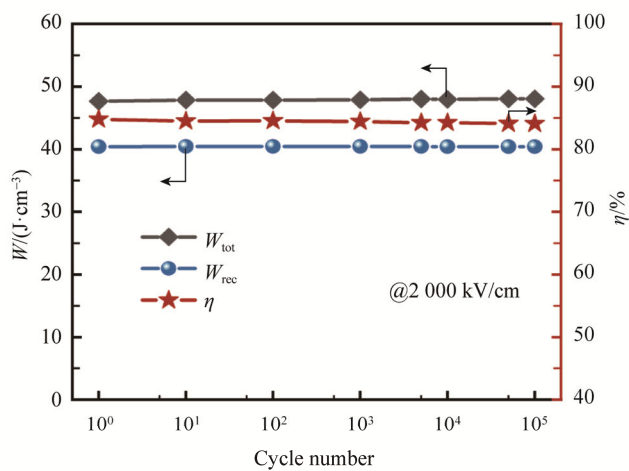
(c) $P-E$ loops with temperature



(d) Energy storage properties with temperature



(e) $P-E$ loops with cycle



(f) Energy storage properties with cycle

图 7 样品 BNT-0.40SBT 在 2000 kV/cm 下的单极 $P-E$ 曲线和储能特性与外加电场频率，工作温度和循环次数的关系

Fig. 7 Unipolar $P-E$ hysteresis loops and the energy storage performances as a function of applied electric field frequency, operating temperature, and number of cycles of BNT-0.40SBT thin film at 2000 kV/cm

3 结论

采用溶胶-凝胶法制备了 $(1-x)(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3-x\text{Sr}_{0.7}\text{Bi}_{0.2}\text{TiO}_3$ (BNT- x SBT, $x=0.30, 0.35, 0.40, 0.45$ 和 0.50) 二元固溶体薄膜, 探究了不同固溶比例对 BNT 基薄膜结构、介电及储能性能的影响。随着 SBT 含量的增加, 晶胞尺寸先增大后降低, 介电常数逐渐降低, 介电损耗维持在较低水平。适量 SBT 的引入可以有效提高 BNT 基薄膜的 BDS 和储能性能, 样品 BNT-0.40SBT 获得了最佳的综合储能性能: 在 $3\ 622.25\ \text{kV/cm}$ 的大击穿电场 E_b 下获得了 $85.99\ \text{J/cm}^3$ 的放电储能密度 W_{rec} 和 74% 的储能效率 η , 并具有良好的温度、频率和疲劳稳定性, 是高储能密度脉冲功率电容器的候选材料。

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Optimization of Electric Energy Storage Performance of $\text{Sr}_{0.7}\text{Bi}_{0.2}\text{TiO}_3$ Modified $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ -Based Films

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Extended Abstract

Introduction The environmentally friendly dielectric capacitors based on lead-free relaxation ferroelectrics have attracted recent attention. The material $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ (BNT) exhibits an intrinsic high saturation polarization due to the hybridization between Bi 6s and O 2p orbitals, surpassing conventional lead-free relaxor ferroelectrics. However, a low breakdown strength (BDS) of BNT results in a relatively poor energy storage performance, restricting its further applications. Therefore, improving the BDS of BNT-based materials is a necessity towards achieving a high energy storage density, and one effective measure is a compositional modification. $\text{Sr}_{0.7}\text{Bi}_{0.2}\text{TiO}_3$ (SBT) as an emerging relaxor ferroelectric material has a higher dielectric constant due to the ion substitution-induced local charge imbalance and dipole fluctuations in nanoscale. It is anticipated that introducing SBT as a solid solution component into BNT matrix films can enhance the BDS of the films, optimizing their energy storage performance. In this paper, the impact of SBT/BNT solid solution ratio on phase structure, microstructure, dielectric, and energy storage properties of the SBT modified BNT-based film was investigated.

Methods The precursor solutions for $(1-x)(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ – $x\text{Sr}_{0.7}\text{Bi}_{0.2}\text{TiO}_3$ (BNT– x SBT, $x=0.30, 0.35, 0.40, 0.45$, and 0.50) were prepared by a sol–gel method. The precursor solutions prepared were aged via static aging for 24 h before spin-coating. Subsequently, the films were heat-treated on a hot plate and rapidly annealed at $630\text{ }^\circ\text{C}$ for 2 min. The film preparation process, including spin-coating, heat treatment, and rapid annealing, was repeated for 8 times to complete the film fabrication.

The crystal structure of the films was analyzed by a model PANalytical X'Pert PRO X-ray diffractometer (XRD). The surface and cross-sectional morphologies of the samples were determined a model Ultra Plus scanning electron microscope (SEM). To evaluate the electrical properties of the samples, platinum electrodes with a diameter of 0.2 mm were deposited on the film surface using magnetron sputtering. The leakage current density of the films was obtained by a model 6517A electrostatic/high-resistance meter. The ferroelectric properties of the samples were tested by a model PolyK CPE1801 ferroelectric workstation. The dielectric properties of the samples were analyzed by a model 4294A precision impedance analyzer.

Results and discussion All the BNT– x SBT films exhibit a single pseudocubic phase structure. The unit cell volume initially increases and then decreases as the SBT content increases, which is affected by a combined effect of Sr^{2+} doping at the A-site and vacancies. The films demonstrate a well-crystallinity, clear grain boundaries, good adhesion to the substrate, and a thickness of

approximately 140 nm. The introduction of SBT results in a reduction in the dielectric constant of the film, improving the temperature stability of the dielectrics. At 2 000 kV/cm, the maximum polarization ($P_{\max}$) and remnant polarization (P_r) of the films both decrease as the SBT content increases, which is consistent with the dielectric performance. The incorporation of an appropriate amount of SBT increases the BDS of the films from 2 975 kV/cm for BNT-0.3SBT to 3 622 kV/cm for BNT-0.40SBT, which is consistent with the leakage current density. Therefore, the optimal composition BNT-0.40SBT film achieves a high recoverable energy storage density (W_{rec}) of 85.99 J/cm³ and an efficiency of 74% at the breakdown electric field (E_b). This film demonstrates some advantages, compared to other film capacitors. In addition, the BNT-0.40SBT film exhibits a superior high-frequency stability, a heat resistance, and a fatigue resistance, showing a promising potential for applications in dielectric capacitors.

Conclusions All the films exhibited a well-crystallinity, having a single perovskite phase. With the introduction of SBT, the unit cell volume initially increased and then decreased, and the BDS firstly increased and then decreased. The dielectric constant and polarization intensity gradually decreased, while dielectric loss remained stable. The optimal component BNT-0.40SBT film achieved a high BDS of 3 622.25 kV/cm and a high energy storage density (W_{rec}) of 85.99 J/cm³. The superior energy storage density and stability indicated that BNT-0.40SBT thin films could be promising candidates for pulse power and power electronics applications in capacitors.

Keywords dielectric capacitor; thin films; breakdown strength; energy storage properties

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