

电介质储能陶瓷薄膜研究进展及改性方法

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摘 要: 电介质陶瓷薄膜材料制备的储能电容器, 具有充放电速率快、功率密度大以及良好的温度稳定性和循环稳定性等优势, 在脉冲激光武器、心脏起搏器等军事、民用领域具有广阔的应用前景。然而, 电介质电容器的储能密度相对较低, 限制了其应用范围, 因此如何提高其储能密度成为当前研究的重点之一。此外, 电介质储能陶瓷薄膜材料种类繁多、制备工艺复杂, 因此选择合适的材料体系和制备工艺至关重要。本文总结了电介质储能陶瓷薄膜材料的研究进展, 重点讨论了 6 种类型的材料, 包括线性电介质、顺电材料、铁电材料、弛豫铁电材料、超顺电材料和反铁电材料。此外, 进一步总结了目前常用的提升电介质储能陶瓷薄膜材料储能性能的方法。期望本文的研究成果能够对开发新一代高性能电介质储能陶瓷薄膜提供有价值的参考。

关键词: 陶瓷薄膜; 电介质; 电容器; 储能性能

中图分类号: TM534 文献标志码: A 文章编号: 0454-5648(2024)04-1413-25

网络出版时间: 2024-03-09



近年来, 随着社会的快速发展, 能源消耗呈不断上升趋势, 对于清洁能源的合理使用的呼声也愈加高涨。合理使用清洁能源对于人类社会的可持续发展十分重要。然而, 清洁能源在使用过程中受到多方面的限制, 如地区间水资源的差异、风力大小的差异等。因此, 通常需要将清洁能源转换成其他能源形式(如电能), 以便进行存储、运输和使用。这对电能存储设备提出了更高的要求, 因此, 发展可靠、高效、无污染的电能存储设备势在必行。目前, 常用的储能设备有电池、超级电容器和电介质电容器等。在这些设备中, 电介质电容器在电磁弹射炮、医疗器械、运输设备和脉冲激光武器等领域具有广泛的应用。相较于电池和超级电容器, 电介质电容器具有更高的功率密度($10^4 \sim 10^5 \text{ W/kg}$), 并且具有更快的充放电特性($\sim \mu\text{s}$)^[1-6], 在新能源汽车和脉冲设备等领域具备广泛的应用前景。

通常, 电介质电容器由 2 个导电金属层和中间的电介质层构成, 呈平行板状, 如图 1a 所示。电介质电容器存储电荷的能力由电容 C 表示, 为存储在金属板上的电荷 Q 与施加电压 V 的比, 即:

$$C = Q / V \quad (1)$$

C 的大小和介电常数 ϵ_r 、金属板之间的距离 d 以及金属板的面积 A 相关, 如式(2)所示:

$$C = \epsilon_0 \epsilon_r A / d \quad (2)$$

式中: ϵ_0 为真空介电常数($8.854 \times 10^{-12} \text{ F/m}$)。当通过 2 个导电金属层对电介质层施加外加电场时, 电介质内部的偶极子沿着电场方向排列, 在导电金属层上积累出与外电场强度相等但方向相反的电荷, 此时, 电能以静电能的形式存储。当外加电场撤去后, 定向排列的偶极子则恢复到无序状态, 导电金属板上的电荷开始转移, 将存储的静电能输出到外部负载, 即电容器完成了一次充电-放电过程。电介质电容器在充电过程中单位体积内所存储的能量(即总的储能密度) U 可以由式(3)计算得到:

$$U = \int_0^{Q_{\max}} V dq / Ad = \int_0^{D_{\max}} E dD \quad (3)$$

其中: $Q_{\max}$ 为导电金属层间积累的最大电荷量; V 为电压; dq 为充电过程中电荷的增量; D 为电介质材料的电位移大小; E 为施加的外加电场。对于线性电介质而言, 其电位移大小与外加电场成线性关系, 其储能密度可以用式(4)表示:

收稿日期: 2023-09-04。 修订日期: 2023-11-09。

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Received date: 2023-09-04. Revised date: 2023-11-09.

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$$U = 1/2 \varepsilon_0 \varepsilon_r E^2 \quad (4)$$

非线性电介质材料的电位移大小约等于极化值 $P(D \approx P = \varepsilon_0 \varepsilon_r E)$ ，其储能密度可表示为：

$$U = \int_0^{P_{\max}} E dP \quad (5)$$

因此，储能密度可以通过 P - E 电滞回线计算得到，如图 1b 所示，蓝色部分的面积为可释放的储能密度 (U_{rec})，绿色部分的面积为充放电过程中的能量损耗 (U_{loss})，充放电过程中的效率用 η 表示， U_{rec} 、 U_{loss} 和 η 可以分别用式(6)~式(8)表示^[7-11]：

$$U_{\text{rec}} = \int_{P_r}^{P_{\max}} E dP \quad (6)$$

$$U_{\text{loss}} = U - U_{\text{rec}} \quad (7)$$

$$\eta = U_{\text{rec}} / U \times 100\% \quad (8)$$

式中： $P_{\max}$ 为电介质材料在最大外加电场时的极化强度； P_r 为剩余极化强度，即外加电场为 0 时的极化强度； E 为外加电场，薄膜击穿前的最大外加电场即为击穿场强 (E_b)。从式(6)可以发现， $P_{\max}$ 、 P_r 和 E_b 共同决定着 U_{rec} 的大小，因此，增大 $P_{\max}$ 、减小 P_r 以及提高 E_b 对于提高电介质电容器的 U_{rec} 和 η

至关重要。因此，目前对于储能电介质电容器的研究主要集中在提高 $P_{\max}$ 和 E_b 以及降低 P_r 等方面的设计和研究^[12-16]。

目前，常用的电介质材料主要分为 2 大类：聚合物和陶瓷。聚合物基电介质电容器具有更高的 E_b 和更好的柔性，更易于制备柔性器件，符合电子元器件可穿戴化的发展趋势。通常情况下，聚合物基介质材料的介电常数 $\varepsilon_r < 10$ ，这对于储能性能是不利的。例如，商用的双向拉伸聚丙烯薄膜(BOPP)的 ε_r 约为 2.25， U_{rec} 仅为 2~3 J/cm³，这严重限制了聚合物基电介质电容器的应用^[17-18]。此外，相对于陶瓷材料，聚合物基电介质电容器的温度稳定性较差，当温度上升时，聚合物基电介质电容器的漏电流密度会急剧上升，导致 U_{rec} 和 η 急剧下降，难以满足高温环境下的使用需求。例如，当温度从 25 °C 升高到 200 °C 时，纯聚酰亚胺膜(PI)的 U_{rec} 和 η 从 5.2 J/cm³ 和 86.7% 急剧下降到 0.9 J/cm³ 和 16.8%^[19]。因此，目前聚合物基电介质电容器研究重点集中于探索具有高 U_{rec} 和出色高温特性的电介质电容器，并在这

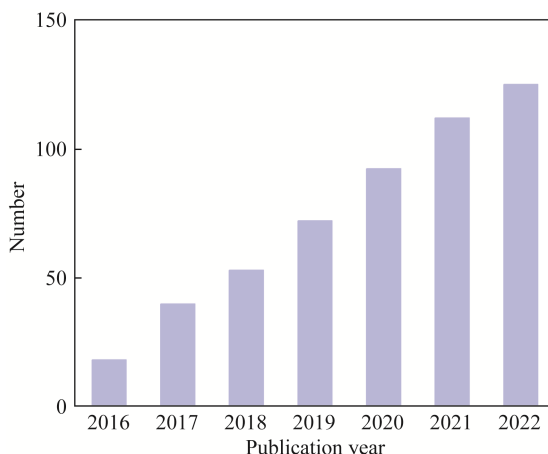
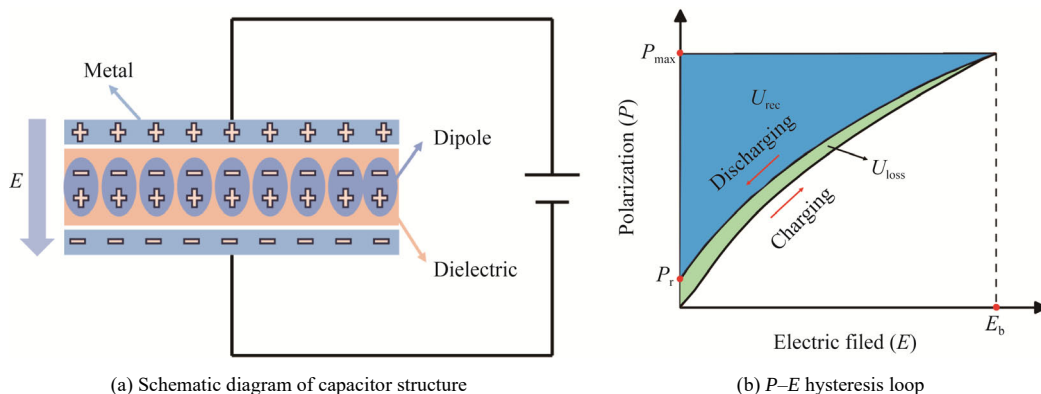


图 1 电介质电容器结构示意图， P - E 电滞回线和储能陶瓷薄膜年度出版物数量

Fig. 1 Dielectric capacitor structure diagram, polarization–electric field (P - E) hysteresis loop and number of annual publications of energy storage ceramic thin films

方面取得了显著进展^[20-25]。如 Fan 等^[26]制备了聚醚酰亚胺(PEI)纳米复合材料, 通过将(Pb,La)(Zr,Sn,Ti)O₃ 反铁电芯和 Al₂O₃ 壳层制备的核壳结构无机颗粒添加到 PEI 中, 显著增强了 PEI 在高温时的储能性能, 其 U_{rec} 在 150 °C 时达到了 10.20 J/cm³, 并且获得了 83.5% 的 η 。

陶瓷基电介质电容器根据其尺寸分为块体陶瓷以及陶瓷薄膜 2 类。与聚合物基电介质电容器相比, 陶瓷基电介质电容器具有更大的 ϵ_r 和 P_{max} , 在较低的电场下能够实现可观的 U_{rec} , 并且可以在较宽的温度范围内稳定工作。此外, 块体陶瓷因较大的体积而具有可观的能量存储容量, 但是其内部通常存在较多的缺陷, 从而降低了 E_b , 进而显著影响了 U_{rec} 。近年来, 研究人员通过改进制备工艺来优化陶瓷材料的致密度、晶粒尺寸和二次相含量, 从而提高材料的 E_b ^[27-37]。此外, 通过制备具有核壳结构的陶瓷电容器, 利用核的高 ϵ_r 和壳的高绝缘性, 有效降低了材料的介电损耗($\tan\delta$), 显著提高了 E_b ^[38-41]。Wang 等^[38]制备了具备核壳结构的 (0.7-x)BiFeO₃-0.3BaTiO₃-xBi(Zn_{2/3}Nb_{1/3})O₃ 陶瓷, 观察到由 BiFeO₃ 核和 BaTiO₃ 壳组成的核-壳微观结构, 显著提高了材料的储能性能。然而, 随着集成电路小型化、集成化和电子设备可穿戴化的发展趋势, 块体陶瓷受自身尺寸和脆性的限制难以满足使用要求。因此, 基于无机陶瓷薄膜制备的电介质电容器的发展受到了广泛关注, 涉及到电介质储能陶瓷薄膜材料的研究论文数量也逐年增加, 如图 1c 所示。陶瓷薄膜材料本身体积较小, 并且内部缺陷较少, 因此其 E_b 相较于块体陶瓷有了显著提高, U_{rec} 也远优于块体陶瓷和聚合物基电介质电容器。此外, 陶瓷薄膜具备可柔性化的条件也符合电子元器件可穿戴化的发展趋势^[42-49]。2018 年, Lee 等^[44]通过在柔性基板超薄金属箔上制备了 La 掺杂的 PbZrO₃ 薄膜电容器, 其 U_{rec} 为 (15.2 ± 0.2) J/cm³, 该

薄膜电容器可以在 2.5 mm 的小曲率半径弯曲, 并且没有对器件及其性能造成损坏, 这是第 1 次文献报道的无机陶瓷薄膜制备的柔性电容器, 也揭开了无机陶瓷薄膜在柔性电子器件领域应用的面纱。Bin 等^[49]在柔性云母衬底上制备了 xMn-BiMg_{0.5}Ti_{0.7}O₃ 陶瓷薄膜, 其 U_{rec} 高达 124 J/cm³, 同时保持了 77% 的 η , 当弯曲半径为 6 mm 时, 并且经历 10⁸ 次循环后, 储能性能的变化可以忽略不计, U_{rec} 从 70.1 J/cm³ 减小到 68.98 J/cm³, η 约 78%。这展示了陶瓷薄膜在柔性储能器件领域良好的应用前景, 为柔性电子产品提供了新的储能选择。

本文总结了近年来基于陶瓷薄膜制备的储能电容器的研究进展, 重点介绍了线性电介质、顺电材料、铁电材料、弛豫铁电材料、超顺电材料以及反铁电材料等不同类型的储能陶瓷薄膜材料。此外, 对现有陶瓷薄膜储能性能的改性方法进行了详细探讨, 文中详细的展示了不同改性方法的机理及改性方法对储能性能的改善, 旨在为储能陶瓷薄膜性能进一步的改善提供有益的借鉴。

1 陶瓷薄膜储能材料研究进展

根据其本征的极化特性, 陶瓷薄膜储能材料可以分为 6 大类: 线性材料(LD)、顺电材料(PE)、铁电材料(FE)、弛豫铁电材料(RFE)、超顺电材料(SPE)和反铁电材料(AFE)^[50-51], 如图 2 所示。

1.1 线性材料

线性电介质材料不存在永久偶极子, 其极化强度随外加电场的升高而线性增加, ϵ_r 为定值, 不受外加电场的影响而变化。常见的线性电介质包括 HfO₂ 和 Al₂O₃^[52-53]。线性电介质通常具有很高的 E_b , 在能量存储与释放过程中几乎没有能量的损耗, 但其 ϵ_r 相对较低, 这制约了 U_{rec} 。因此, 改善线性电介质的储能性能通常需要提高 ϵ_r 。例如, Zhang 等^[52]通过原子层沉积技术(ALD)制备了 HfO₂ 薄膜, 通过

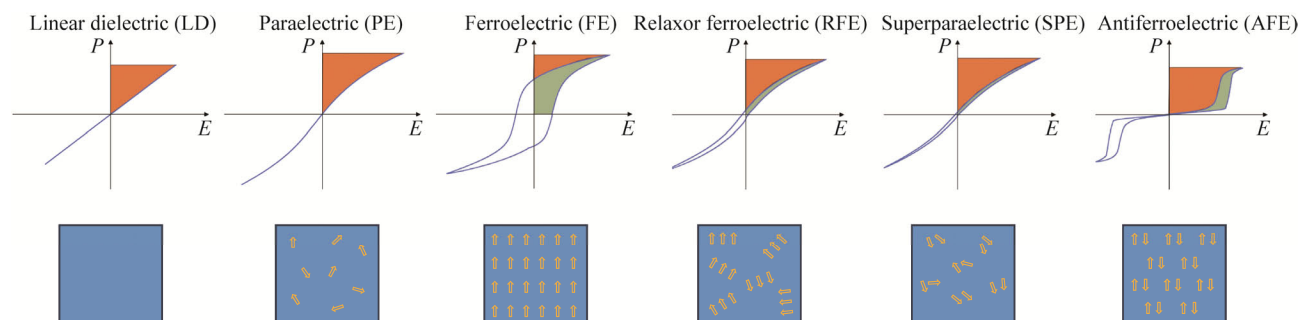
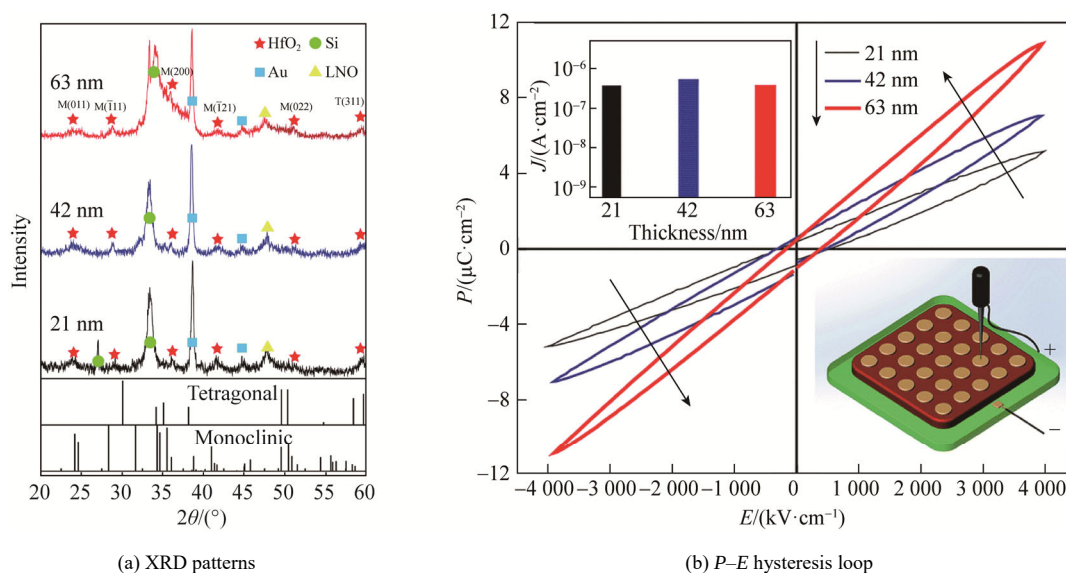


图 2 不同电介质的 P - E 电滞回线和铁电畴

Fig. 2 P - E hysteresis loop and ferroelectric domains of different dielectrics

厚度调节了 HfO_2 薄膜四方相和单斜相混合相结构(如图 3 所示), 进而提高 ε_r , 其 ε_r 达到了 26, 获得了优异的 U_{rec} (21.3 J/cm^3)。Spahr 等^[53]制备了纯 Al_2O_3 薄膜, 通过与大 ε_r 的 ZrO_2 和 TiO_2 进行叠层结构设计, 制备了 $\text{Al}_2\text{O}_3/\text{ZrO}_2$ 和 $\text{Al}_2\text{O}_3/\text{TiO}_2$ 多层薄膜, ε_r 得到提升, 最终在 $\text{Al}_2\text{O}_3/\text{TiO}_2$ 中获得了 60 J/cm^3 的 U_{rec} 。虽然在线性电介质中也获得了不错的 U_{rec} , 但是线性电介质的 ε_r 仍然相对很小, 因此对

于其 ε_r 的进一步提高仍需要更多的研究。此外, 线性介电体较小的 ε_r 也被科研工作者用于储能领域的另一方面。例如, 通过构建 Al_2O_3 和 SrTiO_3 的叠层结构, 利用 Al_2O_3 较高的电阻率来阻止界面处载流子的迁移, 并且 Al_2O_3 的存在使得外加电场更多的分布在 Al_2O_3 层, 从而降低 SrTiO_3 层的电场分布, 提高了薄膜的 E_b , 最终获得了优异的储能性能^[54]。



(a) XRD patterns

(b) P - E hysteresis loop图 3 不同厚度 HfO_2 的 XRD 谱和 P - E 电滞回线^[52]Fig. 3 XRD patterns and P - E hysteresis loop of HfO_2 samples with different thickness^[52]

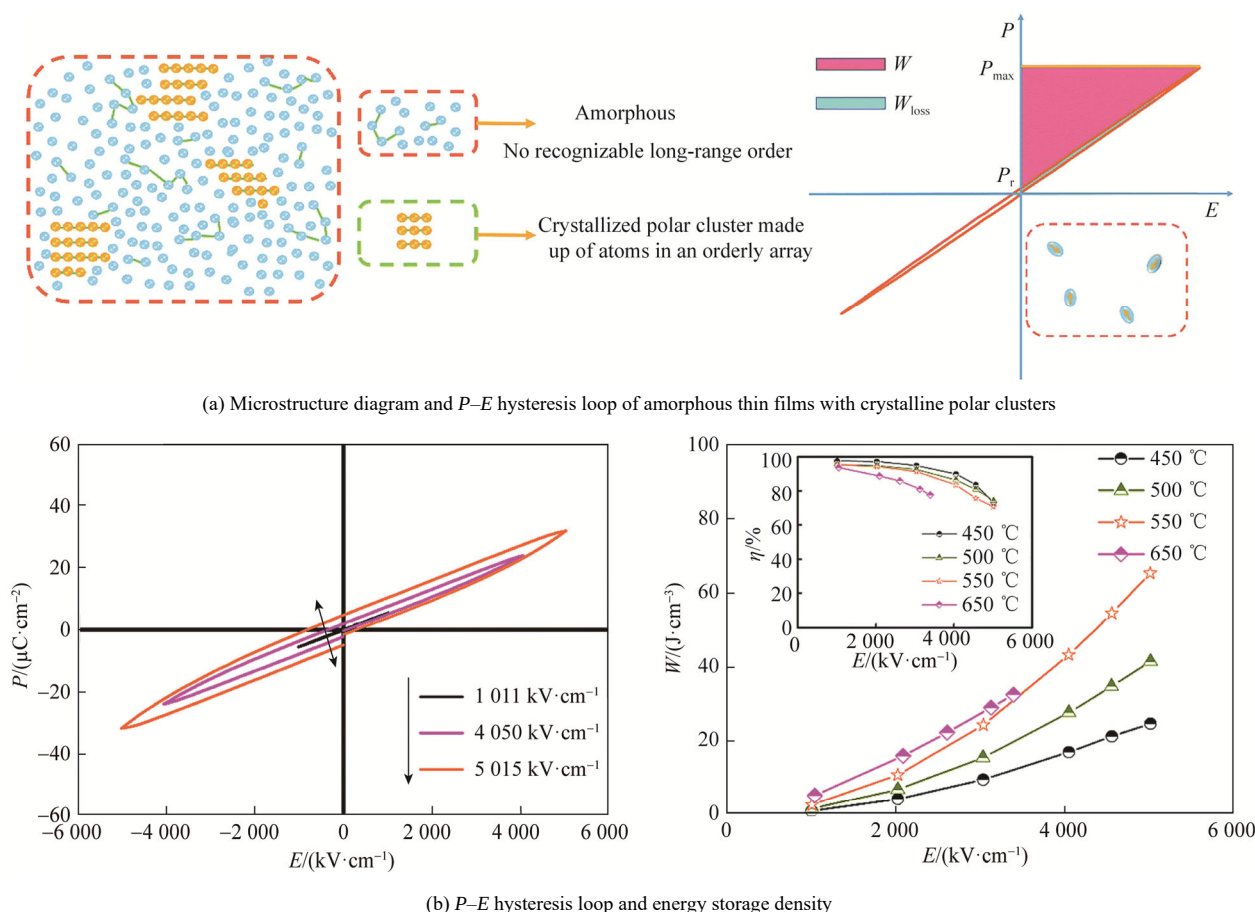
1.2 顺电材料

顺电材料内部存在永久偶极子, 但不具有铁电畴结构, 其电偶极子在外加电场下发生翻转, 导致极化强度和 ε_r 随外加电场呈非线性变化。在外加电场的作用下, 偶极子重新排列, 材料被极化, 当外加电场移除后, 材料仍表现为非极性状态, 不存在自发极化。典型的顺电材料包括 SrTiO_3 、 CaTiO_3 以及 EuTiO_3 等^[55–58]。Liu 等^[55]通过溶胶-凝胶法制备了 SrTiO_3 薄膜, 通过调控退火温度改善介电性能以及储能性能。当退火温度为 650°C 时, 在 SrTiO_3 薄膜中获得了具有顺电特性的 P - E 电滞回线, 并且获得了增强的 ε_r 、 E_b 和 P_{max} 以及低的 $\tan\delta$ 、 P_r 和漏电流密度, 最终在 6.5 MV/cm 的电场下获得了 55 J/cm^3 的 U_{rec} 以及 94.7% 的 η 。有趣的是, 当退火温度达到 750°C 时, 在压缩应变以及增大的晶粒尺寸的作用下, SrTiO_3 展示出了铁电特性, 为顺电材料在储能领域的应用提供了有意思的线索。Diao 等^[57]研究不同退火温度下 1% (摩尔分数) Mn 掺杂的 SrTiO_3 薄膜的储能性能, 其在 550°C 退火的 SrTiO_3 薄膜中获

得了 53.9 J/cm^3 的 U_{rec} 以及 77.2% 的 η , 并且 Mn 掺杂的薄膜在退火温度达到 700°C 时也展现出了典型的铁电性。Zhang 等^[56]通过将 Na 和 Bi 形成的晶体极性簇嵌入到非晶 SrTiO_3 薄膜中, 形成各向异性极性纳米尺度区域, 该区域随电场自由切换, 不受晶体周期结构的约束, 进而导致非晶薄膜中的增强的 P_{max} , 如图 4 所示。同时, 非晶薄膜本身具有良好的绝缘性有利于提高材料的击穿场强, 最终显著提高了材料的储能性能, 实现了 65.3 J/cm^3 的 U_{rec} 以及 70.8% 的 η 。

1.3 铁电材料

铁电材料具有自发极化特性, 其电滞回线通常较胖, 一般情况下, 铁电材料具有较高的 ε_r 和较大的 P_{max} 。但是, 铁电材料的 P_r 以及 $\tan\delta$ 较大, 且存在较多的缺陷, 导致其 E_b 较低。因此传统铁电材料用作储能电容器时其 U_{rec} 和 η 较低, 不太适用于储能应用。这些传统铁电材料包括 BiFeO_3 、 PbTiO_3 以及 BaTiO_3 等^[59–64], 目前主要的研究方向是如何降低铁电材料的 P_r 以及提高其 E_b 。例如, Kim 等^[60]

图 4 非晶薄膜微观结构示意图和储能性能^[56]Fig. 4 Microstructure diagram and energy storage performance of amorphous thin films^[56]

通过向 BaTiO_3 中添加 Sn, 使得 BaTiO_3 中同时存在铁电相和弛豫铁电相, 在降低 P_r 的同时提高了 E_b 。Zhao 等^[61]通过降低磁控溅射过程中衬底的温度来提高导电钙钛矿缓冲层 LaNiO_3 在镀铂硅片上的成核速率, 并降低横向晶粒生长, 获得了(100) LaNiO_3 缓冲层, 该缓冲层促进了 BaTiO_3 薄膜中(001)取向柱状纳米晶粒的生长, 通过调控晶粒大小, 制备了具有大柱状晶粒以及纳米柱状晶粒的 BaTiO_3 薄膜, 通过相场模拟(如图 5 所示)以及实验相互印证, 由超细纳米柱状晶粒构成的薄膜具有超高的 U_{rec} $[(135 \pm 10) \text{ J/cm}^3]$ 和 η (80%±4%)。此外, 通过元素掺杂与组分固溶, 可以将铁电体转变为弛豫铁电体来降低 P_r 并提高 E_b , 从而提高铁电材料的储能性能。

1.4 弛豫铁电材料

弛豫铁电材料和铁电材料一样具有自发极化, 但其畴结构不同, 通常呈现为纳米畴, 对于电场的响应十分灵敏, 这导致了弛豫铁电材料通常具有较小的 P_r 和较大的 P_{max} , 因此在储能性能方面十分优异, 具有广阔的应用前景。目前, 弛豫铁电体的研究主要集中在 PbTiO_3 基、 $(\text{Pb}, \text{La})(\text{Zr}, \text{Ti})\text{O}_3$ 基、 BaTiO_3

基、 BiFeO_3 基以及 $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ 基材料体系^[65-70], 商用电容器中多使用铅基材料制备, 其具有优良的储能性能。Peng 等^[66]通过溶胶凝胶法制备了 $\text{Pb}_{0.97}\text{La}_{0.02}(\text{Zr}_{0.905}\text{Sn}_{0.015}\text{Ti}_{0.08})\text{O}_3$ (PLZST) 弛豫铁电薄膜, 利用低温极化的方式, 在接近液氮温度下进行了极化, 显著提高了室温时的 E_b 以及 U_{rec} , 其 U_{rec} 从 16.6 J/cm^3 提高到了 31.2 J/cm^3 , 这种低温极化为增强材料的 E_b 提供了一种新的策略。然而, 铅基材料中铅的挥发对人体以及环境具有一定的危害, 因此开发无铅材料是势在必行的。Zhang 等^[67]通过在 A 位点采取 Na^+ 和 Bi^{3+} 共取代构成离子对, 诱发局域极化区, 并且通过 B 位点 Mn 掺杂来降低材料的氧空位浓度, 氧空位浓度的降低使得漏电流密度下降, 增强了 E_b , 最终在 A 位掺杂以及 B 位掺杂的共同作用下, 在 $\text{Sr}_{0.99}(\text{Na}_{0.5}\text{Bi}_{0.5})_{0.01}\text{Ti}_{0.99}\text{Mn}_{0.01}\text{O}_3$ 中获得了 53 J/cm^3 的 U_{rec} , 如图 6 所示。

1.5 超顺电材料

超顺电最初是作为磁性材料中的“超顺磁性”的类似物而被提出的^[71-73]。超顺电的铁电体保持局部极性有序, 表现为只有几纳米甚至几个晶胞的极性

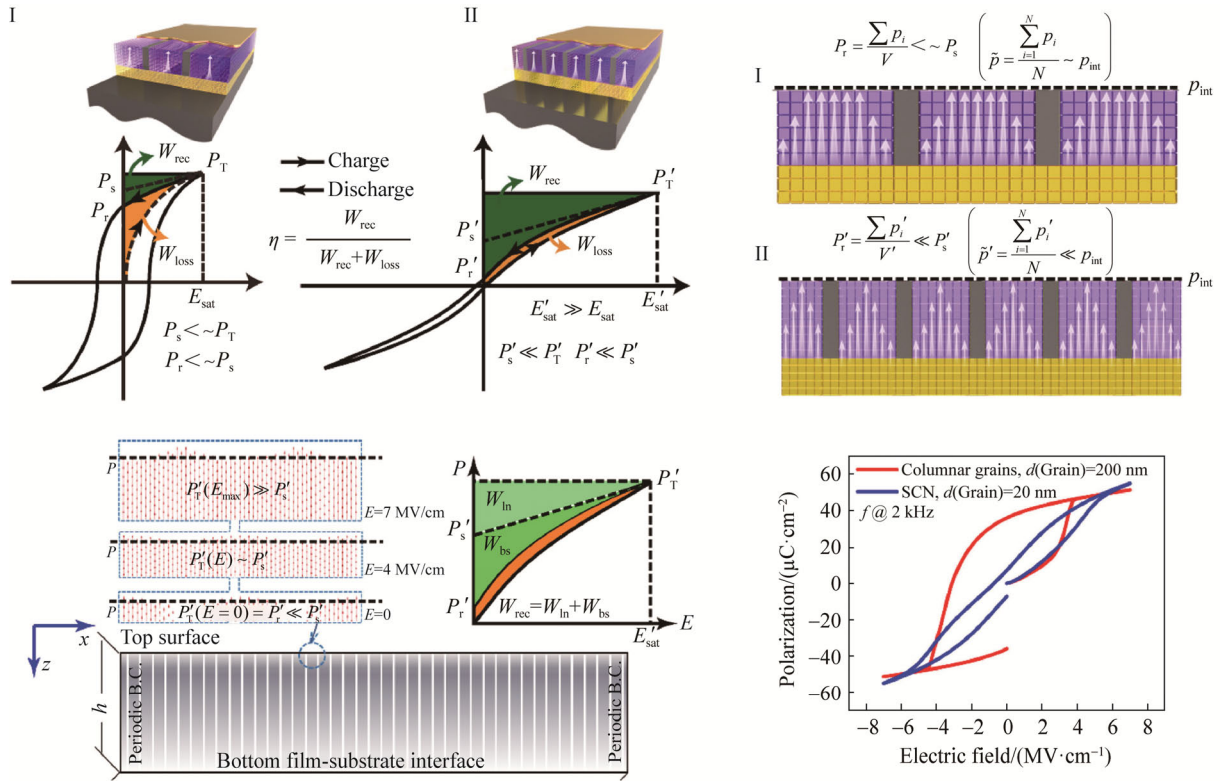


图 5 大晶粒(规则柱状晶粒)和小晶粒(柱状纳米晶粒)铁电薄膜极化特性的示意图和相场模拟^[61]

Fig. 5 Schematics and phase field modeling of the P - E characteristics of large-grained (regular columnar grains) and small-grained (columnar nanograins, SCN) ferroelectric films^[61]

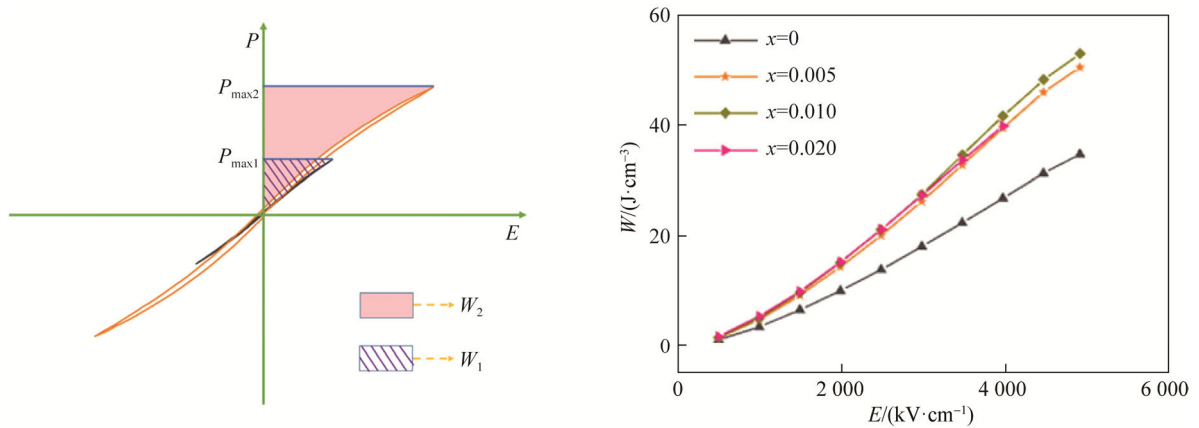


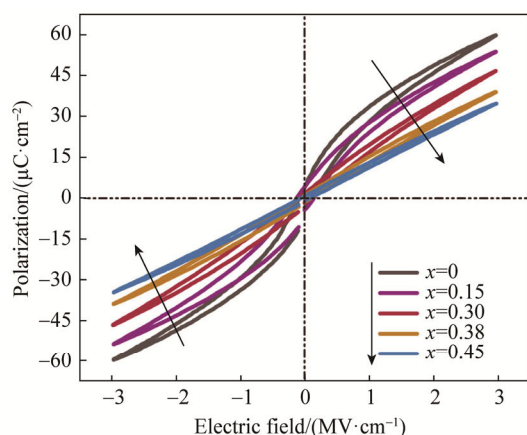
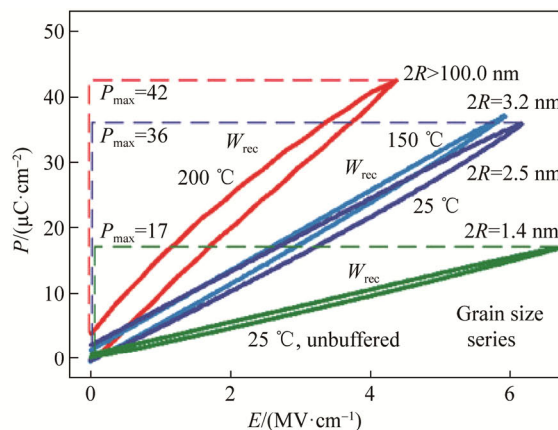
图 6 $\text{Sr}_{0.99}(\text{Na}_{0.5}\text{Bi}_{0.5})_{0.01}\text{Ti}_{0.99}\text{Mn}_{0.01}\text{O}_3$ 薄膜 P - E 电滞回线示意图和储能性能^[67]

Fig. 6 Schematic of P - E hysteresis loops and energy-storage performance of $\text{Sr}_{0.99}(\text{Na}_{0.5}\text{Bi}_{0.5})_{0.01}\text{Ti}_{0.99}\text{Mn}_{0.01}\text{O}_3$ thin films^[67]

簇,这使得畴之间的相互耦合进一步减弱,极性开关能量势垒也随之减小^[74–76]。因此,超顺电中的极性团簇更具有活性,甚至可以通过热扰动来切换,这极大的降低了损耗,显著提高了储能密度和储能效率^[77]。超顺电态出现在长程有序铁电性减弱但未消除的地方,这使得任何使铁电退化的条件都能产生超顺电体,目前常用的产生超顺电的方法有温度驱动和尺寸驱动 2 种手段^[77–79]。

温度驱动的超顺电体是弛豫铁电的一种特殊状

态,在介电常数达到最大值时的相变温度(T_m)开始到 Burns 温度(T_B)时,超顺电态的弛豫体在很宽的温度范围内保持局部极性有序。Pan 等^[77]通过在 BiFeO_3 - BaTiO_3 中掺杂 Sm (Sm - BFBT),利用薄膜内存在局部化学、结构和电学异质性,将 BiFeO_3 - BaTiO_3 相变温度降低到室温以下,如图 7a 所示。并且通过优化成分, P - E 电滞回线的滞回损耗显著降低,如图 7b 所示。最终,在制备的超顺电薄膜中实现了高达 152 J/cm^3 的 U_{rec} ,其 η 保持在 77%。

(a) P - E hysteresis loop of Sm-BFBT(b) P - E hysteresis loop of BSZT thin films图 7 温度驱动和尺寸驱动的超顺电薄膜实例^[77-78]Fig. 7 Examples of temperature-driven and size-driven superparaelectric thin film^[77-78]

尺寸驱动的超顺电材料是通过控制晶粒/极性微区的尺寸(R)处于极化波动的相干长度(R_c)和顺电态出现的极限尺寸(R_{cr})之间来获得, 即 $R_c > R > R_{cr}$ ^[78, 80]。Wang 等^[78]通过降低 $\text{Ba}_{0.95}\text{Sr}_{0.05}\text{Zr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ (BSZT) 薄膜的沉积温度来限制晶粒生长, 在室温沉积的薄膜中, 非极性的非晶基体包围着 2~3 nm 的极性团簇, 随着晶粒/极性团簇尺寸的减小, BSZT 薄膜的 P - E 电滞回线表现出较低的滞后, 如图 7b 所示, 其 U_{rec} 约 102 J/cm^3 , η 约 87%。

1.6 反铁电材料

反铁电材料具有独特的双电滞回线, 这源于其在 2 个相邻的晶格上的自发极化平行且相反的排列。反铁电材料在宏观上不显示自发极化, 并且其在低电场下的 P_r 较低。当外加场强逐渐升高时, 极化就会沿着电场方向平行排列, 具有典型的宏观铁电性, 发生反铁电-铁电相变。这种独特的性质使得反铁电材料在储能领域同样具有良好的应用前景。目前, 最常用的反铁电材料包括 PbZrO_3 、 $(\text{Pb}, \text{La})(\text{Zr}, \text{Ti})\text{O}_3$ 、 AgNbO_3 和 HfO_2 等^[81-91]。

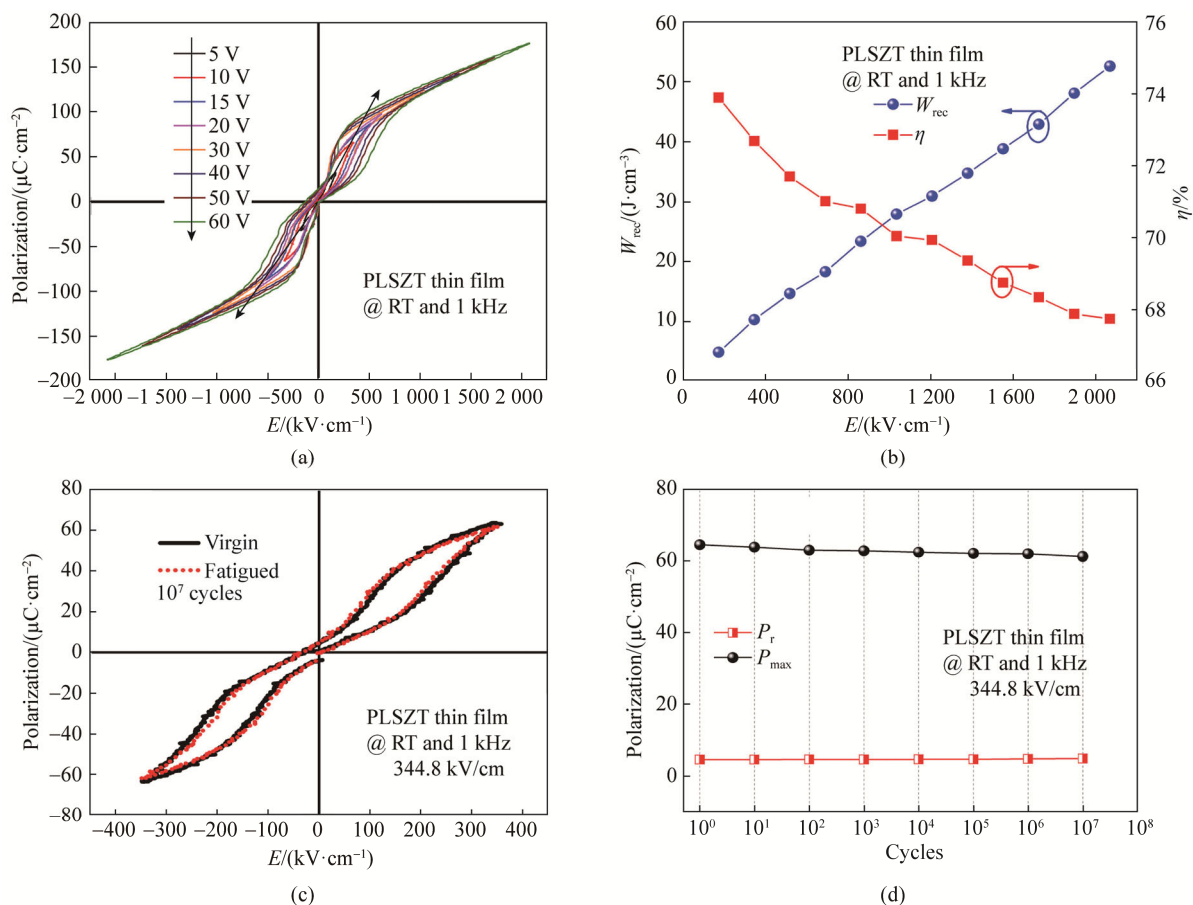
PbZrO_3 是广泛研究的反铁电材料之一, 具有高的 P_{max} 以及较低的 P_r , 适合电介质储能电容器领域。例如, Li 等^[81]研究了掺杂不同浓度 Ca^{2+} 的 $\text{Pb}_{1-x}\text{Ca}_x\text{ZrO}_3$ 反铁电薄膜的反铁电性与储能性能, 发现通过掺杂 Ca^{2+} , 增强了材料反铁电相的稳定性、场致相变的弥散性和 E_b , 最终在 $x=0.12$ 时获得了 50.2 J/cm^3 的 U_{rec} 以及 83.1% 的 η , 这比纯 PbZrO_3 薄膜的 U_{rec} 相比提高了 261%。Tang 等^[82]通过传统固相法制备了 $\text{Pb}_{0.89}\text{La}_{0.06}\text{Sr}_{0.05}(\text{Zr}_{0.95}\text{Ti}_{0.05})\text{O}_3$ (PLSZT) 陶瓷, 并且通过脉冲激光法 (PLD) 制备了 PLSZT 反铁电薄膜电容器, 薄膜电容器的 U_{rec} 达到了 52.6 J/cm^3 , 而陶瓷的

U_{rec} 仅为 1.29 J/cm^3 , 这是因为薄膜电容器的氧空位含量相对于陶瓷电容器显著下降, 降低了材料内部的氧缺陷。这个研究凸显了薄膜电容器优异的 U_{rec} , 并且薄膜电容器具有良好的循环稳定性, 如图 8 所示。除传统铅基材料外, 研究人员通过脉冲激光法制备了 AgNbO_3 外延薄膜, 显著提高了 AgNbO_3 薄膜的 E_b , 当外加场强大于 300 kV/cm 时, $(001)\text{AgNbO}_3$ 外延薄膜出现典型的反铁电滞回线, 当外加电场为 600 kV/cm 时, AgNbO_3 薄膜的 U_{rec} 为 5.8 J/cm^3 , η 为 55.8%^[83]。Ali 等^[84]详细研究了 10 nm 厚的 Si 掺杂 HfO_2 反铁电材料, 其具有纤细的双电滞回线和较大的 P_{max} , 其在 4500 kV/cm 时 U_{rec} 达到了 61.2 J/cm^3 , η 达到了 65%, 并且在 210~400 K 温度范围内显出良好的热稳定性。

总之, 线性电介质、顺电体、铁电、弛豫铁电、超顺电和反铁电材料都在储能领域具有广阔的应用前景。表 1 汇总了近年来不同电介质材料的典型研究成果。这些研究结果表明, 通过不同的制备技术和材料改性方法, 各种电介质材料在储能领域都有望实现更高的能量存储密度和更好的性能, 为电子器件和可穿戴设备等领域的发展提供了重要的支持。

2 陶瓷薄膜储能材料改性方法

为了满足高性能电介质储能电容器的要求, 电介质材料需要大的 P_{max} 、小的 P_r 和大的 E_b 。为了优化电介质材料的性能, 研究人员进行了广泛的研究, 尤其是在薄膜电介质储能材料方面。相对于传统的陶瓷块体材料和聚合物基材料, 薄膜材料具有更加复杂的制备工艺和多种影响性能的因素。下面总结了薄膜电介质储能材料的主要改性方法。



RT is room temperature.

图 8 PLSZT 薄膜的储能性能和循环稳定性^[82]

Fig. 8 Energy storage performance and cyclic stability of $\text{Pb}_{0.89}\text{La}_{0.06}\text{Sr}_{0.05}(\text{Zr}_{0.95}\text{Ti}_{0.05})\text{O}_3$ (PLSZT) thin films^[82]

表 1 近年来不同电介质储能陶瓷薄膜材料的典型研究成果

Table 1 Typical achievements of different dielectric energy storage ceramic thin film materials in recent years

Type	Material	Method	Thickness/nm	$U_{\text{rec}}/(\text{J}\cdot\text{cm}^{-3})$	$\eta/\%$	$E_b/(\text{kV}\cdot\text{cm}^{-1})$	Reference
LD	HfO_2	ALD	63	21.3	75.0	4 250	[52]
	$\text{Al}_2\text{O}_3/\text{TiO}_2$	ALD	15.0/7.8	60.0		13 000	[53]
PE	SrTiO_3	Sol-gel	300	55.0	94.7	6 500	[55]
	$\text{Sr}_{0.995}(\text{Na}_{0.5}\text{Bi}_{0.5})_{0.005}(\text{Ti}_{0.99}\text{Mn}_{0.01})\text{O}_3$	Sol-gel	196	65.3	70.8	5 015	[56]
	SrTiO_3	Magnetron sputtering	610	307.0	89.0	6 600	[92]
FE	$\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$	CSD	480	44.7	78.4	2 040	[59]
	$\text{BiFeO}_3/\text{BaTiO}_3$	RF-magnetron sputtering	300	51.2	73.0	2 600	[93]
	BaTiO_3	RF-magnetron sputtering	200	135.0 ± 10.0	80.0 ± 4.0	6 500	[61]
RFE	$\text{Mn-Pb}_{0.97}\text{La}_{0.02}(\text{Zr}_{0.905}\text{Sn}_{0.015}\text{Ti}_{0.08})\text{O}_3$	Sol-gel	320–350	31.2	58.0	2 000	[66]
	$\text{BiFeO}_3\text{-BaTiO}_3\text{-SrTiO}_3$	PLD	450–500	112.0	80.0	4 900	[94]
	$\text{Sr}_{0.99}(\text{Na}_{0.5}\text{Bi}_{0.5})_{0.01}\text{Ti}_{0.99}\text{Mn}_{0.01}\text{O}_3$	Sol-gel	200	53.0	48.8	4 910	[67]
SPE	$\text{Sm-BiFeO}_3\text{-BaTiO}_3$	PLD	650	152.0	77.0	3 500	[77]
	$\text{Ba}_{0.95}\text{Sr}_{0.05}\text{Zr}_{0.2}\text{Ti}_{0.8}\text{O}_3$	RF-magnetron sputtering	300	102.0	87.0	6 200	[78]
AFE	La-PbZrO_3	CSD	450	23.1	73.0	1 400	[95]
	Ca-PbZrO_3	CSD	300	50.2	83.1	2 800	[81]
	AgNbO_3	PLD	400	5.8	55.8	600	[83]
	Si:HfO_2	ALD	10	61.2	65.0	4 500	[84]

ALD, CSD and PLD represent the atomic layer deposition, chemical solution method and pulsed laser deposition; RF is radio frequency.

2.1 制备工艺

制备工艺在电介质材料的性能调控中起着至关重要的作用。通过对制备工艺进行优化,可以显著的改善薄膜材料的性能。通常,制备工艺的优化包括以下几个方面:制备方法、退火工艺、电极材料、薄膜老化和多层薄膜电容器(MLFC)制备。

1) 制备方法。薄膜材料可以采用多种不同的制备方法,包括脉冲激光沉积法、磁控溅射技术、原子层沉积技术以及溶胶凝胶法等。不同的制备方法通常导致薄膜性能的差异,例如,Nguyen 等^[96]通过溶胶凝胶法以及脉冲激光沉积法制备了反铁电 PbZrO_3 (PZO)薄膜,2 种方法制备的薄膜表现出不同的电滞回线形状,如图 9 所示,最终通过溶胶-凝胶法制备的 PZO 薄膜展现了更高的 U_{rec} (19.4 J/cm^3)和 η (70.8%),并且展现出了良好的循环稳定性。此外,不同的研究团队分别通过溶胶凝胶法和磁控溅射沉积制备了 SrTiO_3 (STO)薄膜,也展现出不同的储能性能。通过溶胶凝胶法制备的 STO 薄膜展现出 55 J/cm^3 的 U_{rec} 和 94.7%的 η ^[55],而磁控溅射制备的 STO 薄膜则具有惊人的储能性能,其 U_{rec} 高达 307 J/cm^3 , η 为 89%^[92],凸显了不同制备方法对电介质材料储能性能的影响。

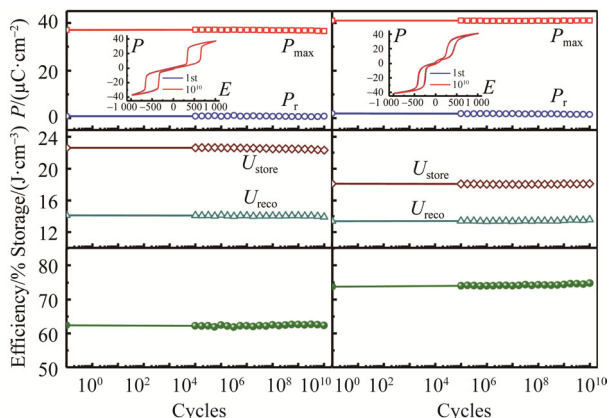


图9 PLD (左)和溶胶-凝胶法(右)制备的PZO薄膜的循环稳定性^[96]

Fig. 9 Cyclic stability of PbZrO_3 (PZO) films prepared by pulsed laser deposition (PLD) (left) and sol-gel (right) method^[96]

2) 退火工艺。退火工艺通常包括退火温度(沉积温度)和退火气氛^[56, 59, 97-105]。Nguyen 等^[97]在脉冲激光沉积法在硅上沉积无铅 $\text{BaZr}_{0.35}\text{Ti}_{0.65}\text{O}_3$ (BZT)薄膜时,通过改变沉积温度调控了 BZT 薄膜的相结构,低温沉积的 BZT 具有顺电相,显著提高了 BZT 薄膜的 E_b ,最终获得了 121.2 J/cm^3 的 U_{rec} 以及 88.2%的 η 。Wang 等^[104]探索了铁电材料 $\text{Ba}_2\text{Bi}_{3.9}\text{Pr}_{0.1}\text{Ti}_5\text{O}_{18}$

的晶粒与 ϵ_r 以及 E_b 之间的关系,发现具有较低 ϵ_r 的非晶薄膜内部的局域态或陷阱束缚载流子,宏观上表现出更高的击穿电场。而具有较大晶粒的铁电薄膜具有大 ϵ_r ,这意味着其具有较大的 P_{max} 。该团队通过调控 $\text{Ba}_2\text{Bi}_{3.9}\text{Pr}_{0.1}\text{Ti}_5\text{O}_{18}$ 的热处理温度将具有高 E_b 的非晶态与大 ϵ_r 的晶粒结合起来优化储能性能,在 4240 kV/cm 的电场下获得了 90.4 J/cm^3 的 U_{rec} 以及 84.2%的 η 。Zhu 等^[103]将 $\text{Pb}_{0.8}\text{La}_{0.1}\text{Ca}_{0.1}\text{Ti}_{0.975}\text{O}_3$ (PLCT)薄膜分别在 N_2 、空气和 O_2 气氛下进行退火,结果表明在 O_2 气氛下退火的 PLCT 薄膜具有显著降低的漏电流密度,增强了储能性能。Yang 等^[105]的研究结果表明 O_2 气氛下可以降低薄膜内部的氧空位数量,从而降低漏电流密度,进而增强薄膜的 E_b 。同时,不同材料在不同气氛下进行退火会影响薄膜材料的取向,如 $\text{Pb}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ (PBT)薄膜随着退火气氛中氧分压的增长其(001)取向度逐渐增加,这不利于 PBT 薄膜的 E_b ,最终该研究团队综合了择优取向和缺陷的影响,在空气气氛下制备了 PBT 薄膜,最终获得了 59.4 J/cm^3 的 U_{rec} 和 81.2%的 η ,如图 10 所示。

3) 电极。在储能电介质电容器制备过程中,需要在电介质材料的两端沉积导电层来构建电容器结构。通常情况下,常用的导电层包括 Au、Pt 等材料,此外,还有一些如 $\text{La}_x\text{Sr}_{1-x}\text{MnO}_3$ (LSMO)、 Nb:SrTiO_3 (STO)、 SrRuO_3 (SRO)和导电玻璃等^[106-112]。一般来说,底部电极的制备发生在薄膜制备之前,因此不同的底部电极会对电介质薄膜产生一定的影响,如影响薄膜的取向和晶格失配应变等^[113-117]。Zhao 等^[110]在 LaNiO_3 底部电极上制备了 $(\text{Pb}_{0.97}\text{La}_{0.02})(\text{Zr}_{0.9}\text{Sn}_{0.05}\text{Ti}_{0.05})\text{O}_3$ (PLZST)薄膜,通过改变薄膜的厚度调控了薄膜内部的压应力,进而增加 PLZST 薄膜中的反铁电相优化了薄膜的储能性能。同样的, Ma 等^[108]在 $(\text{La}_{0.5}\text{Sr}_{0.5})\text{CoO}_3$ 、 LaNiO_3 和 SrRuO_3 底部电极上制备了 AgNbO_3 薄膜,通过底部电极的改变调节 AgNbO_3 薄膜的面内压应力,改善了 AgNbO_3 薄膜的反铁电稳定性,这为反铁电储能薄膜提供了一个思路,如图 11 所示。Li 等^[109]将支撑在(001) SrTiO_3 衬底上的 SrRuO_3 、 LaNiO_3 和 Pt 层作为 $\text{BaZr}_{0.15}\text{Ti}_{0.85}\text{O}_3$ 的底电极,来促进 BZT 薄膜的取向生长,进而改善薄膜的储能性能。Ge 等^[107]研究发现,使用氧化物材料作为顶部电极可以获得更薄的界面层,从而增强反铁电薄膜的储能性能。

4) 老化。最近的研究表明,老化过程中引入的缺陷偶极子可以降低薄膜中的 P_r 并且提高 E_b ,有利

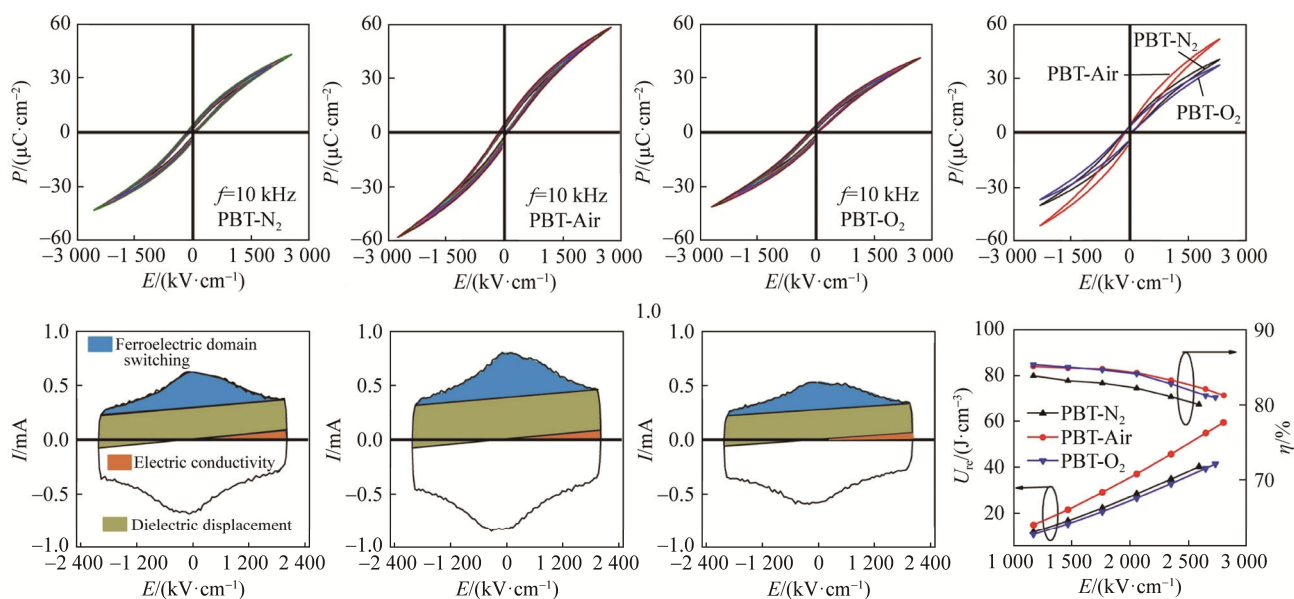


图 10 不同退火气氛下 PBT 薄膜的 P - E 电滞回线、 I - E 曲线以及储能性能^[105]

Fig. 10 P - E hysteresis loop, I - E curves and energy storage performance of $\text{Pb}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ (PBT) films under different annealing atmospheres^[105]

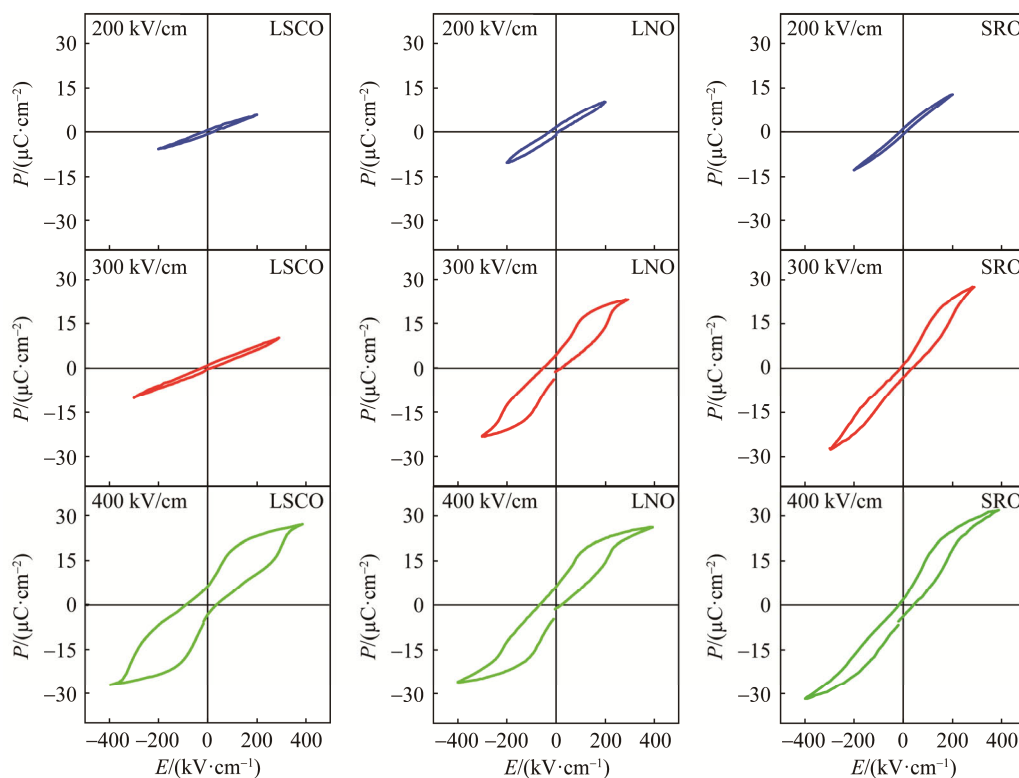


图 11 不同底电极上生长的 ANO 膜的 P - E 电滞回线^[108]

Fig. 11 P - E hysteresis loop of ANO films grown on different bottom electrodes^[108]

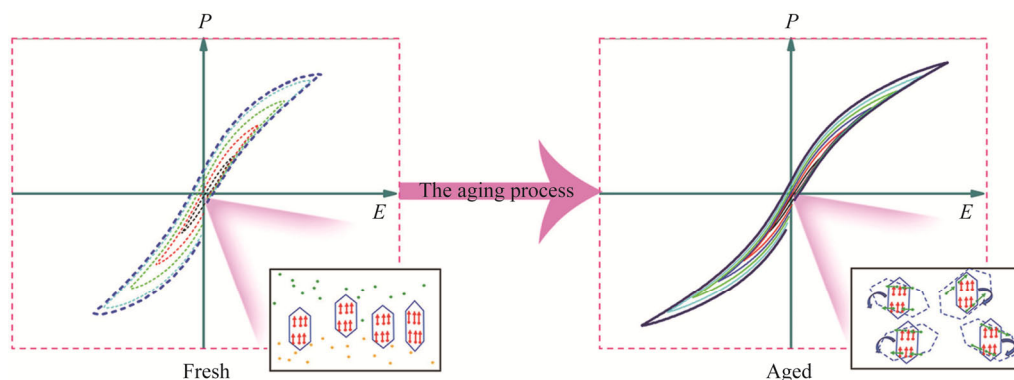
于改善薄膜的储能性能^[118–121]。这一发现对以前的观点进行了颠覆，以前认为老化会对电介质薄膜的极化性能产生负面影响。Yan 等^[120]最先发现了老化在电介质储能领域的正效应，如图 12 所示。该研究

团队通过溶胶-凝胶法制备了 $\text{Na}_{0.5}\text{Bi}_{0.47}\text{La}_{0.03}\text{TiO}_3$ (NBLT) 薄膜和 $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{0.97}\text{Mn}_{0.03}\text{O}_3$ (NBMT) 薄膜，通过老化改善了薄膜的 E_b 和储能性能，之后其将 NBLT 薄膜和 NBMT 薄膜制备成多层薄膜并进行老

化, 获得了 56.8 J/cm^3 的储能性能。之后 Sui 等^[118]制备了 $\text{Na}_{0.5}\text{Bi}_{0.5}(\text{Fe}_{0.03}\text{Ti}_{0.97})\text{O}_3/\text{Na}_{0.5}\text{Bi}_{0.5}(\text{Zr}_{0.02}\text{Ti}_{0.98})\text{O}_3$ (NBFT/NBZT) 基弛豫多层薄膜, 在通过 21 d 的老化之后, 储能性能得到了显著改善, 其 U_{rec} 达到了 71.7 J/cm^3 , η 为 74.1%, 这也是目前报道的老化改善电介质薄膜储能电容器中最高 U_{rec} 。值得注意的是, 之前的老化研究主要侧重于界面工程的综合效应对储能性能的改善, 而针对单一老化行为的研究仍需要进一步探索。

5) MLFC 制备。多层薄膜电容器(MLFC)的制备

是一个重要的领域, 然而, 与块体多层陶瓷电容器 (MLCC) 不同, 薄膜材料领域尚未开发出相应的 MLFC。近日, Yang 等^[122]通过熵设计的方法, 成功增加了薄膜内部的局部不均匀性, 在 $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ 基中熵薄膜中实现了增强的储能性能。并利用该中熵薄膜制备了 MLFC, 如图 13 所示, 其展示了具有内电极(Au)和介电层的交替多层结构, 实现了 78.3 J/cm^3 的高 U_{rec} 和 90.2% 的 η 。这项研究不仅为多层薄膜的商业化提供了思路, 同时为改性薄膜电容器储能性能提供了研究思路。



Such the aging process provides a simple, efficient and low-cost strategy to improve the energy storage performance.

图 12 老化工艺机理示意图^[120]

Fig. 12 Schematic diagram of aging process mechanism^[120]

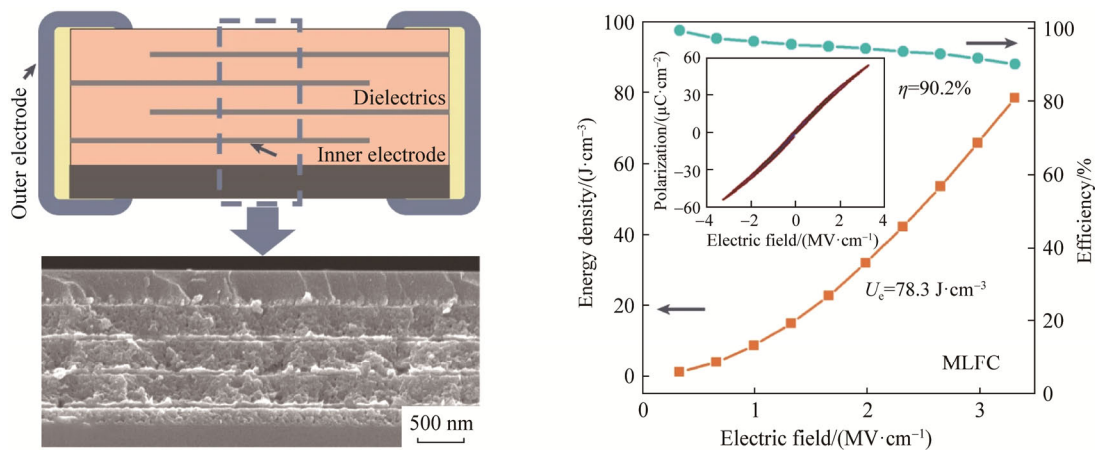


图 13 MLFC 结构示意图和储能性能^[122]

Fig. 13 MLFC structure diagram and energy storage performance^[122]

2.2 组分设计

在组分设计方面, 主要涵盖了元素掺杂和两相或多相固溶 2 个主要方向。此外, 通过熵调控和添加纳米粒子形成复合薄膜也被用来改善电介质电容器的储能性能。

1) 元素掺杂。目前, 广泛使用的元素掺杂包括 La ^[62, 95, 123-125]、 Mn ^[126-131]、 Eu ^[132-133]、 Nd ^[134]、 Sn ^[60, 135]

和 Sr ^[136]等。元素掺杂的效果主要包括细化 $P-E$ 电滞回线、降低 $\tan\delta$ 、抑制泄漏电流、增强 E_b , 从而增强材料的储能性能^[81, 137-140]。例如, 众多科研团队发现, 通过 Mn 元素掺杂, Mn^{2+} 向 Mn^{4+} 的转变可以降低薄膜内部的氧空位含量, 降低薄膜的漏电密度, 提高薄膜的 E_b ^[126-131]。Song 等^[126]利用 Mn^{2+} 与氧空位结合形成缺陷复合物, 抑制了漏电流密度,

最终获得了 47.6 J/cm^3 的 U_{rec} 。Wang 等^[127]在 $0.6\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3\text{--}0.4\text{Sr}_{0.7}\text{Bi}_{0.2}\text{TiO}_3$ 薄膜中引入 Mn 离子来补偿 A 位空位的价态不平衡, 形成缺陷偶极子, 降低漏电流密度, 改善了极化和击穿行为, 最终获得了 85.35 J/cm^3 的 U_{rec} 和 73.17% 的 η 。此外, 如 La、Eu、Sn 等元素多通过 A 位、B 位取代来调控晶格结构、正常铁电到弛豫铁电的相变等, 进而细化电介质薄膜的 $P\text{--}E$ 电滞回线, 并且调控电介质薄膜的介电性能, 以改善储能性能^[60, 62, 95, 123–125]。如 Cai 等^[95]通过将 La^{3+} 引入 PZO 的 A 位来构建化学压力, 增加了反铁电相和铁电相之间的能垒, 增强了反铁电性, 如图 14 所示, 改善了储能性能, 获得了 23.1 J/cm^3 的 U_{rec} 和 73% 的 η 。Nguyen^[124]通过 La 掺杂增强了 $\text{Ba}(\text{Zr}_{0.25}\text{Ti}_{0.75})\text{O}_3$ 薄膜的弛豫行为, 细化了 $P\text{--}E$ 电滞回线, 最终获得了 72.2 J/cm^3 的 U_{rec} 以及 78.6% 的 η 。Kim 等^[60]在 BaTiO_3 外延薄膜电容器中掺杂 Sn, 实现了 92.5 J/cm^3 的 U_{rec} 。

2) 两相或多相固溶。两相或多相固溶一方面通过调控材料的相结构, 来改善材料的储能性能; 另一方面, 通过两相或多相固溶进行成分修饰, 来调控薄膜材料的微观结构、极化行为和相变温度等, 进而增强材料的储能性能^[94, 141–152]。Li 等^[141]通过在 $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ 体系中引入 PbTiO_3 , 制备了一系列 $(1-x)(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3\text{--}x\text{PbTiO}_3$ ($x=0, 0.05, 0.10, 0.15, 0.25$) ($\text{BNT}\text{--}x\text{PT}$) 薄膜, 通过调控 PT 含量, 相结构经历了菱形(R)–菱形+四方(R+T)–四方(T)的演化过程, 最终在菱形相和四方相共存的 $\text{BNT}\text{--}0.10\text{PT}$ 薄膜中获得了 $(13.02\pm0.39) \text{ J/cm}^3$ 的 U_{rec} 。Pan 等^[142]通过 BiFeO_3 来修饰 $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$, 通过引入 BF 调整了晶格中的化学压力, 优化了极化行为。并且通过引入 BF, 显著降低了漏电流密度, 提高了 E_b , 获得了 113 J/cm^3 的 U_{rec} , 并且具有 80.4% 的 η 。Pan 等^[94]在三相固溶体系中, 利用 BiFeO_3 提供大的菱方

相极化、 BaTiO_3 提供四方相极化、 SrTiO_3 提供顺电的立方相, 利用菱方相和四方相共存, 显著降低了畴的尺度、提高了极化的无序度, 如图 15 所示。通过该设计, 降低了铁电畴翻转势垒, 铁电畴的翻转变得容易, 降低了损耗, 获得了纤细的 $P\text{--}E$ 电滞回线, 并且大幅度提升了 η , 最终在 $\text{BiFeO}_3\text{--}\text{BaTiO}_3\text{--}\text{SrTiO}_3$ 体系中获得了 112 J/cm^3 的 U_{rec} 和约 80% 的 η 。值得一提的是, Lv 等^[143]通过弛豫铁电 $0.4\text{BiFeO}_3\text{--}0.6\text{SrTiO}_3$ 和顺电 $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ 交替旋涂, 制备了多层结构, 在界面处辅助元素扩散的帮助下成功制备了 $\text{BiFeO}_3\text{--}\text{BaTiO}_3\text{--}\text{SrTiO}_3$ 薄膜, 优化后的薄膜实现了较大的 ϵ_r 和 E_b , 获得了 98 J/cm^3 的 U_{rec} , η 也达到了 80%, 这为制备多相固溶体系提供了一种思路。

3) 熵调控。熵调控策略通过在体系中引入多种元素, 利用原子尺寸不匹配引起的化学无序形成局部多元极化、增加无序程度、抑制晶粒粗化和增加晶能, 可有效同时调制多种因素, 从而增强高场极化响应、近零剩余极化、延迟极化饱和、增强击穿强度等, 进而改善储能性能^[153–158]。Liu 等^[155]在 $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ (NBT) 的 B 位引入 Hf、Zr、Sn 元素制备了外延高熵 $\text{Na}_{0.5}\text{Bi}_{0.5}\text{Ti}_{0.7}\text{Hf}_{0.1}\text{Zr}_{0.1}\text{Sn}_{0.1}\text{O}_3$ (NBTHZS) 薄膜, U_{rec} 从 NBT 薄膜的 5.1 J/cm^3 提高到 NBTHZS 薄膜的 81 J/cm^3 , 并且保持了 74.1% 的 η 。Yang 等^[154]从铁电体 $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ 开始设计高熵铁电体, 在 Ti 位上引入等摩尔比的 Zr、Hf 和 Sn 元素, 在 Bi 位上引入 La 元素, 其标定组成为 $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_{3-3x}\text{Zr}_x\text{Hf}_x\text{Sn}_x\text{O}_{12}$ 。通过逐步增加 x ($x=0.1, 0.2, 0.3, 0.4, 0.5$) 来增加体系的熵, 利用熵稳定效应获得了热力学上不稳定的 $\text{Bi}_2\text{Ti}_2\text{O}_7$ 基烧绿石相材料, 并且通过多元素在等效晶格位上的无序共存(如图 16 所示)降低了稳定的焦绿石相的漏导和损耗, 同时提升了其击穿场强, 最终在 $x=0.4$ 的高熵薄膜中获得了 182 J/cm^3 的 U_{rec} 和 78% 的 η 。之后 Yang 等^[122]又设计了一系列基于

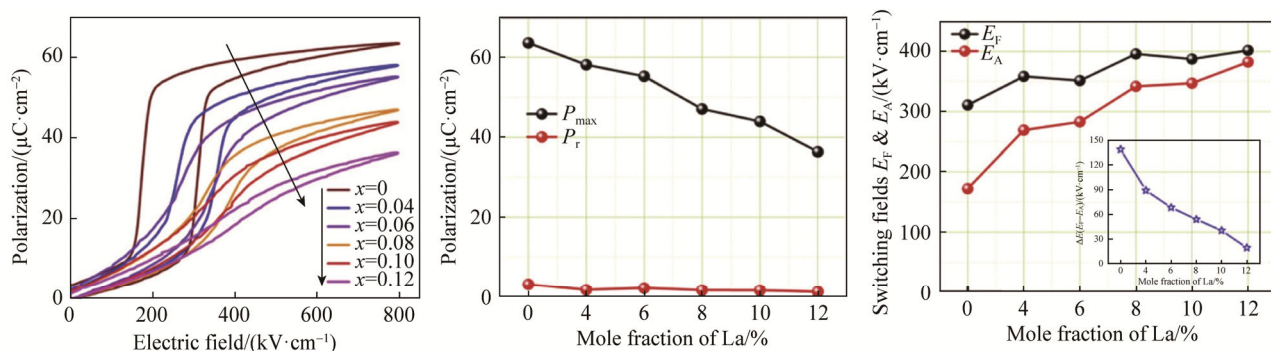
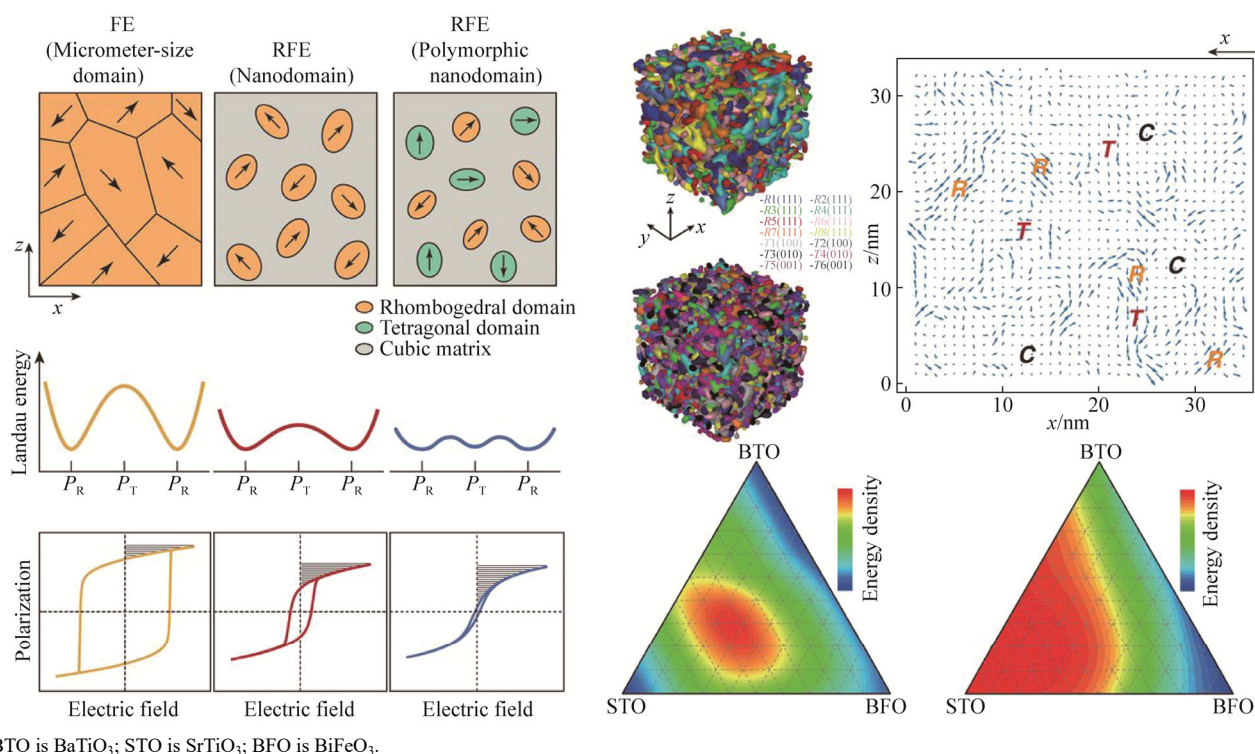
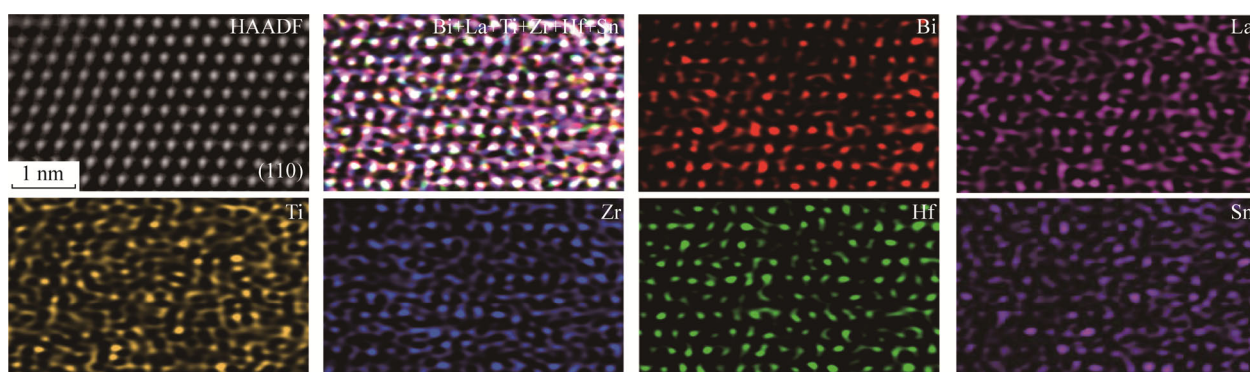
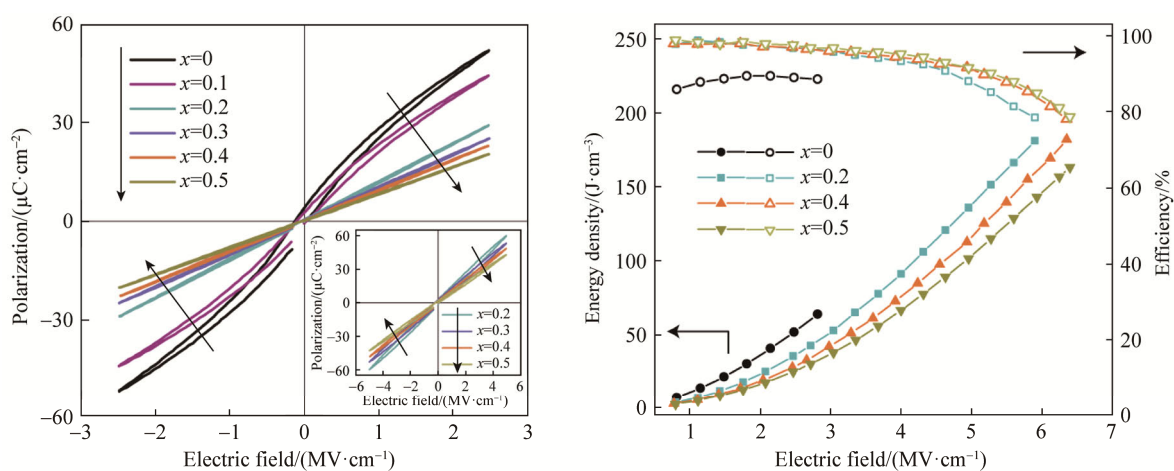


图 14 La-PZO 薄膜的 $P\text{--}E$ 电滞回线和储能性能^[95]

Fig. 14 $P\text{--}E$ hysteresis loop and energy storage performance of La-PZO thin film^[95]

图 15 通过多晶型纳米域设计设计具有增强能量性能的新型 RFE^[94]Fig. 15 Design of new RFEs with enhanced energy performance via polymorphic nanodomain design^[94]

(a) Atomic EDS mapping



(b) P-E hysteresis loop and energy storage performance

图 16 熵调控实例^[154]Fig. 16 Example of entropy control^[154]

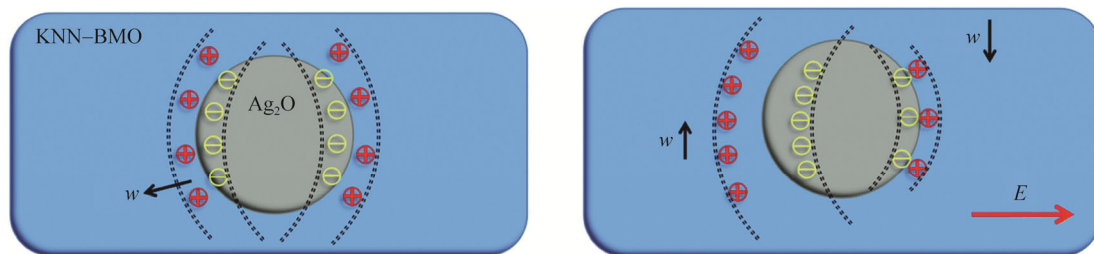
$\text{Bi}_4\text{Ti}_3\text{O}_{12}$ 材料体系的熵调制薄膜, 其将等摩尔的稀土元素(La、Pr、Nd 和 Sm)引入到 $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ 的 A 位点(即 Bi 位), 标称成分为 $\text{Bi}_{4-x}\text{La}_x\text{Pr}_x\text{Nd}_x\text{Sm}_x\text{Ti}_3\text{O}_{12}$ ($x=0, 0.4, 1.0, 1.5, 2.0$ 和 2.2)。该研究证明了通过熵工程来定量评估局部成分不均匀性, 并且以弛豫扩散因子来调控弛豫特征, 最终在 $x=1.5$ 时的中熵薄膜中实现了 178.1 J/cm^3 的 U_{rec} 和 80.5% 的 η , 并且利用该中熵薄膜制备了 MLFC 器件, 为高性能电容器器件提供了替代方案, 如前文所述。

4) 纳米粒子复合材料。纳米粒子复合是通过在基体材料中均匀的添加纳米粒子, 使其与基体材料形成整体来改善材料的储能性能。Sa 等^[159]通过将 $\alpha\text{-Fe}_2\text{O}_3$ 粒子添加到 PZO 薄膜中, $\alpha\text{-Fe}_2\text{O}_3$ 周围出现局域场强化了铁电相, 进而表现出较高的 P_{max} 。Li 等^[160]通过在 PZO 薄膜中添加 Au 纳米颗粒, 研究了 Au 纳米颗粒浓度对 PZO 薄膜储能性能的影响, 结果表明加入适量的 Au 纳米颗粒可以有效提高储能性能。Guo 等^[161]在 $0.92\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3\text{-}0.08\text{BiMnO}_3$ (KNN-BMO)薄膜中添加 Ag_2O 纳米粒子, 利用 Ag_2O 纳米粒子与基体之间构成类 PN 结构(如图 17 所示), 在界面处形成高电阻的损耗层, 这种类 PN 结中高阻区的整流效应提高了薄膜材料的 E_b , 提高了储能性能, 其 U_{rec} 达到了 65.1 J/cm^3 , 相比于纯 $0.92\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3\text{-}0.08\text{BiMnO}_3$ 薄膜 20.1 J/cm^3 的 U_{rec}

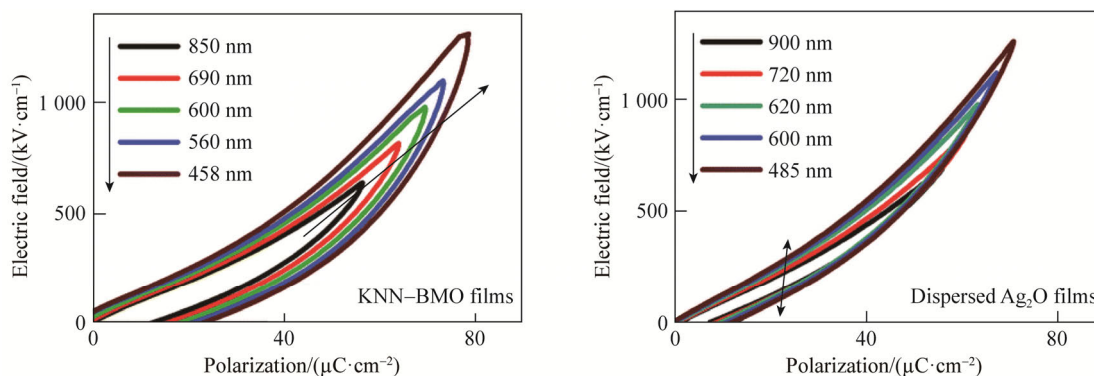
有了极大提升。

2.3 界面工程

1) “死层”效应。该效应是通过在薄膜和衬底之间或薄膜和电极之间引入一层具有高电阻率、宽带隙和低 ϵ_r 的材料, 如 Al_2O_3 和 $\text{Ca}_{0.2}\text{Zr}_{0.8}\text{O}_{1.8}$ 等, 来增加 E_b , 从而提高薄膜的储能性能^[162]。McMillen 等^[163]通过在 $(\text{BiFeO}_3)_{0.6}\text{-(SrTiO}_3)_{0.4}$ (BFST)薄膜与电极之间添加超薄 Al_2O_3 层, 通过 Al_2O_3 层扭曲了极化响应, 将 BFST 的最终极化响应推向了更高电场值。与未添加 Al_2O_3 层的 BFST 薄膜相比, 其 U_{rec} 增加了约 30%。Chen 等^[164]通过在 $\text{Ba}_{0.3}\text{Sr}_{0.7}\text{Zr}_{0.18}\text{Ti}_{0.82}\text{O}_3$ (BSZT)弛豫铁电薄膜中引入了新的“死层”, 即 $\text{Ca}_{0.2}\text{Zr}_{0.8}\text{O}_{1.8}$ 薄膜。相较于 Al_2O_3 而言, 其在具有高电阻率和宽带隙的同时具有大 ϵ_r , 这意味着在引入“死层”时可以在增强 E_b 的同时牺牲更少的极化。该研究通过 $\text{Ca}_{0.2}\text{Zr}_{0.8}\text{O}_{1.8}$ 的引入, 增强了 BSZT 薄膜的 E_b 和储能性能, 其 E_b 由 5.4 MV/cm 提高到 6.3 MV/cm , U_{rec} 由 64.9 J/cm^3 大幅增加至 89.4 J/cm^3 。此外, Wang 等^[165]提出了一种新概念的“死层”, 其将具有低 ϵ_r 的晶界看作“死层”, 并且将传统的在铁电薄膜与电极之间添加的“死层”作为一种柱状结构引入到薄膜本身之中, 通过晶界实现了分布式“死层”, 如图 18 所示。借此设计成功的延缓了薄膜的饱和极化, 降低了 P_r , 并且提高了 E_b , 实现了约 148 J/cm^3



(a) Schematic diagram of the PN-like junction mechanism

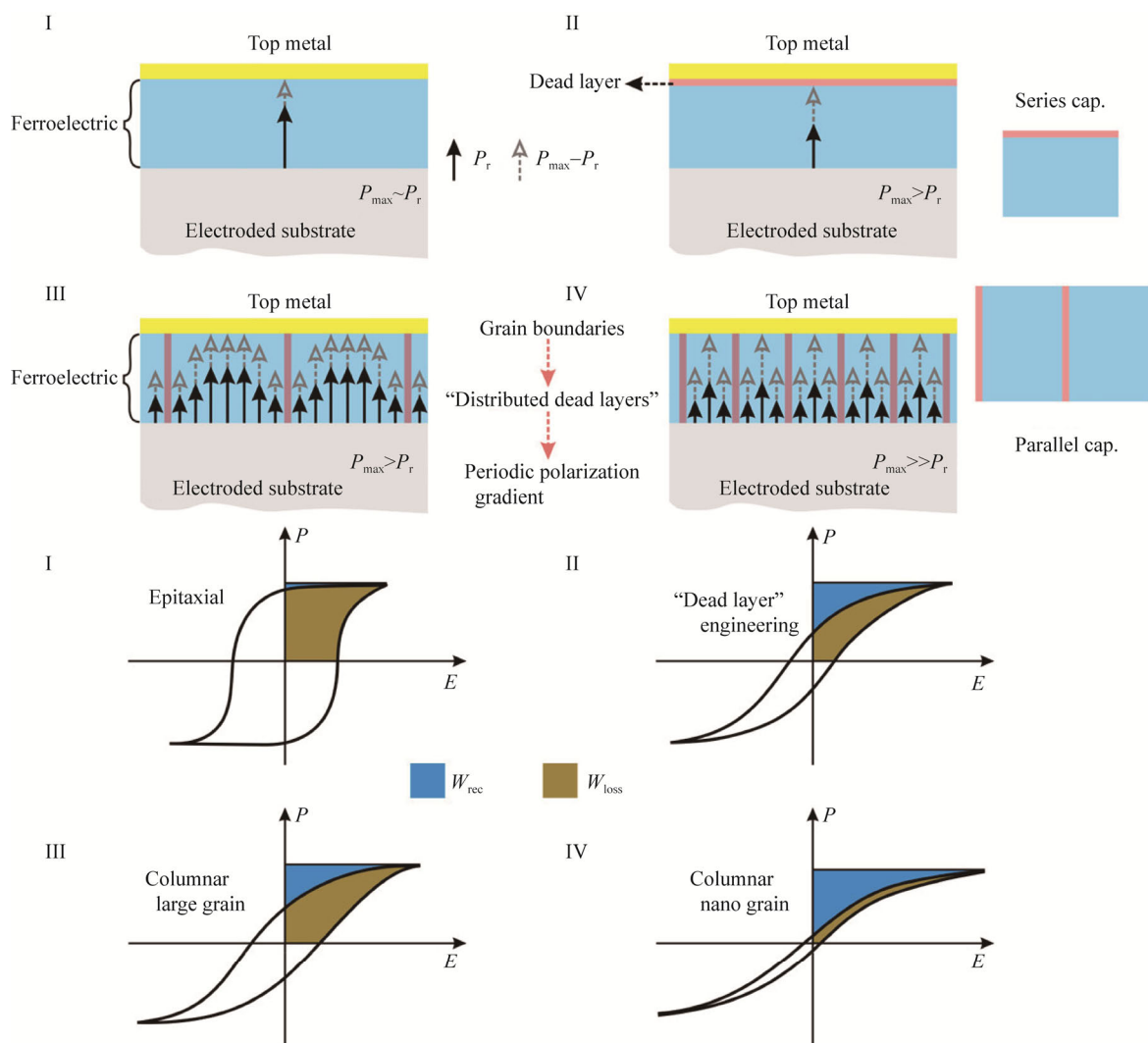


(b) P - E hysteresis loop of KNN-BMO thin film and dispersed Ag_2O thin film

KNN-BMO is $0.92\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3\text{-}0.08\text{BiMnO}_3$.

图 17 纳米粒子复合材料实例^[161]

Fig. 17 Examples of nanoparticle composites^[161]

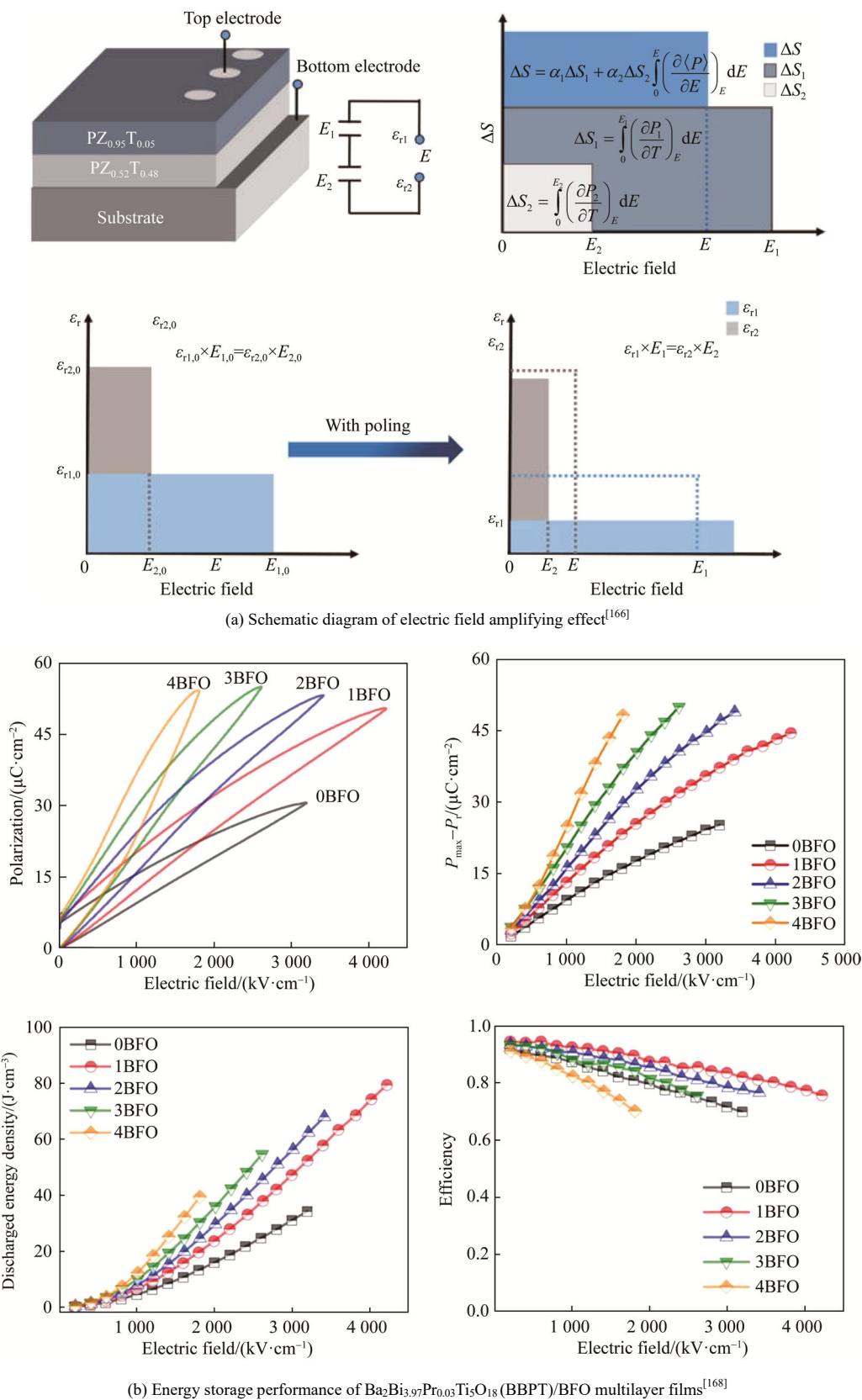
图 18 “死层”工程原理图和相应的 P - E 电滞回线^[165]Fig. 18 Schematics of “dead layer” engineering and corresponding P - E hysteresis loop^[165]

的 U_{rec} 和约 $91\% \pm 3\%$ 的 η , 在储能领域展现了极大的应用潜力。

2) 电场放大效应。对于多层薄膜, 按照 Gauss 定律, 当施加外加电场时, 相邻层的电位移大小应该相等, 这意味着大 ϵ_r 的铁电层共享较小的电场, 小 ϵ_r 的铁电层共享较大的电场, 如图 19a 所示^[166]。通过将大 ϵ_r 与小 ϵ_r 的薄膜构建多层薄膜, 可以放大 ϵ_r 层的电场, 从而提高多层薄膜的 E_b , 改善多层薄膜的储能性能^[167-170]。Zhang 等^[167]通过前期研究发现 $0.7\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3-0.3\text{SrTiO}_3(0.7\text{NBT}-0.3\text{ST})$ 具有大的 P_{max} , $0.6\text{SrTiO}_3-0.4\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3(0.6\text{ST}-0.4\text{NBT})$ 具有高 E_b 。其选取上述 2 种体系薄膜制备了多层薄膜, 利用电场放大效应显著提高了 U_{rec} , 其 U_{rec} 相对于 $0.7\text{NBT}-0.3\text{ST}$ 薄膜提高了 1 倍以上。Wang 等^[168]通过高电阻率的 $\text{Ba}_2\text{Bi}_{3.97}\text{Pr}_{0.03}\text{Ti}_5\text{O}_{18}(\text{BBPT})$ 与大 P_{max}

的 $\text{BiFeO}_3(\text{BF})$ 制备 BBPT/BFO 多层薄膜, 利用电场放大效应实现了增强的 E_b , 并且通过调控 BF 界面层来调节 P_{max} , 最终实现了 79.3 J/cm^3 的 U_{rec} 和超过 75% 的 η , 如图 19b 所示。

3) 空间电荷效应和异质结效应。空间电荷效应的研究表明, 它对铁电薄膜的电学性能产生显著影响^[93, 171-173]。Zubko 等^[172]的研究结果表明空间电荷浓度变化会导致铁电薄膜的 P - E 电滞回线的细化和倾斜。此外, Tagantsev 等^[173]的研究结果也证明了这一说法, 其研究表明厚耗尽层会增加 P - E 电滞回线的倾斜角。这些结果表明通过空间电荷效应可以在铁电薄膜中获得纤细的 P - E 电滞回线, 进而使得铁电薄膜在储能领域得以应用。Zhu 等^[93]将具有大量空间电荷的 $\text{BaTiO}_3(\text{BT})$ 沉积在具有 SrRuO_3 (SRO) 涂层的 $\text{SrTiO}_3(\text{STO})$ 衬底上, 在施加小电场时,



(b) Energy storage performance of Ba₂Bi_{3.97}Pr_{0.03}Ti₅O₁₈ (BBPT)/BFO multilayer films^[168]

图 19 电场放大效应机理示意图和实例

Fig. 19 Schematic diagram and example of electric field amplifying effect

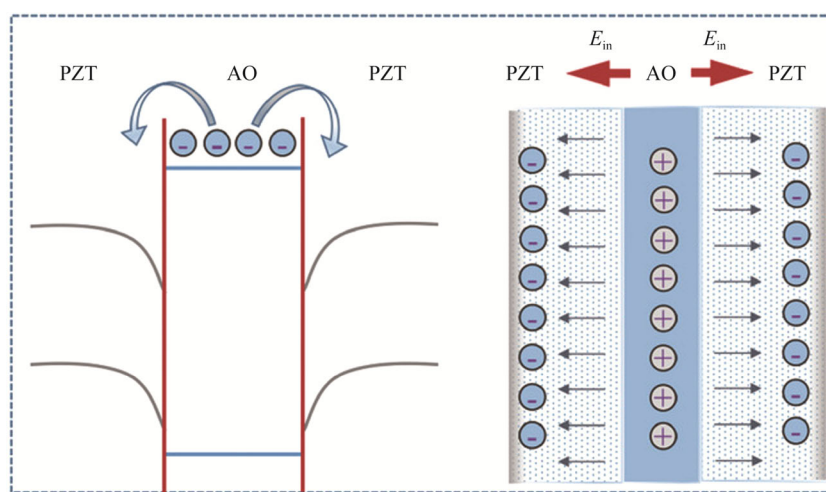
BT/SRO 界面处会形成耗尽层, 使得空间电荷主导的 BT 薄膜具备了纤细的 P - E 电滞回线, 展现了其

在储能领域的应用潜力。之后, 该研究团队通过在 BT/SRO 上沉积 1 层 BiFeO₃, 通过层间耦合作用增

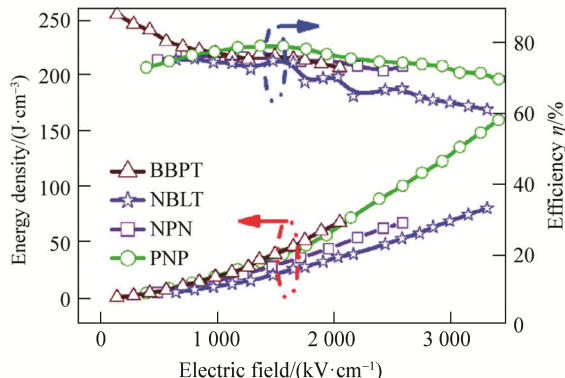
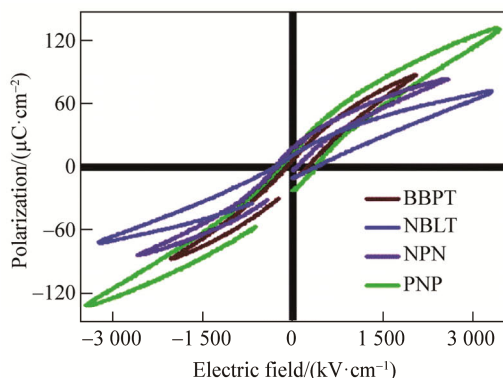
强了薄膜的 $P_{\max}$, 最终实现了 51.2 J/cm^3 的 U_{rec} 。

异质结, 在半导体领域中指 2 种半导体相接触形成的界面区域。在多层薄膜中, 通过选取宽带隙与窄带隙的电介质薄膜构建多层薄膜, 宽带隙的电介质薄膜导带中的电子扩散到窄带隙的电介质薄膜中, 进而在异质界面处形成内置电场, 内置电场的形成抵消了外部电场, 增强多层薄膜的 E_b , 进而改善多层薄膜的储能性能^[174-179]。Zhang 等^[174]选取了 $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ (PZT) 和 Al_2O_3 (AO) 制备多层薄膜, 其中 Al_2O_3 的带隙大于 PZT, AO 层的电子扩散到 PZT 铁电层中, 在 PZT 与 AO 的异质界面处引入内置电场, 如图 20a 所示。通过异质结效应显著

增强了多层薄膜的 E_b , 同时利用 AO 较低的 ϵ_r 实现了电场放大效应, 这进一步增强了多层薄膜的 E_b , 该多层薄膜的 E_b 达到了 5711 kV/cm , 最终获得了 63.7 J/cm^3 的 U_{rec} 和 81.3% 的 η 。Chen 等^[179]选择了具有相似 Aurivillius 相层状钙钛矿结构的化合物: P 型 $\text{Na}_{0.5}\text{Bi}_{3.25}\text{La}_{1.25}\text{Ti}_4\text{O}_{15}$ (P-NBLT) 和 N 型 $\text{BaBi}_{3.4}\text{Pr}_{0.6}\text{Ti}_4\text{O}_{15}$ (N-BBPT), 通过结构设计制备了具有 PNP 异质结构和 NPN 异质结构的电介质储能电容器, 结果表明在 PNP 异质结构中, 损耗区的宽度随着外加电场的增大而增大, 大大改善了绝缘特性, 提高了薄膜的 E_b 。最终, 在设计的 PNP 异质结构薄膜中获得了 159.7 J/cm^3 的 U_{rec} 和 70% 的 η , 如图 20b 所示。



(a) Schematic diagram of opposite double-heterojunction^[174]



(b) Energy storage performance of P-NBLT and N-BBPT multilayer films^[179]

PZT is $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$; AO is Al_2O_3 ; BBPT is N type $\text{BaBi}_{3.4}\text{Pr}_{0.6}\text{Ti}_4\text{O}_{15}$; NBLT is P type $\text{Na}_{0.5}\text{Bi}_{3.25}\text{La}_{1.25}\text{Ti}_4\text{O}_{15}$.

图 20 异质结效应实例

Fig. 20 Examples of heterojunction effects

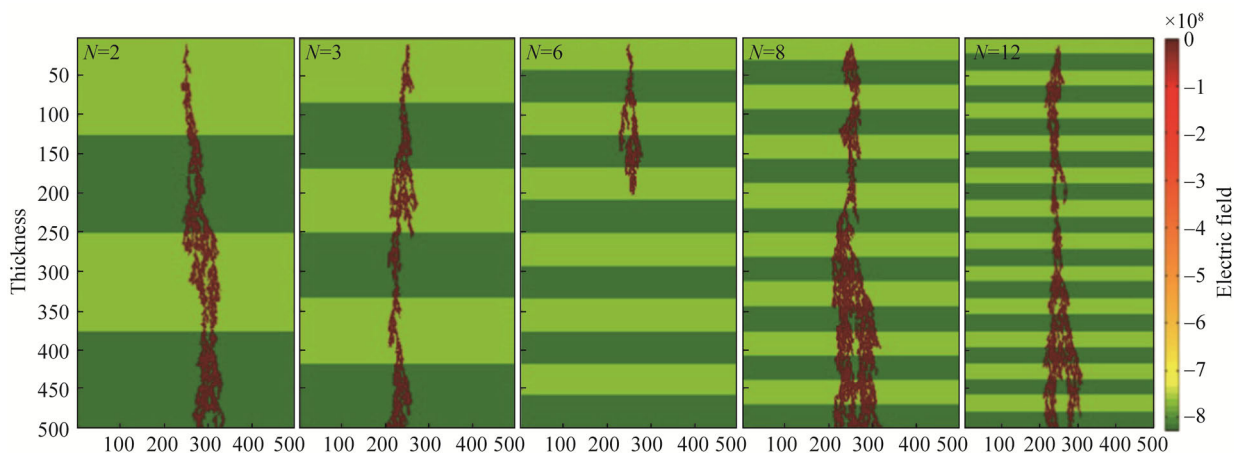
4) 界面阻挡效应和层间耦合效应。多层薄膜中存在的界面会阻碍电树枝的发展, 从而增强薄膜的 E_b , 改善薄膜的储能性能^[180-182]。Fan 等^[180]通过磁控溅射法制备了 $\text{BaZr}_{0.15}\text{Ti}_{0.85}\text{O}_3/\text{BaZr}_{0.35}\text{Ti}_{0.65}\text{O}_3$ (BZT15/BZT35) 多层薄膜, 在保持薄膜的总厚度不

变的同时改变界面数量来优化多层薄膜的储能性能。通过对多层薄膜的电树枝发展进行仿真, 如图 21a 所示, 证明了多层薄膜的界面可以阻挡薄膜中电树枝的穿透, 在 BZT15/BZT35 多层薄膜中实现了 8300 kV/cm 的大 E_b , 获得了 83.9 J/cm^3 的 U_{rec} 和

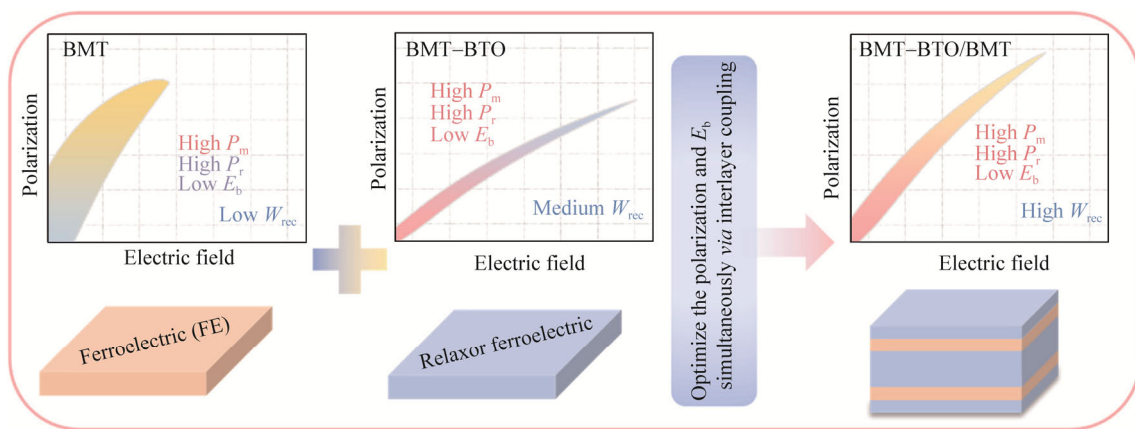
约 78.4% 的 η 。值得一提的是, 在界面阻挡效应的多层薄膜中应考虑界面数量增多对界面阻挡效应的正效应和界面扩散/界面耦合效应的负效应, 在二者之间进行合理选择, 进而获得最佳的储能性能。

在多层薄膜中, 相邻子层之间不同的电学性能会诱发层间耦合效应, 增强多层薄膜的储能性能^[167, 169, 183–184]。Bin 等^[184]利用铁电 BMT 和弛豫铁电 BMT–BTO 制备了多层薄膜, 通过 $\text{BiMg}_{0.5}\text{Ti}_{0.5}\text{O}_3$ (BMT) 和 $\text{BiMg}_{0.5}\text{Ti}_{0.5}\text{O}_3$ – BaTiO_3 (BMT–BTO) 之间的

层间静电耦合降低了 P_r , 增强了 E_b , 其层间耦合对 P – E 电滞回线的影响示意图如图 21b 所示, 在多层薄膜中获得了 106.8 J/cm^3 的 U_{rec} 。Song 等^[170]通过溶胶凝胶法制备了 $\text{Bi}_{0.2}\text{Sr}_{0.7}\text{TiO}_3/\text{BiFeO}_3$ (BST/BFO) 多层薄膜, 2 种材料的 ϵ_r 和电导率的差异使得界面处产生集中电荷, 导致极化增强。Nguyen 等^[183]研究表明在 PbZrO_3 和 $\text{Pb}_{0.9}\text{La}_{0.1}\text{Zr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ 多层薄膜中存在耦合降低了多层薄膜的 P – E 电滞回线的滞后。



(a) Development of electrical tree in multilayer thin film^[180]



(b) Schematic image of interlayer coupling design^[184]

BMT is $\text{BiMg}_{0.5}\text{Ti}_{0.5}\text{O}_3$.

图 21 界面阻挡效应和层间耦合效应实例

Fig. 21 Examples of interface barrier effect and interlayer coupling effect

总的来说, 在多层薄膜中, 各种效应的影响通常是交织在一起, 并不是单一的。通常情况下, 在一种多层薄膜中会存在多种效应共同影响其电学性能和储能性能。因此, 在多层薄膜的设计和研究过程中, 应当综合考虑各种效应来改善多层薄膜的储能性能, 从而使电介质储能薄膜的性能得以进一步提升, 更好地满足实际应用需求。

3 总结与展望

在过去的几年里, 电介质储能陶瓷薄膜材料因其出色的功率密度、高速充放电速率和良好的温度稳定性以及循环稳定性受到广泛研究。本文从线性电介质、顺电材料、铁电材料、弛豫铁电材料、超顺电体材料和反铁电材料 6 个类别中总结了近年来

电介质储能陶瓷薄膜材料的研究进展,并详细介绍了从制备工艺、组分设计以及界面工程 3 个方面改善电介质储能陶瓷薄膜材料储能性能的方法。电介质储能陶瓷薄膜材料种类繁多、提升电介质储能陶瓷薄膜材料储能性能的手段也多种多样,这意味着在实际应用中,可以根据实际条件进行选择合适材料和改性方法,以更好的满足具体的使用需求。然而,电介质储能陶瓷薄膜仍然面临一些挑战,需要在未来的研究中得以解决。

1) 材料层面:目前的研究主要集中在单一材料的探索上,而不同材料体系之间的经验无法通用,这增加了新材料的研发难度。此外,即使在相同材料体系的薄膜制备中,不同研究团队制备出来的结果差异巨大,这反映了薄膜材料制备的过程中存在着一些因素影响薄膜材料的重复性。这使得电介质薄膜材料的研究多以定性分析为主,难以对不同研究团队的不同研究成果进行定量分析,从而严重限制了储能电介质薄膜物理机制的探索与数学模型的建立,阻碍了电介质储能陶瓷薄膜理论基础的发展。电介质储能陶瓷薄膜材料的 $P_{\max}$ 和 E_b 是相互制约的,目前的策略大多是在两者之间寻找平衡,是否存在一种手段可以同时增强 $P_{\max}$ 和 E_b 来增强储能性能,仍需进一步探索。

2) 器件层面:尽管已经完成了某些电介质储能陶瓷薄膜材料的制备,但实际应用的器件并没有得到广泛研发。陶瓷块体材料和聚合物基电介质材料具有相应的器件结构,如 MLCC 陶瓷电容器以及卷绕式聚合物基电容器。然而,目前,电介质储能陶瓷薄膜电容器的商业化应用仍然面临挑战。虽然前文所述清华大学研究团队制备了类似于 MLCC 的电介质薄膜电容器,展现了电介质储能陶瓷薄膜在器件制备方面的更进一步,向着实际应用迈出了步伐,但在器件设计与性能调控仍面临着挑战。研发陶瓷薄膜基新型器件,在器件制备的同时保持材料的卓越储能性能,探索电介质储能陶瓷薄膜电容器的工业化制备等问题仍需进一步解决。

综上所述,电介质储能陶瓷薄膜材料在储能领域具有广阔的应用前景,但在材料层面和器件层面仍然需要进一步的研究和发展。这将需要更多的跨学科合作和创新,以解决当前面临的挑战,推动电介质储能陶瓷薄膜材料的实际应用和工业化制备。

参考文献:

[1] WANG G, LU Z, LI Y, et al. Electroceramics for high-energy density

capacitors: Current status and future perspectives[J]. Chem Rev, 2021, 121: 6124–6172.

- [2] LIU G, LI Y, SHI M, et al. An investigation of the dielectric energy storage performance of $\text{Bi}(\text{Mg}_{2/3}\text{Nb}_{1/3})\text{O}_3$ -modified BaTiO_3 Pb-free bulk ceramics with improved temperature/frequency stability[J]. Ceram Int, 2019, 45(15): 19189–19196.
- [3] GUO B, ZHANG L, DONG J, et al. Enhanced energy storage properties of ZrO_2 -doped $(\text{Na}_{0.5}\text{Bi}_{0.5})_{0.4}\text{Sr}_{0.6}\text{TiO}_3$ Pb-free relaxor ferroelectric ceramics[J]. Ceram Int, 2021, 47(6): 8545–8554.
- [4] KHESRO A, KHAN F A, MUHAMMAD R, et al. Energy storage performance of Nd^{3+} -doped BiFeO_3 - BaTiO_3 -based lead-free ceramics[J]. Ceram Int, 2022, 48(20): 29938–29943.
- [5] LI Z, WANG Z, YANG Q, et al. Phase transition and energy storage properties of $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ - $\text{Bi}(\text{Mg}_{2/3}\text{Nb}_{1/3})\text{O}_3$ lead-free ceramics[J]. Ceram Int, 2023, 49(6): 9615–9621.
- [6] HAN D, WANG C, ZENG Z, et al. Ultrahigh energy efficiency of $(1-x)\text{Ba}_{0.85}\text{Ca}_{0.15}\text{Zr}_{0.1}\text{Ti}_{0.9}\text{O}_3$ - $x\text{Bi}(\text{Mg}_{0.5}\text{Sn}_{0.5})\text{O}_3$ lead-free ceramics[J]. J Alloys Compd, 2022, 902: 163721.
- [7] ZHANG L, WANG Z, LI Y, et al. Enhanced energy storage performance in Sn doped $\text{Sr}_{0.6}(\text{Na}_{0.5}\text{Bi}_{0.5})_{0.4}\text{TiO}_3$ lead-free relaxor ferroelectric ceramics[J]. J Eur Ceram Soc, 2019, 39(10): 3057–3063.
- [8] WANG G, LU Z, LI J, et al. Lead-free $(\text{Ba},\text{Sr})\text{TiO}_3$ - BiFeO_3 based multilayer ceramic capacitors with high energy density[J]. J Eur Ceram Soc, 2020, 40(4): 1779–1783.
- [9] WANG X, FAN Y, BIN Z, et al. High discharge energy density in novel $\text{K}_{1/2}\text{Bi}_{1/2}\text{TiO}_3$ - BiFeO_3 based relaxor ferroelectrics[J]. J Eur Ceram Soc, 2022, 42(15): 7381–7387.
- [10] PENG X, PU Y, DU X, et al. Optical transmittance and energy storage properties of potassium sodium niobate glass-ceramics[J]. J Eur Ceram Soc, 2023, 43(3): 966–973.
- [11] WANG C, LI H, ZHANG Q, et al. Ultrahigh energy storage density in $\text{Ba}_{0.85}\text{Ca}_{0.15}\text{Zr}_{0.1}\text{Ti}_{0.9}\text{O}_3$ -based lead-free ceramics by introducing a relaxor end-member[J]. J Eur Ceram Soc, 2023, 43(15): 6844–6853.
- [12] SHEN Z H, LIU H X, SHEN Y, et al. Machine learning in energy storage materials[J]. Interdiscip Mater, 2022, 1(2): 175–195.
- [13] LI W B, ZHOU D, LIU W F, et al. High-temperature BaTiO_3 -based ternary dielectric multilayers for energy storage applications with high efficiency[J]. Chem Eng J, 2021, 414: 128760.
- [14] ZHOU S, PU Y, ZHANG X, et al. High energy density, temperature stable lead-free ceramics by introducing high entropy perovskite oxide[J]. Chem Eng J, 2022, 427: 131684.
- [15] ZHOU X, XUE G, SU Y, et al. Optimized dielectric energy storage performance in ZnO -modified $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ - $\text{Sr}_{0.7}\text{Bi}_{0.2}\text{Ti}_{0.1}\text{O}_3$ ceramics with composite structure and element segregation[J]. Chem Eng J, 2023, 458: 141449.
- [16] LU Z, BAO W, WANG G, et al. Mechanism of enhanced energy storage density in AgNbO_3 -based lead-free antiferroelectrics[J]. Nano Energy, 2021, 79: 105423.
- [17] LIU H X, ZHU W X, MAO Q, et al. Single-crystalline $\text{BaZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ membranes enabled high energy density in PEI-based composites for high-temperature electrostatic capacitors[J]. Adv Mater, 2023, 35(22): 9.
- [18] ZHANG B, CHEN X M, WU W W, et al. Outstanding discharge energy density and efficiency of the bilayer nanocomposite films with BaTiO_3 -dispersed PVDF polymer and polyetherimide layer[J]. Chem Eng J, 2022, 446: 136926.
- [19] SUN W, LU X, JIANG J, et al. Dielectric and energy storage

- performances of polyimide/BaTiO₃ nanocomposites at elevated temperatures[J]. *J Appl Phys*, 2017, 121: 244101
- [20] FAN Z, ZHANG Y, JIANG Y, et al. Polymer composites with high energy density and charge-discharge efficiency at high temperature using aluminum oxide particles[J]. *J Mater Res Technol*, 2022, 18: 4367–4374.
- [21] ZHANG B, CHEN X M, PAN Z, et al. Superior high-temperature energy density in molecular semiconductor/polymer all-organic composites[J]. *Adv Funct Mater*, 2023, 33: 2210050.
- [22] LI Q, YAO F Z, LIU Y, et al. High-temperature dielectric materials for electrical energy storage[J]. *Annu Rev Mater Res*, 2018, 48(1): 219–243.
- [23] WANG R, ZHU Y, FU J, et al. Designing tailored combinations of structural units in polymer dielectrics for high-temperature capacitive energy storage[J]. *Nat Commun*, 2023, 14(1): 2406.
- [24] BOUHARRAS F E, LABARDI M, TOMBARI E, et al. Dielectric characterization of core-shell structured poly(vinylidene fluoride)-grafted-BaTiO₃ nanocomposites[J]. *Polymers*, 2023, 15(3): 595.
- [25] PAN Z, MAO M, ZHANG B, et al. Excellent energy storage performance in epoxy resin dielectric polymer films by a facile hot-pressing method[J]. *Polymers*, 2023, 15(10): 2315.
- [26] FAN Z, GAO S, CHANG Y, et al. Ultra-superior high-temperature energy storage properties in polymer nanocomposites via rational design of core-shell structured inorganic antiferroelectric fillers[J]. *J Mater Chem A*, 2023, 11(13): 7227–7238.
- [27] JI H, WANG D, BAO W, et al. Ultrahigh energy density in short-range tilted NBT-based lead-free multilayer ceramic capacitors by nanodomain percolation[J]. *Energy Storage Mater*, 2021, 38: 113–120.
- [28] FAN Y, WANG X, LI H, et al. Pb, Bi, and rare earth free X6R barium titanate-sodium niobate ceramics for high voltage capacitor applications[J]. *Appl Phys Lett*, 2023, 122: 143901.
- [29] LI W-B, ZHOU D, XU R, et al. BaTiO₃-based multilayers with outstanding energy storage performance for high temperature capacitor applications[J]. *ACS Appl Energy Mater*, 2019, 2(8): 5499–5506.
- [30] WANG D, FAN Z, ZHOU D, et al. Bismuth ferrite-based lead-free ceramics and multilayers with high recoverable energy density[J]. *J Mater Chem A*, 2018, 6(9): 4133–4144.
- [31] LI Z, YANG Q, WANG C, et al. A brief review of sodium bismuth titanate-based lead-free materials for energy storage: Solid solution modification, metal/metallic oxide doping, defect engineering and process optimizing[J]. *Crystals*, 2023, 13(2): 295.
- [32] LI Z, ZHANG D, WANG C, et al. The influence of BaTiO₃ content on the energy storage properties of Bi_{0.5}Na_{0.5}TiO₃-Bi(Mg_{2/3}Nb_{1/3})O₃ lead-free ceramics[J]. *Crystals*, 2023, 13: 733.
- [33] WANG G, LU Z, YANG H, et al. Fatigue resistant lead-free multilayer ceramic capacitors with ultrahigh energy density[J]. *J Mater Chem A*, 2020, 8(22): 11414–11423.
- [34] MA Z, LI Y, ZHAO Y, et al. High-performance energy-storage ferroelectric multilayer ceramic capacitors via nano-micro engineering[J]. *J Mater Chem A*, 2023, 11(13): 7184–7192.
- [35] ZHAO Q L, WANG Y K, HE G P, et al. Energy storage and thermodynamics of PNZST thick films with coexisting antiferroelectric and ferroelectric phases[J]. *Int J Appl Ceram Technol*, 2020, 18(1): 154–161.
- [36] ZHOU S, PU Y, ZHAO X, et al. Dielectric temperature stability and energy storage performance of NBT-based ceramics by introducing high-entropy oxide[J]. *J Am Ceram Soc*, 2022, 105(7): 4796–4704.
- [37] YANG H, BAO W, LU Z, et al. High-energy storage performance in BaTiO₃-based lead-free multilayer ceramic capacitors[J]. *J Mater Res*, 2021, 36(6): 1285–1294.
- [38] WANG D, FAN Z, LI W, et al. High energy storage density and large strain in Bi(Zn_{2/3}Nb_{1/3})O₃-doped BiFeO₃-BaTiO₃ ceramics[J]. *ACS Appl Energy Mater*, 2018, 1(8): 4403–4412.
- [39] YANG H, LU Z, LI L, et al. Novel BaTiO₃-based, Ag/Pd-compatible lead-free relaxors with superior energy storage performance[J]. *ACS Appl Mater Interfaces*, 2020, 12(39): 43942–43949.
- [40] WANG G, LI J, ZHANG X, et al. Ultrahigh energy storage density lead-free multilayers by controlled electrical homogeneity[J]. *Energy Environ Sci*, 2019, 12(2): 582–588.
- [41] LU Z, WANG G, BAO W, et al. Superior energy density through tailored dopant strategies in multilayer ceramic capacitors[J]. *Energy Environ Sci*, 2020, 13(9): 2938–2948.
- [42] LIANG Z, MA C, SHEN L, et al. Flexible lead-free oxide film capacitors with ultrahigh energy storage performances in extremely wide operating temperature[J]. *Nano Energy*, 2019, 57: 519–527.
- [43] QIAN J, HAN Y, YANG C, et al. Energy storage performance of flexible NKBT/NKBT-ST multilayer film capacitor by interface engineering[J]. *Nano Energy*, 2020, 74: 104862.
- [44] LEE H J, WON S S, CHO K H, et al. Flexible high energy density capacitors using La-doped PbZrO₃ anti-ferroelectric thin films[J]. *Appl Phys Lett*, 2018, 112(9): 092901.
- [45] CHEN Q, ZHANG Y, TANG M, et al. Significantly enhanced energy storage density and efficiency in flexible Bi_{3.15}Nd_{0.85}Ti₃O₁₂ thin film via periodic dielectric layers[J]. *J Appl Phys*, 2022, 131: 114101.
- [46] YANG C, LV P, QIAN J, et al. Fatigue-free and bending-endurable flexible Mn-doped Na_{0.5}Bi_{0.5}TiO₃-BaTiO₃-BiFeO₃ film capacitor with an ultrahigh energy storage performance[J]. *Adv Energy Mater*, 2019, 9: 1803949.
- [47] YANG C, QIAN J, HAN Y, et al. Design of an all-inorganic flexible Na_{0.5}Bi_{0.5}TiO₃-based film capacitor with giant and stable energy storage performance[J]. *J Mater Chem A*, 2019, 7(39): 22366–22376.
- [48] WANG W, QIAN J, GENG C, et al. Flexible lead-free Ba_{0.5}Sr_{0.5}TiO₃/0.4BiFeO₃-0.6SrTiO₃ dielectric film capacitor with high energy storage performance[J]. *Nanomaterials*, 2021, 11: 3065.
- [49] BIN C, HOU X, XIE Y, et al. Ultrahigh energy storage performance of flexible BMT-based thin film capacitors[J]. *Small*, 2022, 18(4): e2106209.
- [50] PALNEEDI H, PEDDIGARI M, HWANG G T, et al. High-performance dielectric ceramic films for energy storage capacitors: Progress and outlook[J]. *Adv Funct Mater*, 2018, 28: 1803665.
- [51] CHU Y-H. The superparaelectric battery[J]. *Science*, 2021, 374(6563): 33–34.
- [52] ZHANG L, LIU M, REN W, et al. ALD preparation of high-k HfO₂ thin films with enhanced energy density and efficient electrostatic energy storage[J]. *RSC Adv*, 2017, 7(14): 8388–8393.
- [53] SPAHR H, NOWAK C, HIRSCHBERG F, et al. Enhancement of the maximum energy density in atomic layer deposited oxide based thin film capacitors[J]. *Appl Phys Lett*, 2013, 103(4): 042907.
- [54] GAO W, YAO M, YAO X. Achieving ultrahigh breakdown strength and energy storage performance through periodic interface modification in SrTiO₃ thin film[J]. *ACS Appl Mater Interfaces*, 2018, 10(34): 28745–28753.
- [55] LIU J, WANG Y, ZHAI X, et al. Energy storage properties of sol-gel-processed SrTiO₃ films[J]. *Materials*, 2022, 16(1): 31.

- [56] ZHANG Y, LI W, WANG Z, et al. Ultrahigh energy storage and electrocaloric performance achieved in SrTiO_3 amorphous thin films via polar cluster engineering[J]. *J Mater Chem A*, 2019, 7(30): 17797–17805.
- [57] DIAO C, LIU H, LI Z, et al. Simultaneously achieved high energy storage density and efficiency in sol–gel-derived amorphous Mn-doped SrTiO_3 thin films[J]. *J Alloys Compd*, 2020, 845: 155636.
- [58] ZHANG G-F, LIU H, YAO Z, et al. Effects of Ca doping on the energy storage properties of (Sr, Ca) TiO_3 paraelectric ceramics[J]. *J Mater Sci Mater Electron*, 2015, 26(5): 2726–2732.
- [59] YANG B B, GUO M Y, SONG D P, et al. $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ thin film capacitors for energy storage applications[J]. *Appl Phys Lett*, 2017, 111: 183903.
- [60] KIM T Y, CHOI J O, ANOOP G, et al. (111)-oriented Sn-doped BaTiO_3 epitaxial thin films for ultrahigh energy density capacitors[J]. *Ceram Int*, 2021, 47(19): 26856–26862.
- [61] ZHAO Y, OUYANG J, WANG K, et al. Achieving an ultra-high capacitive energy density in ferroelectric films consisting of superfine columnar nanograins[J]. *Energy Storage Mater*, 2021, 39: 81–88.
- [62] SONG H, SON J Y. Energy storage and multiferroic properties of La-doped epitaxial BiFeO_3 thin films according to La doping concentration[J]. *J Energy Storage*, 2023, 68: 107729.
- [63] LIM K W, PEDDIGARI M, ANNAPUREDDY V, et al. Energy storage characteristics of {001} oriented $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ thin film grown by chemical solution deposition[J]. *Thin Solid Films*, 2018, 660: 434–438.
- [64] NGUYEN M D, NGUYEN C T Q, VU H N, et al. Experimental evidence of breakdown strength and its effect on energy-storage performance in normal and relaxor ferroelectric films[J]. *Curr Appl Phys*, 2019, 19(9): 1040–1045.
- [65] WANG F, CHEN J, TANG Z, et al. High energy storage properties for the lead-free NBT–0.1BFO–0.068La relaxor ferroelectric film[J]. *J Alloys Compd*, 2021, 854: 157306.
- [66] PENG B, TANG S, LU L, et al. Low-temperature-poling awakened high dielectric breakdown strength and outstanding improvement of discharge energy density of $(\text{Pb},\text{La})(\text{Zr},\text{Sn},\text{Ti})\text{O}_3$ relaxor thin film[J]. *Nano Energy*, 2020, 77: 105132.
- [67] ZHANG Y, LI W, WANG Z, et al. Perovskite $\text{Sr}_{1-x}(\text{Na}_{0.5}\text{Bi}_{0.5})_x\text{Ti}_{0.99}\text{Mn}_{0.01}\text{O}_3$ thin films with defect dipoles for high energy-storage and electrocaloric performance[J]. *ACS Appl Mater Interfaces*, 2019, 11(41): 37947–37954.
- [68] PAN H, ZENG Y, SHEN Y, et al. BiFeO_3 – SrTiO_3 thin film as a new lead-free relaxor-ferroelectric capacitor with ultrahigh energy storage performance[J]. *J Mater Chem A*, 2017, 5(12): 5920–5926.
- [69] LI D, ZHOU D, WANG D, et al. Lead-free relaxor ferroelectric ceramics with ultrahigh energy storage densities via polymorphic polar nanoregions design[J]. *Small*, 2023, 19(8): e2206958.
- [70] XIE Z, YUE Z, RUEHL G, et al. $\text{Bi}(\text{Ni}_{1/2}\text{Zr}_{1/2})\text{O}_3$ – PbTiO_3 relaxor-ferroelectric films for piezoelectric energy harvesting and electrostatic storage[J]. *Appl Phys Lett*, 2014, 104: 243902.
- [71] ZHAO W, LIU Z, SUN Z, et al. Superparamagnetic enhancement of thermoelectric performance[J]. *Nature*, 2017, 549(7671): 247–251.
- [72] WASER R. Dielectric analysis of integrated ceramic thin film capacitors[J]. *Integ Ferroelectr*, 2006, 15(1/4): 39–51.
- [73] CROSS L E. Relaxor ferroelectrics[J]. *Ferroelectrics*, 1987, 76(1): 241–267.
- [74] FAN J, WANG J, HE G, et al. Ultrahigh energy storage performance of a $0.75\text{Bi}_{0.47}\text{Na}_{0.47}\text{Ba}_{0.06}\text{TiO}_3$ – $0.25\text{CaTi}_{0.8}\text{Sn}_{0.2}\text{O}_3$ ceramic under moderate electric fields[J]. *Inorg Chem Front*, 2023, 10(18): 5475–5487.
- [75] YANG D, TIAN J, TIAN S, et al. Composition design of BNB–ST relaxor ferroelectric ceramics in superparaelectric state with ultrahigh energy density[J]. *Ceram Int*, 2023, 49(17): 27750–27757.
- [76] CAO W, CHEN P, LIN R, et al. Boosting energy-storage performance in lead-free ceramics via polyphase engineering in the superparaelectric state[J]. *Compos Part B Eng*, 2023, 255: 110630.
- [77] PAN H, LAN S, XU S, et al. Ultrahigh energy storage in superparaelectric relaxor ferroelectrics[J]. *Science*, 2021, 374(6563): 100–104.
- [78] WANG K, OUYANG J, WUTTIG M, et al. Superparaelectric $(\text{Ba}_{0.95}\text{Sr}_{0.05})(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ ultracapacitors[J]. *Adv Energy Mater*, 2020, 10(37): 2001778.
- [79] LIU Y, YANG B, LAN S, et al. Perspectives on domain engineering for dielectric energy storage thin films[J]. *Appl Phys Lett*, 2022, 120: 150501.
- [80] GLINCHUK M D, ELISEEV E A, MOROZOVSKA A N. Superparaelectric phase in the ensemble of noninteracting ferroelectric nanoparticles[J]. *Phys Rev B*, 2008, 78: 134107.
- [81] LI Y Z, WANG Z J, BAI Y, et al. High energy storage performance in Ca-doped PbZrO_3 antiferroelectric films[J]. *J Eur Ceram Soc*, 2020, 40(4): 1285–1292.
- [82] TANG Z, HU S, YAO D, et al. Enhanced energy-storage density and temperature stability of $\text{Pb}_{0.89}\text{La}_{0.06}\text{Sr}_{0.05}(\text{Zr}_{0.95}\text{Ti}_{0.05})\text{O}_3$ anti-ferroelectric thin film capacitor[J]. *J Materiomics*, 2022, 8(1): 239–246.
- [83] ZHANG Y, LI X, SONG J, et al. AgNbO_3 antiferroelectric film with high energy storage performance[J]. *J Materiomics*, 2021, 7(6): 1294–1300.
- [84] ALI F, LIU X, ZHOU D, et al. Silicon-doped hafnium oxide anti-ferroelectric thin films for energy storage[J]. *J Appl Phys*, 2017, 122(14): 144105.
- [85] ZHANG W L, MAO Y H, CUI L, et al. Impact of the radiation effect on the energy storage density and wake-up behaviors of antiferroelectric-like Al-doped HfO_2 thin films[J]. *Phys Chem Chem Phys*, 2020, 22(38): 21893–21899.
- [86] PAYNE A, BREWER O, LEFF A, et al. Dielectric, energy storage, and loss study of antiferroelectric-like Al-doped HfO_2 thin films[J]. *Appl Phys Lett*, 2020, 117(22): 221104.
- [87] FANG Y, BAI Y, LI Y Z, et al. Improved energy storage performance of PbZrO_3 antiferroelectric thin films crystallized by microwave radiation[J]. *Rsc Adv*, 2021, 11(30): 18387–18394.
- [88] NGUYEN M D, RIJNDERS G. Electric field-induced phase transition and energy storage performance of highly-textured PbZrO_3 antiferroelectric films with a deposition temperature dependence[J]. *J Eur Ceram Soc*, 2018, 38(15): 4953–4961.
- [89] LI Y Z, LIN J L, BAI Y, et al. Ultrahigh-energy storage properties of $(\text{PbCa})\text{ZrO}_3$ antiferroelectric thin films via constructing a pyrochlore nanocrystalline structure[J]. *ACS Nano*, 2020, 14(6): 6857–6865.
- [90] SHU L, ZHANG X, LI W, et al. Phase-pure antiferroelectric AgNbO_3 films on Si substrates: Chemical solution deposition and phase transitions[J]. *J Mater Chem A*, 2022, 10(23): 12632–12642.
- [91] ZHAI X, CHENG H, OUYANG J, et al. Achieving a high energy storage density in $\text{Ag}(\text{Nb},\text{Ta})\text{O}_3$ antiferroelectric films via nanograin engineering[J]. *J Adv Ceram*, 2023, 12(1): 196–206.

- [92] HOU C, HUANG W, ZHAO W, et al. Ultrahigh energy density in SrTiO₃ film capacitors[J]. ACS Appl Mater Interfaces, 2017, 9(24): 20484–20490.
- [93] ZHU H, LIU M, ZHANG Y, et al. Increasing energy storage capabilities of space-charge dominated ferroelectric thin films using interlayer coupling[J]. Acta Mater, 2017, 122: 252–258.
- [94] PAN H, LI F, LIU Y, et al. Ultrahigh-energy density lead-free dielectric films via polymorphic nanodomain design[J]. Science, 2019, 365(6453): 578–582.
- [95] CAI H, YAN S, ZHOU M, et al. Significantly improved energy storage properties and cycling stability in La-doped PbZrO₃ antiferroelectric thin films by chemical pressure tailoring[J]. J Eur Ceram Soc, 2019, 39(15): 4761–4769.
- [96] NGUYEN M D, TRINH T T, DANG H T, et al. Understanding the effects of electric-field-induced phase transition and polarization loop behavior on the energy storage performance of antiferroelectric PbZrO₃ thin films[J]. Thin Solid Films, 2020, 697: 137794.
- [97] NGUYEN M D. Towards low-temperature processing of lead-free BZT thin films for high-temperature energy storage performance[J]. J Alloys Compd, 2023, 959: 170597.
- [98] WU M, YU S, WANG X, et al. Influence of substrate temperature on the energy storage properties of bismuth magnesian niobium thin films prepared by magnetron sputtering[J]. Ceram Int, 2021, 47(6): 8265–8270.
- [99] HUANG R, WANG H, TAO C, et al. Evolution of polarization crystallites in 0.92BaTiO₃-0.08Bi(Ni_{0.5}Zr_{0.5})O₃ microcrystal-amorphous composite thin film with high energy storage capability and thermal stability[J]. Chem Eng J, 2022, 433: 133579.
- [100] LI Z, LIU H, YAO Z, et al. Novel BiAlO₃ dielectric thin films with high energy density[J]. Ceram Int, 2019, 45(17): 22523–22527.
- [101] LI X, SUN Z, SUN Y, et al. Effect of argon-oxygen ratio on dielectric and energy storage properties of Ba(Zr_{0.35}Ti_{0.65})O₃ thin films[J]. Ceram Int, 2022, 48(20): 29951–29958.
- [102] REDDY S R, PRASAD V V B, BYSAKH S, et al. Superior energy storage performance and fatigue resistance in ferroelectric BCZT thin films grown in an oxygen-rich atmosphere[J]. J Mater Chem C, 2019, 7(23): 7073–7082.
- [103] ZHU H, FENG G, CHEN X, et al. Energy storage and leakage current characteristics of low-temperature-derived Pb_{0.8}La_{0.1}Ca_{0.1}Ti_{0.975}O₃ thin films tailored by an annealing atmosphere[J]. J Phys Chem C, 2021, 125(5): 2831–2840.
- [104] WANG P, WANG X S, LI G R, et al. Nanocrystalline engineering induced high energy storage performances of fatigue-free Ba₂Bi_{3.9}Pr_{0.1}Ti₅O₁₈ ferroelectric thin films[J]. ACS Appl Mater Interfaces, 2022, 14(15): 17642–17651.
- [105] YANG B B, TONG H Y, LAN S, et al. Annealing atmosphere-dependent capacitive energy storage[J]. Rare Met, 2023, 42(5): 1465–1471.
- [106] FANG X G, LIN S X, ZHANG A H, et al. Effect of bottom electrodes on polarization switching and energy storage properties in Pb_{0.97}La_{0.02}(Zr_{0.95}Ti_{0.05})O₃ antiferroelectric thin films[J]. Solid State Commun, 2015, 219: 39–42.
- [107] GE J, DONG X, CHEN Y, et al. Enhanced polarization switching and energy storage properties of Pb_{0.97}La_{0.02}(Zr_{0.95}Ti_{0.05})O₃ antiferroelectric thin films with LaNiO₃ oxide top electrodes[J]. Appl Phys Lett, 2013, 102(14): 142905.
- [108] MA Q, LI X, ZHANG Y, et al. Dielectric and antiferroelectric properties of AgNbO₃ films deposited on different electrodes[J]. Coatings, 2022, 12(12): 1826.
- [109] LI Y, FANG X, HU F, et al. The effect of bottom electrode on structure and electrical properties of BaZr_{0.15}Ti_{0.85}O₃ films on SrTiO₃ substrates[J]. J Mater Sci Mater Electron, 2023, 34(8): 746.
- [110] ZHAO Q, LEI H, HE G, et al. Effects of thickness on energy storage of (Pb, La)(Zr, Sn, Ti)O₃ antiferroelectric films deposited on LaNiO₃ electrodes[J]. Ceram Int, 2016, 42(1): 1314–1317.
- [111] ZHU X, SHI P, LOU X, et al. Remarkably enhanced energy storage properties of lead-free Ba_{0.53}Sr_{0.47}TiO₃ thin films capacitors by optimizing bottom electrode thickness[J]. J Eur Ceram Soc, 2020, 40(15): 5475–5482.
- [112] HU G, MA C, WEI W, et al. Enhanced energy density with a wide thermal stability in epitaxial Pb_{0.92}La_{0.08}Zr_{0.52}Ti_{0.48}O₃ thin films[J]. Appl Phys Lett, 2016, 109: 193904.
- [113] ZHU X, GUO M, SUN B, et al. Significantly enhanced energy storage density of epitaxial Ba_{0.53}Sr_{0.47}TiO₃ thin films by optimizing bottom electrode material[J]. Ceram Int, 2020, 46(9): 13900–13906.
- [114] TONG S, MA B, NARAYANAN M, et al. Lead lanthanum zirconate titanate ceramic thin films for energy storage[J]. ACS Appl Mater Interfaces, 2013, 5(4): 1474–1480.
- [115] WU S, XU L, ZHU K, et al. Improved piezoelectricity and energy storage performance simultaneously achieved in [001]-preferentially oriented Bi_{0.5}Na_{0.5}TiO₃-BaTiO₃-BiMnO₃ thin films grown on Nb-doped SrTiO₃ single-crystalline substrates[J]. J Eur Ceram Soc, 2021, 41(4): 2539–2547.
- [116] ZHENG D, GENG W, QIAO X, et al. High energy storage of La-doped PbZrO₃ thin films using LaNiO₃/Pt composite electrodes with wide temperature range[J]. J Sol Gel Sci Technol, 2021, 98(1): 264–270.
- [117] LV P, HUANG S, CHENG X, et al. Enhanced energy storage property and dielectric tunability of Na_{0.5}Bi_{0.5}(Ti, W, Ni)O₃ thin film on Bi(Fe, Mn)O₃ buffered LaNiO₃(100)/Si substrate[J]. J Mater Sci Mater Electron, 2018, 29(17): 14479–14486.
- [118] SUI H, SUN H, XIAO S, et al. Boosting energy storage performance of relaxor Na_{0.5}Bi_{0.5}(Fe_{0.03}Ti_{0.97})O₃/Na_{0.5}Bi_{0.5}(Zr_{0.02}Ti_{0.98})O₃-based multilayer thin films under moderate electric field via aging & treating processing[J]. J Power Sources, 2021, 506: 230190.
- [119] XIAO S, SUN H, LIU X, et al. High-performance (Na_{0.5}Bi_{0.5})(Ti_{0.97}Fe_{0.03})O₃-based heterostructure thin films for energy storage capacitors[J]. Ceram Int, 2022, 48(15): 21407–21415.
- [120] YAN C, LIU X, YUE C, et al. Outstanding enhanced breakdown field strength and energy storage properties in Na_{0.5}Bi_{0.5}TiO₃-based thin film by the aging process[J]. J Power Sources, 2021, 508: 230331.
- [121] YUE C, SUN H, YAN C, et al. Optimized energy storage performance by a depolarization field in BaMn_{0.01}Ti_{0.99}O₃/Na_{0.5}Bi_{0.5}TiO₃ multilayer thin films[J]. J Mater Chem C, 2022, 10(28): 10356–10364.
- [122] YANG B, ZHANG Q, HUANG H, et al. Engineering relaxors by entropy for high energy storage performance[J]. Nat Energy, 2023, 8: 956–964.
- [123] HU J, LI W, TANG X, et al. Enhancement of energy storage density and efficiency of PbHfO₃ doped with La antiferroelectric thin films[J]. ACS Appl Energy Mater, 2022, 6(1): 120–126.
- [124] NGUYEN M D. Ultrahigh energy-storage performance in lead-free BZT thin-films by tuning relaxor behavior[J]. Mater Res Bull, 2021, 133: 111072.
- [125] ZHAN X, HUI Z, YANG J, et al. Energy storage performances of La

- doping BaBi₄Ti₄O₁₅ thin films capacitors[J]. Results Phys, 2023, 44: 106160.
- [126] SONG B, WU S, YAN H, et al. Fatigue-less relaxor ferroelectric thin films with high energy storage density via defect engineer[J]. J Mater Sci Technol, 2021, 77: 178–186.
- [127] WANG H, HAO H, LI D, et al. Synergistic effect enhances energy storage properties of BNT-based relaxor ferroelectric thin films[J]. Ceram Int, 2023, 49(8): 12443–12451.
- [128] GENG J, LI D, HAO H, et al. Tunable phase structure in Mn-doped lead-free BaTiO₃ crystalline/amorphous energy storage thin films[J]. Crystals, 2023, 13(4): 649.
- [129] LUO B, DONG H, WANG D, et al. Large recoverable energy density with excellent thermal stability in Mn-modified NaNbO₃-CaZrO₃ lead-free thin films[J]. J Am Ceram Soc, 2018, 101(8): 3460–3467.
- [130] SONG H, SON J Y. Examining imprinted ferroelectric hysteresis loops and improved energy storage properties of Mn-doped epitaxial SrTiO₃ thin films using heat treatment[J]. Mater Sci Eng B, 2022, 285: 115925.
- [131] LIU Y, HAO X, AN S. Significant enhancement of energy-storage performance of (Pb_{0.91}La_{0.09})(Zr_{0.65}Ti_{0.35})O₃ relaxor ferroelectric thin films by Mn doping[J]. J Appl Phys, 2013, 114: 174102.
- [132] YE M, SUN Q, CHEN X, et al. Effect of Eu doping on the electrical properties and energy storage performance of PbZrO₃ antiferroelectric thin films[J]. J Am Ceram Soc, 2011, 94(10): 3234–3236.
- [133] RATH M, MIRYALA M, MURAKAMI M, et al. Controlled piezotronic properties on recoverable energy storage density in rare-earth ions doped epitaxial PZT thin films[J]. J Phys D Appl Phys, 2019, 52: 304001.
- [134] SONG D P, YANG J, SUN J X, et al. Controlling the crystallization of Nd-doped Bi₄Ti₃O₁₂ thin-films for lead-free energy storage capacitors[J]. J Appl Phys, 2020, 127: 224102.
- [135] GUO X, GE J, PONCHEL F, et al. Effect of Sn substitution on the energy storage properties of high (001)-oriented PbZrO₃ thin films[J]. Thin Solid Films, 2017, 632: 93–96.
- [136] HAO X, ZHAI J, YAO X. Improved energy storage performance and fatigue endurance of Sr-doped PbZrO₃ antiferroelectric thin films[J]. J Am Ceram Soc, 2009, 92(5): 1133–1135.
- [137] THATIKONDA S K, HUANG W, DU X, et al. Sm-doping induced large enhancement of antiferroelectric and energy storage performances of (111) oriented PbZrO₃ thin films[J]. Ceram Int, 2019, 45(17): 23586–23591.
- [138] XIE Y, HAO H, HUANG Z, et al. Large energy-storage density with good dielectric property in bismuth sodium titanate-based thin films[J]. J Alloys Compd, 2021, 884: 161031.
- [139] WU S, CHEN P, ZHAI J, et al. Enhanced piezoelectricity and energy storage performances of Fe-doped BNT-BKT-ST thin films[J]. Ceram Int, 2018, 44(17): 21289–21294.
- [140] QIAN J, YANG C H, HAN Y J, et al. Reduced leakage current, enhanced energy storage and dielectric properties in (Ce,Mn)-codoped Ba_{0.6}Sr_{0.4}TiO₃ thin film[J]. Ceram Int, 2018, 44(17): 20808–20813.
- [141] LI P, ZHAI J, SHEN B, et al. High recoverable energy storage density and large piezoelectric response in (Bi_{0.5}Na_{0.5})TiO₃-PbTiO₃ thin films prepared by a sol-gel method[J]. J Eur Ceram Soc, 2017, 37(10): 3319–3327.
- [142] PAN Z, WANG P, HOU X, et al. Fatigue-free Aurivillius phase ferroelectric thin films with ultrahigh energy storage performance[J]. Adv Energy Mater, 2020, 10: 2001536.
- [143] LV P, QIAN J, YANG C, et al. 4-inch ternary BiFeO₃-BaTiO₃-SrTiO₃ thin film capacitor with high energy storage performance[J]. ACS Energy Lett, 2021, 6(11): 3873–3881.
- [144] DONG H, LUO B, JIN K. Structural, electrical and energy storage properties of lead-free NaNbO₃-BaHfO₃ thin films[J]. J Phys Chem Solids, 2022, 162: 110513.
- [145] YU S, ZHANG C, WU M, et al. Energy storage and dielectric properties of a novel Bi_{1.5}MgNb_{1.5}O₇-Bi₂Mg_{2/3}Nb_{4/3}O₇ thin film[J]. Ceram Int, 2021, 47(1): 1238–1243.
- [146] WANG C, SUN N, LI Y, et al. Dielectric property and energy-storage performance of (100)-preferred (1-x)PbTiO₃-xBi(Mg_{0.5}Ti_{0.5})O₃ relaxor ferroelectric thin films[J]. J Alloys Compd, 2019, 810: 151796.
- [147] CHO S, YUN C, KIM Y S, et al. Strongly enhanced dielectric and energy storage properties in lead-free perovskite titanate thin films by alloying[J]. Nano Energy, 2018, 45: 398–406.
- [148] CHEN P, WU S, LI P, et al. High recoverable energy storage density in (1-x)Bi_{0.5}(Na_{0.8}K_{0.2})_{0.5}TiO₃-xSrZrO₃ thin films prepared by a sol-gel method[J]. J Eur Ceram Soc, 2018, 38(14): 4640–4645.
- [149] YANG B B, GUO M Y, SONG D P, et al. Energy storage properties in BaTiO₃-Bi_{3.25}La_{0.75}Ti₃O₁₂ thin films[J]. Appl Phys Lett, 2018, 113: 183902.
- [150] QIAN J, LI G, ZHU K, et al. High energy storage performance and large electrocaloric response in Bi_{0.5}Na_{0.5}TiO₃-Ba(Zr_{0.2}Ti_{0.8})O₃ thin films[J]. ACS Appl Mater Interfaces, 2022, 14(48): 54012–54020.
- [151] AFIFI M, TURKY A O, RASLY M, et al. Field-induced polarization response and energy storage behavior of lead-free BNT-BKT-SZ films[J]. Ceram Int, 2020, 46(16): 26061–26068.
- [152] HAN Y, JIAO P, YANG Y, et al. Energy storage properties in a Bi(Mg_{1/2}Ti_{1/2})O₃ modified BiFeO₃-Sr_{0.7}Bi_{0.2}TiO₃ film[J]. Appl Phys Lett, 2021, 119: 162901.
- [153] QI H, CHEN L, DENG S, et al. High-entropy ferroelectric materials[J]. Nat Rev Mater, 2023, 8(6): 355–356.
- [154] YANG B, ZHANG Y, PAN H, et al. High-entropy enhanced capacitive energy storage[J]. Nat Mater, 2022, 21(9): 1074–1080.
- [155] LIU M, GONG C Z, YANG B B, et al. Achieving high energy storage performances in high-entropy epitaxial Na_{0.5}Bi_{0.5}Ti_{0.7}Hf_{0.1}Zr_{0.1}Sn_{0.1}O₃ thin film[J]. Appl Phys Lett, 2022, 121: 263903.
- [156] WANG Y J, LAI H C, CHEN Y A, et al. High entropy nonlinear dielectrics with superior thermally stable performance[J]. Adv Mater, 2023: e2304128.
- [157] SHARMA Y, LEE M C, PITIKI K C, et al. High entropy oxide relaxor ferroelectrics[J]. ACS Appl Mater Interfaces, 2022, 14(9): 11962–11970.
- [158] ZHANG Y, CHEN L, LIU H, et al. High-performance ferroelectric based materials via high-entropy strategy: Design, properties, and mechanism[J]. Infor Mater, 2023: e12488.
- [159] SA T, CAO Z, WANG Y, et al. Enhancement of charge and energy storage in PbZrO₃ thin films by local field engineering[J]. Appl Phys Lett, 2014, 105(4): 043902.
- [160] LI Y Z, WANG Z J, BAI Y, et al. Enhancement of energy storage density in antiferroelectric PbZrO₃ films via the incorporation of gold nanoparticles[J]. J Am Ceram Soc, 2019, 102(9): 5253–5261.
- [161] GUO F, SHI Z, YANG B, et al. The role of PN-like junction effects in energy storage performances for Ag₂O nanoparticle dispersed lead-free K_{0.5}Na_{0.5}NbO₃-BiMnO₃ films[J]. Nanoscale, 2020, 12(14): 7544–7549.
- [162] SILVA J P B, SILVA J M B, OLIVEIRA M J S, et al.

- High-performance ferroelectric–dielectric multilayered thin films for energy storage capacitors[J]. *Adv Funct Mater*, 2018, 29: 1807196.
- [163] MCMILLEN M, DOUGLAS A M, CORREIA T M, et al. Increasing recoverable energy storage in electroceramic capacitors using “dead-layer” engineering[J]. *Appl Phys Lett*, 2012, 101: 242909.
- [164] CHEN X, PENG B, DING M, et al. Giant energy storage density in lead-free dielectric thin films deposited on Si wafers with an artificial dead-layer[J]. *Nano Energy*, 2020, 78: 105390.
- [165] WANG K, ZHANG Y, WANG S, et al. High Energy performance ferroelectric (Ba,Sr)(Zr,Ti)O₃ film capacitors integrated on Si at 400 °C[J]. *ACS Appl Mater Interfaces*, 2021, 13(19): 22717–22727.
- [166] ZHANG T, LI W, CAO W, et al. Giant electrocaloric effect in PZT bilayer thin films by utilizing the electric field engineering[J]. *Appl Phys Lett*, 2016, 108: 162902.
- [167] ZHANG Y, LI W, XU S, et al. Interlayer coupling to enhance the energy storage performance of Na_{0.5}Bi_{0.5}TiO₃–SrTiO₃ multilayer films with the electric field amplifying effect[J]. *J Mater Chem A*, 2018, 6(47): 24550–24559.
- [168] WANG P, WANG X, LI G, et al. Interface engineering to optimize polarization and electric breakdown strength of Ba₂Bi_{3.97}Pr_{0.03}Ti₅O₁₈/BiFeO₃ ferroelectric thin-film for high-performance capacitors[J]. *Chem Eng J*, 2022, 433: 133676.
- [169] SHEN B, LI Y, SUN N, et al. Enhanced energy-storage performance of an all-inorganic flexible bilayer-like antiferroelectric thin film *via* using electric field engineering[J]. *Nanoscale*, 2020, 12(16): 8958–8968.
- [170] SONG B, ZHU K, YAN H, et al. High energy storage density with high power density in Bi_{0.2}Sr_{0.7}TiO₃/BiFeO₃ multilayer thin films[J]. *J Mater Chem C*, 2021, 9(13): 4652–4660.
- [171] SUI H, SUN H, YAN C, et al. The construction of relaxor perovskite Na_{0.5}Bi_{0.5}(Fe_{0.03}Ti_{0.97})O₃/Ba(Ti_{1-x}Sr_x)O₃ multilayer thin film and explorations on origin of the enhanced energy storage performance[J]. *Appl Surface Sci*, 2021, 543: 148755.
- [172] ZUBKO P, JUNG D J, SCOTT J F. Space charge effects in ferroelectric thin films[J]. *J Appl Phys*, 2006, 100(11): 114112.
- [173] TAGANTSEV A K, LANDIVAR M, COLLA E, et al. Identification of passive layer in ferroelectric thin films from their switching parameters[J]. *J Appl Phys*, 1995, 78(4): 2623–2630.
- [174] ZHANG T, LI W, ZHAO Y, et al. High energy storage performance of opposite double-heterojunction ferroelectricity-insulators[J]. *Adv Funct Mater*, 2018, 28(10): 1706211.
- [175] YE Y, GUO K, CUI R, et al. Enhancing the energy storage density of Bi_{0.5}Na_{0.5}TiO₃ thin films by adding an amorphous alumina[J]. *Surf Interfaces*, 2022, 33: 102229.
- [176] LI Z, ZHAO Y, LI W, et al. Enhanced energy storage properties of amorphous BiFeO₃/Al₂O₃ multilayers[J]. *J Mater Res Technol*, 2021, 11: 1852–1858.
- [177] ZHANG T, YIN C, ZHANG C, et al. Self-polarization and energy storage performance in antiferroelectric-insulator multilayer thin films[J]. *Compos Part B Eng*, 2021, 221: 109027.
- [178] YIN C, ZHANG T, SHI Z, et al. High energy storage performance of all-inorganic flexible antiferroelectric-insulator multilayered thin films[J]. *ACS Appl Mater Interfaces*, 2022, 14(25): 28997–29006.
- [179] CHEN J, TANG Z, YANG B, et al. Ultra-high energy storage performances regulated by depletion region engineering sensitive to the electric field in PNP-type relaxor ferroelectric heterostructural films[J]. *J Mater Chem A*, 2020, 8(16): 8010–8019.
- [180] FAN Q, LIU M, MA C, et al. Significantly enhanced energy storage density with superior thermal stability by optimizing Ba(Zr_{0.15}Ti_{0.85})O₃/Ba(Zr_{0.35}Ti_{0.65})O₃ multilayer structure[J]. *Nano Energy*, 2018, 51: 539–545.
- [181] MAHESH M L V, PAL P, PRASAD V V B, et al. Improved tunability and energy storage density properties of low-loss, lead-free (Ba_{0.50}Sr_{0.50})TiO₃ and Ba(Zr_{0.15}Ti_{0.85})O₃ bilayer thin film stacks[J]. *J Electron Mater*, 2021, 51(2): 727–735.
- [182] YUE W, LI T, YU L, et al. High energy storage density of Bi_{3.25}La_{0.75}Ti₃O₁₂/SrTiO₃ multilayer thin films by structural design[J]. *Mater Lett*, 2023, 333: 133576.
- [183] NGUYEN M D, BIRKHÖLZER Y A, HOUWMAN E P, et al. Enhancing the energy-storage density and breakdown strength in PbZrO₃/Pb_{0.9}La_{0.1}Zr_{0.52}Ti_{0.48}O₃-derived antiferroelectric/relaxor-ferroelectric multilayers[J]. *Adv Energy Mater*, 2022, 12(29): 2200517.
- [184] BIN C, HOU X, WANG K, et al. Interlayer coupling enhanced energy storage performance in a flexible BMT–BTO/BMT multilayer ferroelectric film capacitor[J]. *ACS Appl Mater Interfaces*, 2022, 14(45): 50880–50889.

Research Progress and Modification Methods of Dielectric Energy Storage Ceramic Thin Films

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Extended Abstract

In recent years, with a rapid societal development, the utilization of clean energy becomes a necessity. This demand emphasizes on energy storage equipment, prompts some research on efficient energy storage, energy loss reduction, and environmental impact mitigation. The existing prevalent energy storage devices encompass batteries, supercapacitors, and dielectric capacitors. Batteries boast a maximum energy storage density, but exhibit a comparatively lower power density. Supercapacitors strike a balance with a moderate energy storage and a power density. Dielectric capacitors, characterized by their unparalleled power density and rapid charge/discharge rate, have extensive applications in various domains such as pulsed laser weaponry, cardiac pacemakers, and energy vehicles.

Thin film materials emerge as a favorable option for addressing device miniaturization and enhancing energy density due to their smaller volume and higher energy storage density compared to polymers and block ceramics. The energy storage ceramic thin film materials can be classified based on intrinsic polarization states, *i.e.*, encompassing linear dielectric (LD), paraelectric (PE), ferroelectric (FE), relaxation ferroelectric (RFE), superparaelectric (SPE), and antiferroelectric (AFE) materials.

LD exhibits notable breakdown strength (E_b) and energy storage efficiency (η). However, their low dielectric constant (ϵ_r) and polarization (P) result in a diminished energy storage density (U_{rec}). Elevating ϵ_r stands as a pivotal for enhancing the U_{rec} of LD. PE demonstrates non-linear changes in P and ϵ_r with applied electric fields (E). For the removal of E , PE maintains a non-polar state without spontaneous polarization, featuring a medium P and a substantial E_b . FE exhibits a spontaneous polarization with large P and ϵ_r . Nevertheless, their prominent residual polarization (P_r), dielectric loss ($\tan\delta$), and increased defect density contribute to a lowered E_b , constraining the application of FE in energy storage. Recent research in FE focuses on mitigating P_r and augmenting E_b . In contrast to FE, RFE typically exhibits nanodomains or polar nanodomains in their domain structure. The coupling among these domains is relatively weak, rendering them highly responsive to electric fields. RFE often displays a substantial P , a minimal P_r , and a slender P - E hysteresis loop. This characteristic facilitates the attainment of elevated U_{rec} and η . SPE maintains a local polar order, manifesting as polarity clusters spanning only a few nanometers or cells. This arrangement further diminishes mutual coupling between domains, reducing a polarity-switching energy barrier. Losses are minimized, significantly enhancing both U_{rec} and η . AFE features a distinctive double hysteresis loop, stemming from the parallel and opposite alignment of spontaneous polarization on adjacent lattices. This configuration results in near-zero P_r , undergoing a reversible AFE-FE phase transition under specific E , and yielding a high ϵ_r and substantial P . This property enables the achievement of a heightened U_{rec} , presenting promising applications in energy storage.

In the realm of energy storage ceramic thin film materials, enhancing P_{max} , E_b , and minimizing P_r are pivotal for improving energy storage performance. To achieve these objectives, diverse modification methods are used to encompass the preparation technology, component design, and interface engineering.

For the effective preparation, optimization of preparation methods, alteration of annealing processes, substitution of electrode materials, aging, and the fabrication of multi-layer film capacitors (MLFC) are employed. These interventions regulate the orientation growth and oxygen vacancy content of the material, thereby enhancing the energy storage performance of the ceramic thin film capacitor. Note that the preparation of MLFC demonstrates a substantial U_{rec} (*i.e.*, 78.3 J/cm³) and η (*i.e.*, 90.2%) and offers valuable insights for the commercialization of ceramic film capacitors.

The composition design encompasses elements such as doping, two-phase or multiphase solid solutions, entropy control, and incorporation of nanoparticles. Specifically, element doping and the creation of two-phase or multiphase solid solutions can achieve a slender P - E hysteresis loop *via* transforming FE to RFE. Using Mn²⁺ to form defect complexes with oxygen vacancies is investigated. This reduces the oxygen vacancy content and curbs leakage current density, thereby enhancing the energy storage performance for various energy storage ceramic thin film materials. This method offers a universal approach to mitigating leakage current issues. Entropy control strategies introduce multiple elements into the system, utilizing chemical disorder caused by atomic size mismatch to reduce P_r and delay saturation polarization, thereby improving energy storage performance. Nanoparticle composite can be prepared *via* adding the nanoparticles into matrix material evenly, with the base materials to improve the energy storage of materials performance as a whole.

Interface engineering primarily enhances E_b *via* manipulating material structures, incorporating effects (*i.e.*, ‘dead-layer’ effect, electric field amplification effect, space charge effect, heterojunction effect, interface barrier effect, and interlayer coupling effect). This optimization aims to achieve a superior energy storage performance. Multilayer films in interface engineering typically involve the use of two or more component materials, allowing the strategic utilization of diverse material characteristics to maximize effectiveness. For instance, ‘dead-layer’ engineering involves the incorporation of high resistivity and low ϵ_r Al₂O₃ layer as the top layer, enhancing the E_b of the multilayer film. In multilayer films, the interplay of various effects collectively affects their electrical properties and energy storage performance. The comprehensive consideration of these effects is crucial in the design and research of multilayer films. The energy storage performance of multilayer films can be improved, further aligning dielectric energy storage films with the practical applications.

Summary and prospects Dielectric energy storage ceramic thin film materials have attracted recent attention due to their superior power density and rapid charge/discharge rate. This review summarized recent research progress on dielectric energy storage ceramic thin film materials (*i.e.*, linear dielectric, paraelectric, ferroelectric, relaxation ferroelectric, superparaelectric, and antiferroelectric materials). This review also represented the enhanced energy storage performance *via* the preparation processes, component design, and interface engineering. With a diverse range of dielectric energy storage ceramic thin film materials and various methods for improving their energy storage performance, the practical applications can tailor material selection and modification approaches. To achieve the commercialization of dielectric energy storage ceramic thin films, efforts should be made for strengthening theoretical research and developing new types of ceramic thin film-based devices. This can maintain the superior energy storage performance while preparing devices, thereby laying a foundation for the application of dielectric energy storage ceramic thin film capacitors.

Keywords ceramic thin film; dielectrics; capacitor; energy storage performance