

NaNbO₃ 基无铅储能介质陶瓷研究进展

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摘 要: 高性能环境友好型 NaNbO₃(NN)基储能介质陶瓷由于其功率密度高、放电时间短, 在脉冲功率电子器件方面具有广泛的应用。优异的储能性能及其温度稳定性、抗疲劳特性及工艺重复性等综合性能是 NN 基无铅陶瓷被广泛应用的前提。本文主要综述近几年来国内外有关 NN 基储能陶瓷的相结构调控、微观形貌优化、掺杂改性(A 位、B 位及 A/B 位共掺)以及相关机理研究方面的进展和动向。最后, 对 NN 基无铅储能陶瓷在原料制备、烧结工艺、成型工艺、理论研究和器件研制方面的未来发展进行展望。

关键词: 无铅反铁电陶瓷; 铌酸钠; 掺杂改性; 电介质储能

中图分类号: TQ174 文献标志码: A 文章编号: 0454-5648(2024)04-1460-17

网络出版时间: 2024-03-09



电介质电容器是通过电介质在电场的作用下极化和退极化来存储和释放电能的储能装置^[1]。和超级电容器及电池相比, 电介质电容器可以实现超快的充放电速率($<100\text{ ns}$)及超高的功率密度(10^7 W/kg), 广泛应用于各种场合, 比如混合动力电动汽车、起搏器和电子电路^[2-3]。但是, 电介质电容器的储能密度相对较低($10^{-2}\sim 10^{-1}\text{ W}\cdot\text{h/kg}$), 不能满足电子器件小型化、轻量化的要求, 极大的限制了其实际应用。如果能够研发出和电池相媲美的储能密度, 电介质电容器更广泛的应用将成为可能。电介质电容器目前有 5 大类, 分别为聚合物电容器、玻璃电容器、陶瓷电容器、玻璃陶瓷电容器及陶瓷聚合物复合材料电容器^[4-5]。相比之下, 陶瓷电容器拥有高的介电常数、中等的击穿场强、良好的频率和温度稳定性

等特点被认为是非常有潜力的电介质电容器。

目前, 陶瓷电容器主要分为线性电介质、铁电体、弛豫铁电体及反铁电体, 如图 1 所示。线性电介质的极化强度随着电场的增加呈现线性变化, 不存在滞后的现象, 因此储能效率较高, 如图 1a 所示。但是其低的极化强度及介电常数严重限制了其在储能方面的应用。铁电体在去除外加电场后, 极化不会立刻丧失。如图 1b 所示, 在铁电体中, 由于畴内的偶极子具有相同的极化取向, 外加电场使畴可以自由切换, 这使得其具有高的介电常数及介电损耗, 伴随着高的剩余极化, 导致较低的可恢复能量密度, 不适用于储能应用。弛豫铁电体具有细长的电滞回线, 其内部的极性纳米微区对外加电场非常敏感, 去掉电场后可以迅速恢复到原始状态, 因此具有低

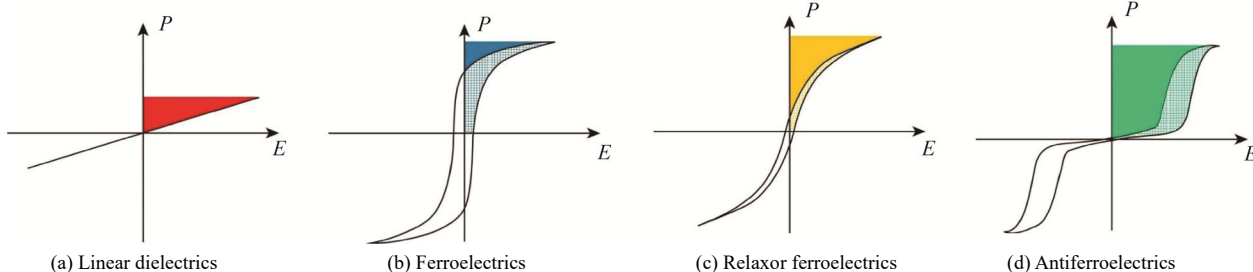


图 1 电滞回线示意图^[6]

Fig. 1 Schematic diagrams of hysteresis loops^[6]

收稿日期: 2023-12-07. 修订日期: 2023-12-23.

基金项目: 国家重点研发计划(2021YFB3800602); 国家自然科学基金项目(51972260, 52072295); 中央高校基本科研业务费。

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Received date: 2023-12-07. Revised date: 2023-12-23.

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的剩余极化,高的储能效率,其在储能陶瓷领域被广泛研究,但击穿场强有待进一步提高,如图 1c 所示。和其他电介质相比,反铁电体因具有可自发的反平行极化偶极矩,当施加的电场为零时,单位晶胞内的极化相互抵消,剩余极化几乎为零,如图 1d 所示。目前,弛豫反铁电体的研究被大量的科研工作者广泛关注。通常来讲,在铁电体中通过调控畴的尺寸到微米或者纳米尺度可以获得拥有低损耗的细电滞回线。由于局部随机场的存在,拥有极性纳米微区的弛豫铁电体表现出无迟滞极化响应的特点,需要极高的外加电场才能形成饱和的长程有序铁电态。基于同样的原因,弛豫反铁电体是指长程有序的反铁电畴被打破,形成具有微米或者纳米尺度的畴尺寸,其对外加电场有快速的响应,减少施加或者卸载电场之间的极化滞后,进而获得优异的储能性能。

由于含铅材料对环境有较大的污染及对人体有害,欧盟已经发布了有关“废弃电子电器设备(WEEE)”的指令,因此发展新型无铅陶瓷体系迫在眉睫^[7]。目前,研究最多的无铅储能陶瓷主要有 BaTiO_3 (BT) 基、 $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ (BNT) 基、 $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ (KNN) 基、 AgNbO_3 (AN) 基、 NaNbO_3 (NN)基等。BT 基陶瓷具有较高的极化强度,但是 Curie 温度较低,因此其具有较差的温度稳定性。BNT 基陶瓷在储能方面表现出了较大的优势,可以通过引入弛豫态获得较高的储能效率,但是其击穿场强还需进一步提高。KNN 基陶瓷拥有高的介电常数及高的 Curie 温度等特点,但是其在烧结过程中 K 和 Na 的挥发使得其烧成温度区间较窄,可重复性较差。AN 陶瓷在室温呈现双电滞回线,并且通过化学改性可以明显改善其储能性能。但是,制备 AN 陶瓷需要一定的烧结气氛,同时 Ag 原料非常昂贵,很难控制烧结过程中的变量,因此进行工业生产有一定的困难。和其他材料相比,NN 基陶瓷具有更宽的带隙,更低廉的成本(Na 原料比较低廉,在空气气氛即可烧结,无需其他气氛),较高的极化强度等特点受到了学者们的广泛关注。

NN 是一个典型的反铁电陶瓷材料,最早谈论其反铁电特性可追溯到 20 世纪 50 年代^[8]。对于 AN 陶瓷而言,其在室温可呈现出双电滞回线,但是 NN 陶瓷由于表现出反铁电相和铁电相的不可逆转变,因此纯 NN 陶瓷目前并没有表现出双电滞回线的特征。随后, Cross 等^[9]以单晶 NN 为研究对象,施加一个沿 *c* 轴的电场,当达到一定电场强度(90 kV/cm)时, NN 单晶呈现出双电滞回线。但是, NN 单晶经过多次循

环后反铁电特性被铁电特性取代,双电滞回线特性消失,表明其反铁电是不稳定的。

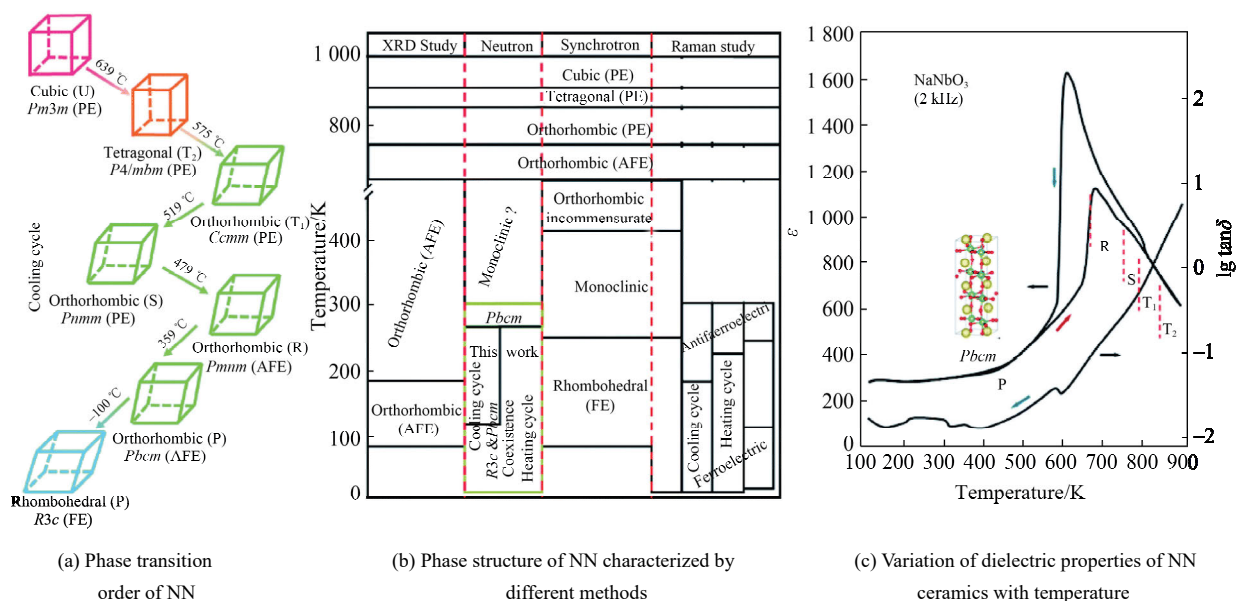
目前,还没有双电滞回线在纯的 NN 多晶陶瓷中呈现出来。大量的科研工作者采用固溶的方式来稳定反铁电相,以期室温下在多晶陶瓷中获得双电滞回线。直到 20 世纪末,很多学者对 NN 陶瓷的研究重点主要是介电性能、电场导致的相转变行为,并且通过一些先进的表征技术(如原位 X 射线衍射、中子衍射等)来深入研究其结构特性。最近,科学界对新型储能陶瓷材料的研究兴趣越来越大,学者们通过掺杂改性在室温获得了具有优异储能性能的新型 NN 基陶瓷材料。

本文主要以 NN 陶瓷为研究对象,介绍了材料的基本结构及储能性能,重点阐述了 NN 陶瓷在微观形貌优化及电学性能增强方面的研究进展,并展望了 NN 基无铅储能陶瓷材料的发展趋势。

1 铌酸钠不同相结构的关系

NN 陶瓷随着温度的升高或者降低表现出复杂的相转变。图 2a 为 NN 从高温至低温的相变序列。在降温过程中, NN 大致依次经历:顺电立方相 $U(Pm3m) \xrightarrow{630^\circ\text{C}}$ 顺电四方相 $T2(P4/mbm) \xrightarrow{575^\circ\text{C}}$ 顺电正交相 $T1(Ccm) \xrightarrow{519^\circ\text{C}}$ 顺电正交相 $S(Pnmm) \xrightarrow{479^\circ\text{C}}$ 反铁电正交相 $R(Pmnm) \xrightarrow{359^\circ\text{C}}$ 反铁电正交相 $P(Pbcm) \xrightarrow{-100^\circ\text{C}}$ 铁电三方相 $N(R3c)$ 。不同的相结构是由 2 种因素决定: Nb^{5+} 在氧八面体中心的位移和氧八面体的倾斜程度^[10]。虽然对 NN 的结构做了大量的研究,但是具体的结构变化仍然存在较大的争议。Mishra 等^[11]对不同测试方法得到的结果进行了较为详细的总结,如图 2b 所示。此外,正如图 2c 所展示, NN 从室温到高温的介电谱上,仅仅在 360 °C 附近出现明显的介电峰,其对应反铁电 P 相到反铁电 R 相的相变。通常为了方便研究,有时把该峰位所对应的温度称为 Curie 温度^[12]。

值得注意的是,如图 3 所示,在 150 °C 附近出现了一个明显的介电损耗色散,产生这种现象的真正原因目前仍存在争议。先前的学者认为这种现象和二级相变、非对称相的出现有关^[13-14]。在电场作用之后,150 °C 附近的介电异常峰消失同时在 270 °C 附近出现一个新的介电异常峰,此峰在不同的频率下拥有明显的介电损耗弥散,如图 3b 所示。Zhang 等^[15]认为这种新的介电异常峰归因于 $P2_1ma$ 相结构至 $Pbcm$ 相结构的非对称相变,这可以通过观察强极化电流峰现象得到证实。



AFE is antiferroelectric; FE is ferroelectric; PE is paraelectric.

图2 NN相变顺序, 采用不同的方法表征的NN的相结构和NN介电常数和介电损耗在2 kHz的频率下随着温度的变化曲线^[7]
Fig. 2 Phase transition order of NaNbO₃ (NN), phase structures of NN characterized by different methods and variation of dielectric constant and dielectric loss of NN ceramics with temperature in the 2 kHz^[7]

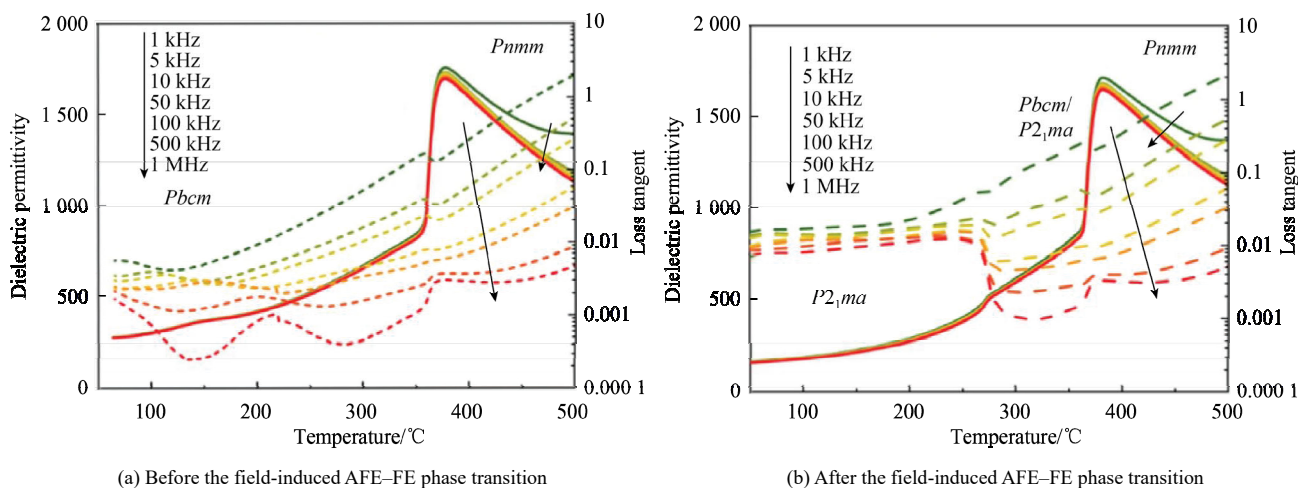


图3 在1 kHz~1 MHz的频率范围内, NN陶瓷材料介电常数和介电损耗(虚线)与温度的关系^[15]
Fig. 3 Dielectric constant and dielectric loss (dashed line) of NN ceramic in the 1 kHz to 1 MHz^[15]

除了温度变化会引起相转变, 电场、外部应变、不同的晶粒尺寸及初始原料也会引起反铁电相到铁电相的转变。例如, Ulinzhev等^[16]研究了静电场方向变化时晶体结构的变化, 发现不同的静电场方向会引起AFE到FE相转变。Schwarzkopf等^[17]采用化学气象沉积的方法在NN薄膜中产生拉伸和压缩晶格应变, 这会引起r相与c相(铁电相)和aa相(反铁电相)之间的转变。Shiratori等^[18]研究了不同晶粒尺寸对NN陶瓷结构的影响, 发现粗大和近微米的晶粒分别呈现出 $Pbcm$ 和 $Pmc2_1$ 结构。值得注意的是, 当晶粒尺寸小于70 nm时, 晶体转变为 $Pmma$ 结构。Li等^[19]研究了不同Nb₂O₅前驱体对NN晶体

结构、烧结行为、铁电性能及介电性能的影响, 发现其对结构和性能有较大的影响。

图4为反铁电P相和铁电Q相的晶体结构。由图4可见, 反铁电P相的晶胞为 $\sqrt{2} \times \sqrt{2} \times 4$ 型钙钛矿超晶格, 但是铁电Q相呈现出 $\sqrt{2} \times \sqrt{2} \times 2$ 的超晶格。除了拥有不同的原子构型, 两相连续的氧八面体沿着(001)方向的倾斜角也不同, 反铁电P相沿着主轴方向交替出现 $a^-b^+a^-$ 和 $a^-b^-a^-$ 2种扭转模式, Nb⁵⁺和Na⁺沿着(110)方向每2层自发位移反向, 使得宏观不显极性。铁电Q相具有 $a^-a^-b^+$ 倾斜模式, 表明氧八面体沿主轴方向倾斜且与其他2个轴倾斜的幅度不同^[20]。Zhang等^[21]采用第一性原理预测了

SrSnO_3 掺杂 NN 陶瓷, 同时使用实验证实了 SrSnO_3 掺杂可以稳定 NN 陶瓷的反铁电 P 相, 发现反铁电

P 相和铁电 Q 相之间的平衡归因于 AFE 相和 FE 相之间的微小能量差。

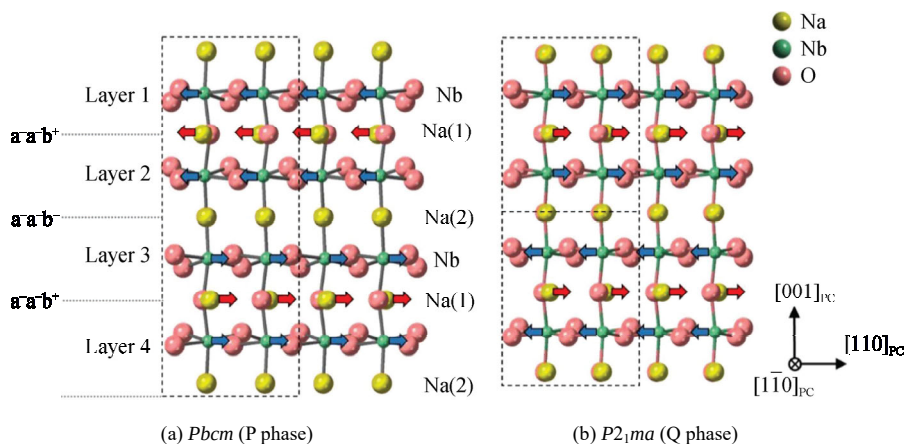


图 4 反铁电 P 相($Pbcm$ 空间群)和铁电 Q 相($P2_1ma$ 空间群)的晶体结构, 沿 $[1\bar{1}0]_{PC}$ 方向观察^[20]

Fig. 4 Crystallographic structures of the P phase ($Pbcm$ space group) and the Q phase ($P2_1ma$ space group), viewed along the $[1\bar{1}0]_{PC}$ direction^[20]

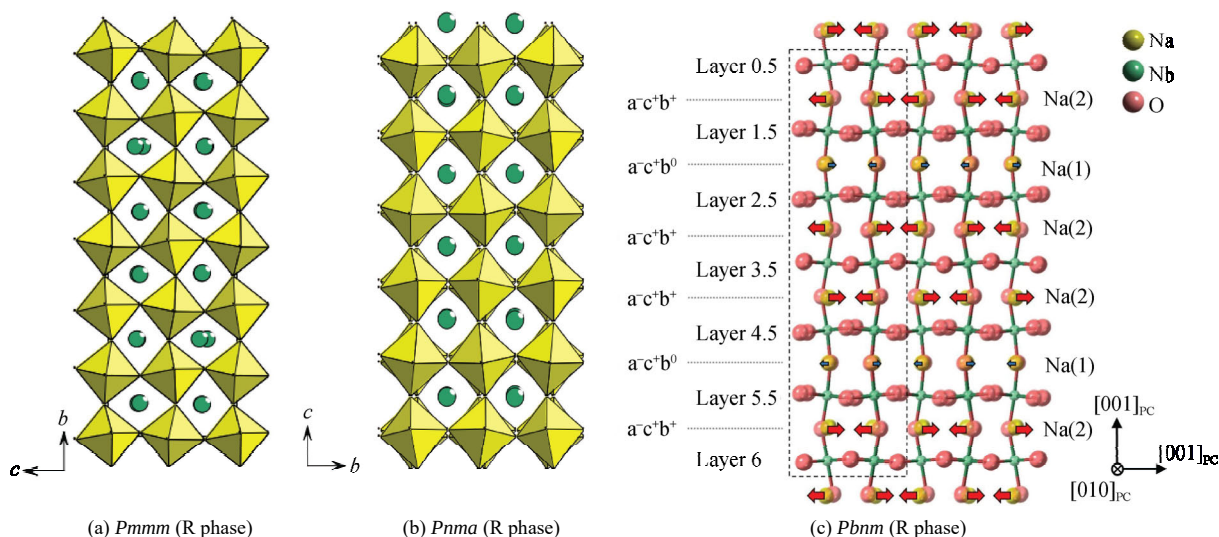


图 5 R 相的晶体结构^[20]

Fig. 5 Crystallographic structure of the R phase^[20]

Li 等^[22]通过 $\text{Bi}(\text{Mg}_{2/3}\text{Nb}_{1/3})\text{O}_3$ 掺杂 NN 陶瓷在室温观察到了 $1/6$ 超晶格衍射峰, 认为此现象为反铁电 R 相的存在。相比于反铁电 P 相, 学者们对反铁电 R 相的关注较少且此结构目前还存在争议。Megaw 等^[10]提出 R 相中 Nb 离子拥有 1 个方向的位移, 并且沿着 3 个方向都有一定的倾斜, 猜测是 $a^-b^+c^+$ 类型的倾斜, 因此认为反铁电 R 相的空间群为 $Pnmm$ 。此后, Peel 等^[23]通过高分辨中子衍射和 X 射线衍射结合第一性原理计算认为反铁电 R 相有 2 种可能的结构模型: $Pmnm$ 和 $Pnma$, 如图 5a 和图 5b 所示, 他们发现和 $Pnma$ 空间群相比, $Pmnm$ 空间群可以更好的拟合所测试的温度的函数, 且其具有更低的能量, 因此认为 $Pmnm$ 结构优于 $Pnma$ 。

Mishra 等^[24]采用原位高分辨中子粉末衍射发现反铁电 R 的结构为类似 CaTiO_3 的 $Pbnm$ 结构, 他们在 680 K 的温度下进行高分辨粉末衍射表征观察到在 35.8° 附近存在 1 个明显的衍射峰, 即沿着 $[001]$ 方向拥有 $1/6$ 超晶格衍射峰。图 5c 为基于 $Pbnm$ 空间群的 R 相晶体结构。由图 5c 可见, 反铁电 R 相的晶胞拥有 $\sqrt{2} \times \sqrt{2} \times 6$ 型钙钛矿超晶格, 和反铁电 P 相 $\sqrt{2} \times \sqrt{2} \times 4$ 钙钛矿超晶格有明显的区别。因此, Qi 等^[25]在 $0.76\text{NaNbO}_3-0.24\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ 材料中使用透射电子显微镜(TEM)观察到了 $1/6$ 超晶格衍射峰。Xie 等^[26]以 NN 为基体, 通过引入第二相 CaTiO_3 将反铁电 R 相调至室温, 通过 TEM 发现了 $1/6$ 超晶格衍射峰, 引入弛豫特性, 进一步提高储能性能。Li

等^[22]采用 $\text{Bi}(\text{Mg}_{2/3}\text{Nb}_{1/3})\text{O}_3$ 掺杂 NN 陶瓷, 在[011] 方向也观察到了 1/6 超晶格衍射斑点, 证实了反铁电 R 相的存在。R 相的反铁电性起源于 Na 离子的反平行原子位移。Na 离子拥有反平行原子位移, 使得其结构内部具有反向的极化偶极子, 因此拥有 R 相反铁电性。

2 铌酸钠介质陶瓷的微观结构

2.1 不同烧结工艺的影响

烧结工艺对无铅 NN 陶瓷材料的储能性能有较大的影响。Bian 等^[27]采用放电等离子烧结(SPS)成功制备了 $\text{NaNb}_{1-x}\text{Ta}_x\text{O}_3$ 陶瓷材料, 相比于传统烧结, 并没有第二相的产生, 同时获得了良好的储能性能(可回收储能密度 $W_{\text{rec}}=0.9 \text{ J/cm}^3$, 效率 $\eta=87\%$)。此后, Yang 等^[28]采用传统烧结和 SPS 烧结制备了 $\text{Na}_{0.7}\text{Bi}_{0.1}\text{Nb}_{0.9}\text{Ta}_{0.1}\text{O}_3$ 陶瓷, 发现 SPS 烧结拥有更均匀的微观结构、更细小的晶粒尺寸及更高的氧空位浓度, 同时储能效率从 81.1%升高至 90.5%, 但是其储能密度略微下降。Wang 等^[29]采用传统固相烧结在 O_2 气氛下成功制备了 A 位 Sm^{3+} 掺杂 $0.88\text{NaNbO}_3-0.12\text{Sr}_{0.7}\text{Bi}_{0.2}\text{TiO}_3$ 无铅储能陶瓷, 在较低的电场(200 kV/cm)获得了 3.58 J/cm^3 的储能密度和 82%的储能效率。Fan 等^[30]采用压力辅助烧结的方法在 1030°C 的温度下 1 h 制备了致密的 $0.91\text{NaNbO}_3-0.09\text{Bi}(\text{Zn}_{0.5}\text{Ti}_{0.5})\text{O}_3$ 陶瓷样品, 获得了 2.20 J/cm^3 的储能密度, 但是储能效率较低, 仅为 62.5%。Xie 等^[31]采用两步烧结的方法制备了 $0.83\text{NaNbO}_3-0.17\text{SrTiO}_3$ 陶瓷材料, 所有烧结样品的致密度均大于 95%, 但是其储能性能较低, 储能密度为 1.60 J/cm^3 , 储能效率仅为 55%。因此, 烧结工艺还需进一步的改善来获得更高的储能密度及储能效率。

2.2 不同烧结助剂的影响

烧结助剂在陶瓷制备过程中起着非常重要的作用。一方面, 添加烧结助剂通常会形成液相, 进而提高陶瓷的致密化过程; 另一方面, 添加烧结助剂可以降低烧结温度, 起到细化晶粒的作用, 这有利于增加陶瓷的电阻进而提高其击穿场强^[32]。

目前, 常见的烧结助剂主要有 MnO_2 , CuO , ZnO , Bi_2O_3 , B_2O_3 等等。最近, MnO_2 成为了一个比较受欢迎的烧结助剂来优化 NN 陶瓷的储能性能。例如, Tian 等^[33]研究了不同的烧结助剂(MnO_2 、 CuO 和 CeO_2)对 $\text{NaNbO}_3-\text{Bi}(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_3$ 陶瓷击穿场强及储能性能的影响。烧结助剂的添加可以抑制

氧空位的形成, 提高击穿场强, 但是相比于 CuO 和 CeO_2 , MnO_2 烧结助剂的添加具有更高的击穿场强, 这归因于当温度高于 1020°C 时 Mn 具有不同的价态, 更有助于抑制 Ti^{4+} 到 Ti^{3+} 的转变, 减少氧空位的含量, 进而提高击穿场强。Luo 等^[34]研究了不同的 MnO_2 掺杂含量对 $0.84\text{NaNbO}_3-0.16\text{CaTiO}_3$ (NN-CT16)陶瓷相结构、微观形貌及储能性能的影响, 发现随着 MnO_2 含量的增加, 样品的致密度逐渐提高, 孔隙率逐渐降低, 同时提高了击穿场强。当 MnO_2 的掺杂含量为 1.5%时(质量分数), NN-CT16 获得了 5.8 J/cm^3 的储能密度和 81%的储能效率, 在 $25\sim140^\circ\text{C}$ 的温度下 $\Delta W_{\text{rec}}<10\%$ 且 $\Delta\eta<5\%$ 。值得注意的是, 在 $1\sim300 \text{ Hz}$ 的频率下 $\Delta W_{\text{rec}}<4\%$ 且 $\Delta\eta<1\%$ 。因此, 陶瓷拥有良好的温度和频率稳定性。Yang 等^[35]添加 0.5% (质量分数) MnO_2 进入 $(\text{Na}_{0.8}\text{Bi}_{0.1})(\text{Nb}_{0.9}\text{Ti}_{0.1})\text{O}_3$ 陶瓷, 其密度从 4.80 g/cm^3 增加至 4.83 g/cm^3 , 储能效率从 82.0%提高至 93.4%, 储能密度基本保持不变。有趣的是, 他们测试了 $-70\sim170^\circ\text{C}$ 宽温区陶瓷样品的温度稳定性, 发现其储能密度的变化率低于 12%, 储能效率一直维持在 90%以上, 变化率低于 4%, 具有优异的温度稳定性。Zhang 等^[36]以 $\text{NaNbO}_3-\text{SrSnO}_3$ 为研究对象, 研究了不同的 MnO_2 掺杂含量对相结构、微观形貌及储能性能的影响。发现 MnO_2 的掺杂可以促进物质的扩散, 抑制第二相的生成, 且不改变相转变行为; 同时可以明显提高其击穿场强, 相比于未掺杂的 $0.95\text{NaNbO}_3-0.05\text{SrSnO}_3$ (NN5SS)陶瓷, 储能密度提高了近 14 倍。同时, 对于掺杂 1% (质量分数) MnO_2 的样品 NN5SS, 从室温至 140°C 具有良好的温度稳定性。击穿场强的提高可能与 MnO_2 掺杂之后电子-空穴对的降低有关。对于一些拥有易挥发元素(K、Na 等)的陶瓷样品, 在高温下元素的挥发将会形成大量的氧空位, 氧空位的产生伴随着电子-空穴对的形成, 导致较高的漏电流密度。当 MnO_2 掺杂之后, 由于 Mn 拥有多种价态, Mn 可以作为缓冲元素抑制材料中电子-空穴对的增加, 进而降低了漏电流密度, 提高了击穿场强。Emmanuel 等^[37]采用 Bi_2O_3 作为烧结助剂研究了不同的 $\text{Sr}_{0.55}\text{La}_{0.3}\text{TiO}_3$ 掺杂对 NN 相结构、微观结构及储能性能的影响, 获得了 5.8 J/cm^3 的储能密度及 85%的储能效率。但是, 温度稳定性未见报道。

值得注意的是, 添加一种烧结助剂在降低烧结温度的同时可能会恶化陶瓷的储能性能。通过组合烧结助剂的方式[例如: $\text{BaO}-\text{CuO}-\text{B}_2\text{O}_3$ (BCB)等]

一定程度上有利于提高陶瓷的储能性能。例如, Chen 等^[38]分别用 1%(质量分数)的 CuO 、 ZnF_2 和 BCB 作为烧结助剂来研究其对 $(\text{Na}_{0.91}\text{La}_{0.09})(\text{Nb}_{0.82}\text{Ti}_{0.18})\text{O}_3$ 陶瓷微观结构、烧结温度及击穿场强的影响。发现相比于 CuO 和 ZnF_2 , BCB 烧结助剂的添加更有利于细化晶粒, 降低烧结温度及提高击穿场强。虽然 ZnF_2 拥有较低的熔点 (872°C), 可以通过颗粒重排、溶质扩散和晶粒生长过程促进烧结, 但是 BCB 相倾向于填充晶界, 阻止晶粒长大, 在较低温度下通过黏性流动增强致密化, 因此更加明显的增加击穿场强, 最终获得 6.5 J/cm^3 的储能密度。

2.3 不同制备工艺的影响

目前, NN 基陶瓷的制备工艺主要包括传统固相反应、轧膜成型工艺、流延成型工艺、多层陶瓷电容器(MLCC)制备工艺等等。Zhou 等^[39]采用传统固相烧结制备了 $0.80\text{NaNbO}_3\text{--}0.20\text{SrTiO}_3$ 陶瓷, 在 323 kV/cm 的电场下获得了 3.02 J/cm^3 的可回复储能密度及 80.7% 的储能效率。为了进一步优化储能性能, Xie 等^[31]采用两步烧结在 $0.83\text{NaNbO}_3\text{--}0.17\text{SrTiO}_3$ 陶瓷中获得了拥有不同晶粒尺寸 ($1.2\sim 8.2\text{ }\mu\text{m}$) 的样品, 发现随着晶粒尺寸的增加, 储能性能得到明显的提升, 在最大的晶粒尺寸下储能密度达到 1.6 J/cm^3 。此后, Wang 等^[40]采用黏性聚合物加工方法(VPP)结合两步烧结制备了 $0.84\text{NaNbO}_3\text{--}0.06\text{BiFeO}_3\text{--}0.1\text{SrTiO}_3$ 陶瓷, 研究发现相比于传统两步烧结制备的样品, VPP 制备的样品击穿场强从 221.4 kV/cm 提升至 379.0 kV/cm , 储能密度得到了大幅度的提升(从 2.70 J/cm^3 升至 5.29 J/cm^3), 但是储能效率略微下降。Zhu 等^[41]采用两步烧结结合 MLCC 工艺制备了 $(0.96-x)\text{NaNbO}_3\text{--}0.04\text{CaZrO}_3\text{--}x\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ 陶瓷, 在 400 kV/cm 的电场下获得了优异的储能性能(储能密度 3.7 J/cm^3 及储能效率 82.1%)。总而言之, 采用 VPP 及 MLCC 工艺在一定程度上可以提高储能性能, 但是储能效率仍然较低。

除了 NN 基陶瓷的制备工艺外, 一些科研工作者将 NN 与聚合物进行复合, 获得了一系列具有高击穿场强的 NN 基储能薄膜材料。Pan 等^[42]通过两步熔盐法制备了 NN 二维板材料, 然后与聚合物聚偏氟乙烯(PVDF)进行复合, 击穿场强高达 400 MV/m , 同时获得了 13.5 J/cm^3 的储能密度。此后, Pan 等^[43]采用水热法制备了 NN 纳米线, 与 PVDF 复合之后在 410 MV/m 的击穿场强下获得了 12.26 J/cm^3 的储

能密度。Pan 等^[44]采用化学微晶转换法制备了二维 NN 板材料, 将 Al_2O_3 包覆在其表面形成核壳结构, 与聚合物 P(VDF-HFP)复合之后获得了优异的储能性能(储能密度达 14.59 J/cm^3 及储能效率达 70.1%)。

3 掺杂改性对铌酸钠介质陶瓷储能特性的影响

尽管通过改进烧结工艺和添加烧结助剂的方式可以提高陶瓷样品的致密化程度, 但是其储能性能还是相对偏低。最近, 大量的科研工作者对 NN 陶瓷进行了 A 位、B 位及 A/B 位复合取代来提高储能性能, 并且取得了长足的进步, 获得了一系列具有优良储能性能的 NN 基陶瓷体系。

3.1 A 位掺杂

NN 基陶瓷的 A 位离子取代主要包含 Bi^{3+} 及一些 Ln 系离子(La^{3+} 、 Sm^{3+} 、 Dy^{3+} 等), 其中研究较多的主要是 A 位 Bi^{3+} 取代, 如表 1 所示。Zhou 等^[45]研究了 A 位 Bi^{3+} 取代对 NN 陶瓷相结构、微观结构及储能性能的影响。添加 Bi_2O_3 改性 NN 陶瓷主要是基于以下 3 点原因: 1) Bi_2O_3 可以作为烧结助剂, 陶瓷的击穿强度可以显著提高, 同时它降低了烧结温度, 抑制了元素 Na 的挥发, 从而使陶瓷变得更致密和更均匀; 2) O^{2-} 2p 轨道和 Bi^{3+} 6p 轨道之间的杂化可以提高最大极化强度; 3) 一价 Na^+ 被三价 Bi^{3+} 阳离子取代导致电荷不平衡, 这可以产生钠空位。研究发现掺杂 Bi^{3+} 之后最大极化强度从 $1.918\text{ }\mu\text{C/cm}^2$ 增加至 $37.51\text{ }\mu\text{C/cm}^2$, 剩余极化从 $0.025\text{ }\mu\text{C/cm}^2$ 增加至 $1.115\text{ }\mu\text{C/cm}^2$, 在 250 kV/cm 的电场下, 储能密度达到了 3.44 J/cm^3 , 储能效率为 85.4%。此后, Yang 等^[28]在此基础上在用 Ta 置换 Nb 离子并且通过 SPS 烧结制备出了具有更优异的储能性能 ($W_{\text{rec}}=6.68\text{ J/cm}^3$, $\eta=90.5\%$), 这可能归因于 SPS 烧结细化了晶粒尺寸、增加了晶界数量, 进而提高了击穿场强所致。

另外, 研究比较多的是 A 位取代镧系离子。Emmanuel 等^[46]研究了 A 位不同的 Dy^{3+} 对 $\text{Na}(\text{Nb}_{0.9}\text{Ta}_{0.1})\text{O}_3$ 陶瓷相结构及储能性能的影响。发现当掺杂含量为 2% 时(摩尔分数), 储能性能最优: 储能密度为 4.61 J/cm^3 , 储能效率为 84%。此后, Wang 等^[29]以二元体系 $0.88\text{NaNbO}_3\text{--}0.12\text{Sr}_{0.7}\text{Bi}_{0.2}\text{TiO}_3$ 为研究对象, 系统探究了不同的 Sm^{3+} 取代 A 位 Na^+ 对其储能性能的影响, 在 200 kV/cm 的低电场下获得了 3.58 J/cm^3 的储能密度及 82% 的储能效率。

表 1 NaNbO₃ 基 A 位掺杂陶瓷的烧结温度及储能性能

Table 1 Sintering temperature and energy storage performance of NaNbO₃-based A-position doped ceramics

Composition	$E_b/(\text{kV}\cdot\text{cm}^{-1})$	$W_{\text{rec}}/(\text{J}\cdot\text{cm}^{-3})$	$\eta/\%$	$\varepsilon'(\text{at } 1 \text{ kHz})$	(Sintering	Sample thickness/ μm	Electrode area/ mm^2	Reference
					Temperature/ $^{\circ}\text{C}$)/ (Time/h)			
Na _{0.7} Bi _{0.1} NbO ₃	351	3.44	85.4	1 600	1 150/2	200	15.900	[45]
Na _{0.7} Ag _{0.3} NbO ₃	220				1 080–1 250/3			[47]
Na _{0.5} K _{0.5} NbO ₃	100	0.22	10.0	725	1 030–1 070/3		3.140	[48]
Na _{0.7} Bi _{0.1} Nb _{0.9} Ta _{0.1} O ₃	560	6.68	90.5	1 400	1 050/0.083	150	3.140	[28]
(Na _{0.84} Bi _{0.08})(Nb _{0.92} Zr _{0.08})O ₃	430	4.90	88.0	970	1 250–1 350/2	100	3.140	[49]
(Na _{0.91} Bi _{0.09})(Nb _{0.94} Mg _{0.06})O ₃	760	10.90	83.0	900	1 200/3	80–100	0.785	[50]
(Na _{0.8} Bi _{0.1})(Nb _{0.9} Ti _{0.1})O ₃	390	4.30	90.0	1 300	1 210–1 320/1	100	3.140	[35]
Dy _{0.8} Na _{0.2} (Nb _{0.9} Ta _{0.1})O ₃	478	4.61	84.0	1 500	1 350/3	180	7.065	[46]
(Na _{0.73} Bi _{0.08} Sm _{0.01})(Nb _{0.91} Ta _{0.09})O ₃	214	1.66	83.6	1 400	1 250–1 300/2	150–200	3.140	[51]
0.96Na _{0.88} La _{0.04} NbO ₃ –0.04CaSnO ₃	250	2.10	62.0	1 000	1 350–1 390/2	150		[52]
0.94(Na _{0.88} Sm _{0.04} NbO ₃)–0.06(BiFeO ₃)	460	4.00	80.0	800	1 080–1 120/3	80–100	3.140	[53]
(0.88Na _{0.94} Sm _{0.02} NbO ₃ –0.12Sr _{0.7} Bi _{0.2} TiO ₃)	200	3.58	82.0	1 100	1 160/3	100	0.196	[29]

E_b is breakdown electric field strength; W_{rec} is recoverable energy density; η is energy storage efficiency; ε' is real part of the permittivity.

3.2 B 位掺杂

NN 陶瓷 B 位取代主要为 Ta⁵⁺和 Sb⁵⁺，如表 2 所示。Bian 等^[27]采用 SPS 烧结制备了不同 Ta⁵⁺含量对 NN 陶瓷相结构及储能性能的影响，发现少量的 Ta 取代可以稳定铁电相，大量的 Ta 取代可以诱导铁电相到顺电相的转变。当掺杂含量为 6%时(摩尔分数)，得到的储能密度和储能效率分别为 0.9 J/cm³和 87%。Cheng 等^[54]研究了 0.88Na(Nb_{1-x}Ta_x)O₃–0.12Bi_{0.2}Sr_{0.7}TiO₃ (x=0–0.075)陶瓷的储能性能，当

掺杂含量为 7.5% (摩尔分数)时，150 kV/cm 的电场下获得了 2.16 J/cm³的储能密度。Yang 等^[55]在研究 Ta⁵⁺取代的(Na_{0.8}Bi_{0.1})(Nb_{0.9}Ti_{0.1})O₃ 陶瓷时，发现掺杂的 Ta 元素会降低在高电场下的漏电流，提高晶粒和晶界的激活能，进而提升储能性能。Qiao 等^[56]在研究 Sb⁵⁺取代部分 Nb⁵⁺时，发现 Sb 元素的掺杂可以降低剩余极化强度，稳定反铁电相，储能密度能够提升至 3.4 J/cm³，但是储能效率只有 44%。

表 2 NaNbO₃ 基 B 位掺杂陶瓷的烧结温度及储能性能

Table 2 Sintering temperature and energy storage performance of NaNbO₃-based B-position doped ceramics

Composition	$E_b/(\text{kV}\cdot\text{cm}^{-1})$	$W_{\text{rec}}/(\text{J}\cdot\text{cm}^{-3})$	$\eta/\%$	$\varepsilon'(\text{at } 1 \text{ kHz})$	(Sintering	Sample thickness/ μm	Electrode area/ mm^2	Reference
					Temperature/ $^{\circ}\text{C}$)/ (Time/h)			
NaNb _{0.94} Ta _{0.06} O ₃	160	0.90	87.0	700	1 300–1 500/2	100		[27]
Na(Nb _{0.9} Sb _{0.1})O ₃	350	3.40	44.0		1 350–1 370/2	200	4.900	[56]
0.88Na(Nb _{0.925} Ta _{0.075})O ₃ –0.12Bi _{0.2} Sr _{0.7} TiO ₃	150	2.16	80.7	1 400	1 160/3	100	0.196	[54]
(Na _{0.8} Bi _{0.1})(Nb _{0.75} Ta _{0.15} Ti _{0.1})O ₃	450	6.50	94.0	1 030	1 180–1 250/2	80	1.770	[55]

3.3 A、B 位复合掺杂

目前，A 位、B 位复合取代 NaNbO₃ 陶瓷的研究是报道最多的，A 位离子可以是+1 价和 B 位离子+5 价的组合；A 位+2 价和 B 位+4 价的组合；A 位+3 价和 B 位+3 价的组合。另外，在 A 位和 B 位的基础上，添加第三组分来提高其储能性能越来越成为研究者们青睐的方式。

3.3.1 A 位+1 价，B 位+5 价 目前，对于 A 位离子是+1 价(Li)和 B 位离子+5 价(Ta)的组合取代 NN 储能性能的研究较少，主要是以提高压电性能为主，如表 3 所示。例如，Mitra 等^[57]研究不同的 LiNbO₃

来掺杂 NN 陶瓷，发现介电温谱中存在弥散相变，这可能归因于 Li 离子的掺杂导致 A 位结构的无序。观察极化曲线发现形状类似矩形，因此具有较低的储能性能。Sun 等^[58]研究了不同 LiTaO₃ 对微观结构、电性能及电场引起的相变行为的影响，发现随着掺杂含量的增加，晶体结构从具有 *Pbcm* 正交相向 *P222*₁ 正交相转变。少量的 LiTaO₃ 掺杂可以诱导反铁电相部分转变为铁电相，大量的掺杂将会导致晶粒的异常长大。观察 *P–E* 曲线发现其储能密度较低。因此，对于+1 和+5 价的组合还需要进一步探究新的方式(如新工艺等)来提高其储能性能。

表 3 $\text{NaNbO}_3\text{-(A, B)O}_3$ (A 为+1、B 为+5)陶瓷的烧结温度及储能性能Table 3 Sintering temperature and energy storage performance of $\text{NaNbO}_3\text{-(A, B)O}_3$ (A is +1, B is +5) ceramics

Composition	$E_b/(\text{kV}\cdot\text{cm}^{-1})$	(Sintering Temperature/ $^{\circ}\text{C}$)/(Time/h)	Reference
$0.84\text{NaNbO}_3\text{-}0.16\text{LiNbO}_3$	90	1 180–1 260/2	[57]
$0.82\text{NaNbO}_3\text{-}0.18\text{LiTaO}_3$	90	1 310/2	[58]

3.3.2 A 位+2 价, B 位+4 价 目前, 有关 A 位 +2 价和 B 位+4 价的组合取代 NN 陶瓷已经被大家广泛研究, 比如 A 位可以是 Ca^{2+} 、 Sr^{2+} 、 Ba^{2+} 、 $(\text{Ca}_{0.7}\text{Bi}_{0.2})^{2+}$ 、 $(\text{Sr}_{0.7}\text{Bi}_{0.2})^{2+}$ 、 $(\text{Li}_{0.5}\text{Bi}_{0.5})^{2+}$ 、 $(\text{Na}_{0.5}\text{Bi}_{0.5})^{2+}$ 、 $(\text{K}_{0.5}\text{Bi}_{0.5})^{2+}$ 等, B 位可以是 Ti^{4+} 、 Zr^{4+} 、 Hf^{4+} 、 $(\text{Mg}_{1/3}\text{Nb}_{2/3})^{4+}$ 、 $(\text{Mg}_{1/3}\text{Sb}_{2/3})^{4+}$ 、 $(\text{Fe}_{0.5}\text{Nb}_{0.5})^{4+}$ 等。除了二元体系, 在此基础上添加第三组分(一般为线性电介质)也成为学者们比较关注的研究方向。

1) 二元体系

A 位+2 价和 B 位+4 价取代主要是通过 2 种途径来提高储能性能:1) 通过添加第二相来稳定反铁电 P 相; 2) 在 NN 陶瓷中引入弛豫反铁电特征。

添加第二相可以稳定反铁电特性的材料主要包含 CaZrO_3 、 CaTiO_3 、 BaZrO_3 、 CaHfO_3 、 SrZrO_3 等, 如表 4 所示。通过添加第二相组分, 降低体系的容差因子, 进而稳定反铁电 P 相, 在一定的组分下表现出明显的双电滞回线。但是较大的滞后和较低的击穿场强使得其具有较低的储能效率和储能密度。例如, Shimizu 等^[59]提出可以通过降低容差因子的方式来稳定反铁电相, 他们预测了几个可能稳定反铁电相的组分, 并且选择了 $(1-x)\text{NaNbO}_3\text{-}x\text{CaZrO}_3$ 为例子来研究。发现通过 Ca 和 Zr 离子的掺杂可以稳定反铁电相, 这归因于随着掺杂含量的增加容忍因子的降低。他们使用 TEM 表征发现在未掺杂的

表 4 二元 $\text{NaNbO}_3\text{-(A, B)O}_3$ (A 为+2、B 为+4)陶瓷的烧结温度及储能性能Table 4 Sintering temperature and energy storage performance of binary $\text{NaNbO}_3\text{-(A, B)O}_3$ (A is +2, B is +4) ceramics

Composition	$E_b/(\text{kV}\cdot\text{cm}^{-1})$	$W_{\text{rec}}/(\text{J}\cdot\text{cm}^{-3})$	$\eta/\%$	$\varepsilon'(\text{at } 1 \text{ kHz})$	(Sintering Temperature/ $^{\circ}\text{C}$)/(Time/h)	Sample thickness/ μm	Electrode area/ mm^2	Reference
$0.88\text{NaNbO}_3\text{-}0.12\text{CaZrO}_3$	650	8.56	80.00	1 600	1 360–1 400/2	100	3.140	[63]
$0.97\text{NaNbO}_3\text{-}0.3\text{CaTiO}_3$	560	5.52	83.30	300	1 120–1 160/2	100		[64]
$0.84\text{NN-}0.16\text{CaTiO}_3$	500	6.60	80.00	800	1 290–1 310/2	100	3.140	[26]
$0.96\text{NaNbO}_3\text{-}0.04\text{CaZrO}_3$	141	0.55	63.00	400	1 370/2	300		[62]
$0.825\text{NaNbO}_3\text{-}0.175\text{BaZrO}_3$	440	5.00	85.00	1 000	1 320–1 330/3	100	3.140	[65]
$0.97\text{NaNbO}_3\text{-}0.3\text{Bi}_{0.2}\text{Ca}_{0.7}\text{TiO}_3$	360	4.43	79.00	500	1 100–1 350/2	100–130	0.785	[66]
$0.84\text{NaNbO}_3\text{-}0.16\text{CaTiO}_3$	470	5.80	81.00		1 150–1 240/3	100	3.140	[34]
$0.85\text{NaNbO}_3\text{-}0.15\text{Ca}_{0.7}\text{Sm}_{0.2}\text{TiO}_3$	800	9.10	80.10	500	1 190–1 250/2.5	35	3.140	[67]
$\text{NaNbO}_3\text{-}0.2\text{SrTiO}_3$	300	3.02	80.70	1 500	1 250/2	400	12.250	[39]
$0.83\text{NaNbO}_3\text{-}0.17\text{SrTiO}_3$	207	1.60	55.00	2 000	1 300/4	130	5.000	[31]
$0.87\text{NaNbO}_3\text{-}0.13\text{Sr}(\text{Mg}_{1/3}\text{Sb}_{2/3})\text{O}_3$	640	6.17	76.72		1 365/3	100	3.140	[68]
$0.74\text{NaNbO}_3\text{-}0.26\text{Sr}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$	453	4.28	89.30	800	1 275/2			[69]
$0.90\text{NaNbO}_3\text{-}0.10\text{Sr}(\text{Fe}_{0.5}\text{Ta}_{0.5})\text{O}_3$	790	11.50	86.20	800	1 180–1 220/3	50	0.785	[70]
$0.76(\text{NaNbO}_3)\text{-}0.24(\text{Sr}_{0.55}\text{La}_{0.3})\text{TiO}_3$	440	5.80	85.00	1 000	1 230–1 340/2	200		[37]
$0.8\text{NaNbO}_3\text{-}0.2\text{Sr}_{0.7}\text{Bi}_{0.2}\text{TiO}_3$	288	4.50	90.30	1 100	1 140/3			[71]
$0.8\text{NaNbO}_3\text{-}0.3\text{Bi}_{0.2}\text{Ca}_{0.7}\text{TiO}_3$	360	4.43	79.00	500	1 100–1 350/2	100–130	0.785	[66]
$0.8\text{NaNbO}_3\text{-}0.2\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$	320	3.04	88.33	2 200	1 225–1 300/3	100	3.140	[72]
$0.82\text{NaNbO}_3\text{-}0.18\text{Ba}(\text{Fe}_{0.5}\text{Nb}_{0.5})\text{O}_3$	450	3.55	84.10	1 000	1 140–1 240/2	100	0.785	[73]
$0.77\text{NaNbO}_3\text{-}0.23\text{BaTiO}_3$	175	1.50	68.20	2 000	1 180–1 230/5	200		[74]
$0.92\text{NaNbO}_3\text{-}0.08\text{Bi}_{2/3}\text{HfO}_3$	260	4.26	60.00	1 440	1 280–1 320/2	200	3.140	[75]
$0.76\text{NaNbO}_3\text{-}0.24(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$	690	12.20	69.00	1 300	1 200–1 350/2	150		[25]
$0.86\text{NaNbO}_3\text{-}0.14(\text{Bi}_{0.5}\text{Na}_{0.5})\text{HfO}_3$	350	3.51	80.10	800	1 160–1 290/5	150		[76]
$0.68\text{NaNbO}_3\text{-}0.32(\text{Bi}_{0.5}\text{Li}_{0.5})\text{TiO}_3$	485	8.73	80.10	1 500	1 040–1 350/3	120	3.140	[77]
$0.82\text{NaNbO}_3\text{-}0.18(\text{Bi}_{1/2}\text{Li}_{1/2})\text{HfO}_3$	560	7.10	85.90	550	1 250–1 320/3			[78]
$0.89\text{NaNbO}_3\text{-}0.11(\text{Bi}_{0.5}\text{K}_{0.5})\text{ZrO}_3$	425	4.40	40.00	700	1 310–1 330/2	100	3.140	[79]

NN 陶瓷中存 1/4 和 1/2 超晶格衍射峰, 这表明材料中存在反铁电 P 相和铁电 Q 相; 掺杂 CaZrO_3 之后陶瓷中只存在反铁电 P 相, 表明掺杂之后稳定了反铁电 P 相。但是, 其双电滞回线在高温下(120 °C)取得, 并且随着掺杂含量的升高最大极化逐渐降低, 反铁电到铁电的转变场逐渐增加。Guo 等^[60]以 $(1-x)\text{NaNbO}_3-x\text{SrZrO}_3$ 陶瓷为研究对象, 发现 SrZrO_3 的掺杂可以稳定反铁电相, 在掺杂含量 x 大于 0.04 时, 在 120 °C 的温度和 0.1 Hz 的频率下获得了双电滞回线。Gao 等^[61]在 NN 基陶瓷中掺杂 CaHfO_3 组分, 当掺杂含量大于 3% 时(摩尔分数), 稳定了反铁电相, 在室温获得了良好的双电滞回线。

随后, Liu 等^[62]通过工艺调控在 $(1-x)\text{NaNbO}_3-x\text{CaZrO}_3$ 陶瓷中室温获得了具有双电滞回线的极

化曲线图。随着掺杂含量的升高, 陶瓷的击穿场强逐渐升高, 这归因于缺陷含量的降低。最后, 在 141 kV/cm 的电场下获得了 0.55 J/cm^3 和 63% 的储能密度及储能效率。此后, Qi 等^[63]以 CaZrO_3 为第二组分掺杂进入 NaNbO_3 陶瓷中, 通过引入弛豫特性在 650 kV/cm 的电场下获得了 8.56 J/cm^3 和 80% 的高储能密度和储能效率。

虽然通过取代之后样品的储能效率得到了提高, 但是储能密度相对较低, Chen 等^[38]开发了一些弛豫反铁电陶瓷来提高其储能密度, 如图 6 所示。在纯的 NaNbO_3 陶瓷中, 由于电场引起的不可逆反铁电和铁电转变, 其具有较差的储能性能。稳定反铁电之后储能效率得到明显的提升, 但是较大的双电滞回线滞后使得其具有中等的储能密度和储能效

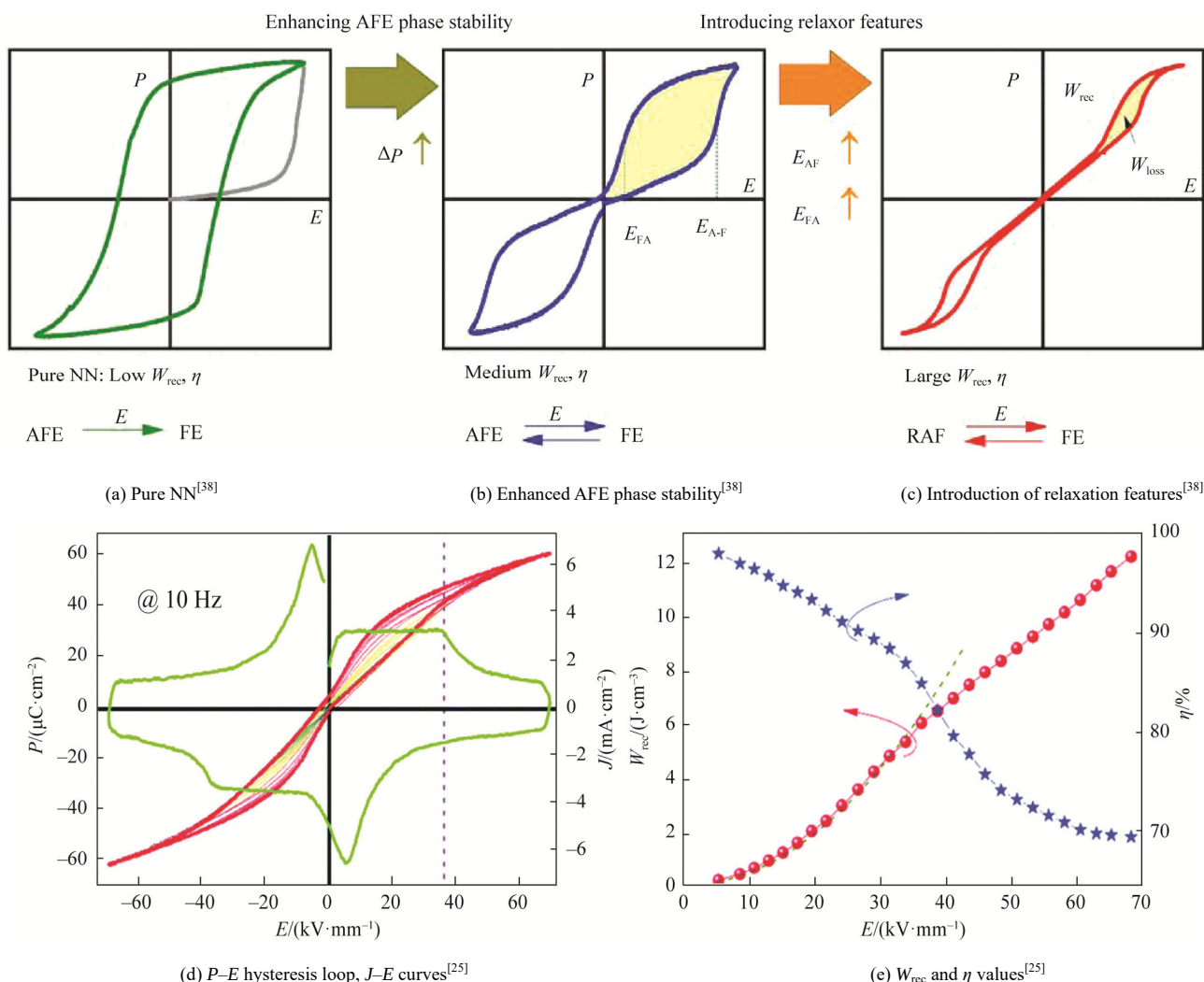


图 6 纯 NN, 增强 AFE 相稳定性, 引入弛豫特征的 P - E 曲线和储能性能的演变示意图以及不同电场和室温下 0.76NN-0.24BNT 陶瓷的 P - E 电滞回线、电流密度(J)- E 曲线和 W_{rec} 和 η 值

Fig. 6 Pure NN, enhanced AFE phase stability, introduction of relaxor features, evolution diagram of P - E curves and energy storage performance and P - E hysteresis loop, current density (J)- E curves and W_{rec} and η values of 0.76NN-0.24BNT ceramics at different electric fields and room temperature

率。在此基础上,引入弛豫行为可以抑制双电滞回线的滞后行为及提高反铁电相向铁电相的转变电场,因此获得高的储能密度和储能效率。通过这种设计方式,Chen 等^[38]采用拥有小的离子半径和大的电负性元素 La 来稳定反铁电相;同时 Ti 离子置换 Nb 离子来提高弛豫行为,因此获得了较高的储能密度(6.5 J/cm³)和中等的储能效率 66%。Qi 等^[25]以 (Bi_{0.5}Na_{0.5})TiO₃ 为第二组分掺杂进入 NN 储能陶瓷中,在 680 kV/cm 的电场下获得了 12.2 J/cm³ 的储能密度及 69% 的储能效率。作为一种新的材料体系,弛豫反铁电体拥有较高的储能密度及储能效率,这使得其在未来的脉冲电容器应用方面可能成为非常受欢迎的材料之一。

2) 三元体系

为了进一步提高陶瓷的储能密度和储能效率,

部分研究者在上一节的基础上添加第三组分以期打破储能密度和储能效率两者之间的制衡关系,如表 5 所示。Zhu 等^[41]在二元陶瓷 0.96NaNbO₃-0.04CaZrO₃ 基础上添加 Bi_{0.5}Nb_{0.5}TiO₃ 陶瓷,并且通过两步烧结优化及多层低温共烧的方式在 400 kV/cm 的电场下获得了 3.7 J/cm³ 的储能密度及 82.1% 的储能效率,这为进一步商业化提供了一种途径。Wang 等^[40]以 NN 为基体,引入二元组分(BiFeO₃-SrTiO₃)同时使用两步烧结及黏性聚合物制备协同优化储能性能,当掺杂含量为 1% (摩尔分数)时获得了最优的储能性能($W_{\text{rec}}=5.29 \text{ J/cm}^3$ 、 $\eta=82\%$)。Feng 等^[80]在弛豫反铁电体 0.76NaNbO₃-0.24(Bi_{0.5}Na_{0.5})TiO₃ 陶瓷的基础上引入线性电介质 SrTiO₃ 以期进一步的提高击穿场强,但是遗憾的是击穿场强从 690 kV/cm 下降至 270 kV/cm,储能密度也仅为 2.64 J/cm³。

表 5 三元 NaNbO₃-(A, B)O₃(A 为+2、B 为+4)陶瓷的烧结温度及储能性能

Table 5 Sintering temperature and energy storage performance of ternary NaNbO₃-(A, B)O₃(A is +2, B is +4) ceramics

Composition	$E_b/$ (kV·cm ⁻¹)	$W_{\text{rec}}/$ (J·cm ⁻³)	$\eta/\%$	ε' (at 1 kHz)	(Sintering Temperature/°C)/(Time/h)	Sample thickness/ μm	Electrode area/mm ²	Reference
0.8NaNbO ₃ -0.04CaZrO ₃ -0.16Bi _{0.5} Na _{0.5} TiO ₃	400	3.70	82.1	750	1 200-1280/2.0	170		[41]
0.84NaNbO ₃ -0.06BiFeO ₃ -0.1SrTiO ₃	379	5.29	82.1	700	1 160/3.0	100	12.56	[40]
0.90NaNbO ₃ -0.06BaZrO ₃ -0.04CaZrO ₃		1.59	30.0		1 350-1380/2.0	200	4.90	[81]
0.97[0.76NaNbO ₃ -0.24(Bi _{0.5} Na _{0.5})TiO ₃]-0.03SrTiO ₃	270	2.64	89.9	800	1 150/2.5	120		[80]
0.85(0.92NaNbO ₃ -0.08Bi(Mg _{0.5} Ti _{0.5})O ₃)-0.15SrTiO ₃	590	6.00	81.0	600	1 100-1 260/2.0	150	3.14	[82]

3.3.3 A 位+3 价, B 位+3 价 目前, A 位+3 价和 B 位+3 价的组合取代是最受学者们的欢迎的材料体系, A 位主要为 Bi³⁺、La³⁺ 离子, B 位为 (Mg_{2/3}Nb_{1/3})³⁺、(Ni_{0.67}Ta_{0.33})³⁺、(Zn_{2/3}Nb_{1/3})³⁺、(Zn_{0.5}Ti_{0.5})³⁺、(Mg_{0.5}Zr_{0.5})³⁺、(Zn_{0.5}Sn_{0.5})³⁺、(Mg_{0.5}Hf_{0.5})³⁺、(Mn_{0.5}Ni_{0.5})³⁺、(Li_{0.5}Nb_{0.5})³⁺、(Al_{0.5}Y_{0.5})³⁺ 等等(如表 6 和表 7)。由于二元体系有限且储能性能有待进一步的提升,大量的学者采取引入第三组分来优化储能性能,以期获得更优异的性能。

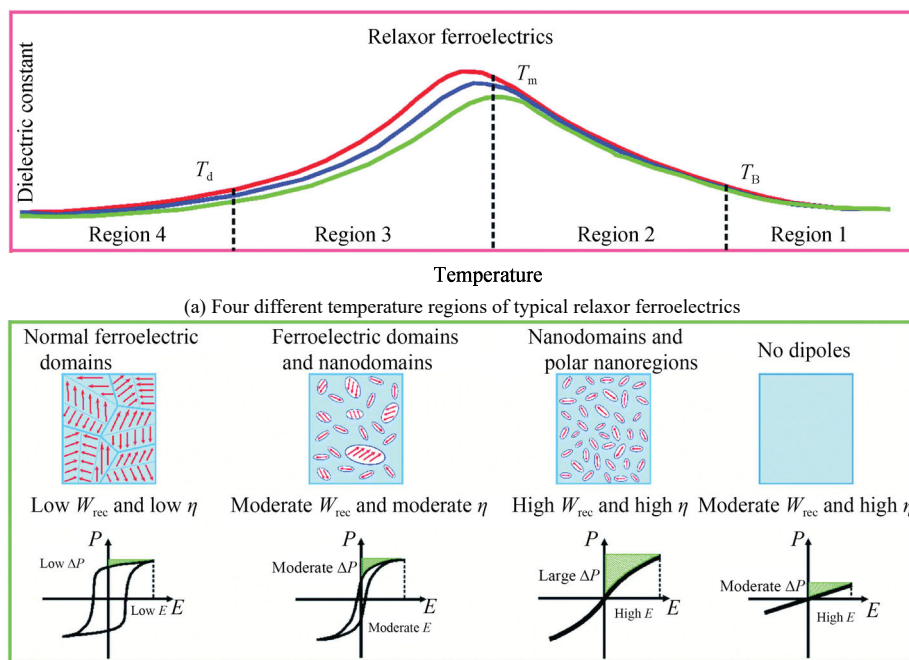
1) 二元体系

A 位+3 价和 B 位+3 价的组合主要是在 NN 陶瓷中引入弛豫特性。图 7 为设计原理图。对于典型的弛豫铁电体,介电光谱中存在 3 个特性温度,分别是 Burns 温度 T_B , 最大的介电常数对应的温度 T_m 及冷冻温度 T_f 。

3 个特征温度将图形分为 4 区域,分别对应着不同的畴尺寸和不同形状的电滞回线。当温度高于 Burns 温度 T_B 时,即区域 1,电介质处于顺电相,此时的 $P-E$ 曲线具有中等的极化差值 ΔP 和较高的击穿场强 E_b , 通常表现出较高的效率 η 及中等的储能密度 W_{rec} 。当温度介于 T_B 和 T_m 之间时(区域 2),

此时电介质中纳米畴和极性纳米微区(PNRs)共存,呈现出弛豫特性,其 $P-E$ 曲线具有较高的 ΔP 和 E_b , 有利于高的 W_{rec} 和 η 。在区域 3 中,随着温度从 T_m 下降至冷冻温度 T_f , 宏观铁电畴出现,纳米畴逐渐减少,在外加电场作用下,电畴随着电场转向,表现出较高的 P_{max} , 撤掉电场后,大多数纳米畴恢复原状,而大多数铁电畴仍保持极化方向,导致较高的剩余极化 P_r , 不利于储能密度的提高。在区域 4 中,当温度降至 T_f 以下,纳米畴消失,只存在宏观铁电畴,此时电介质为典型的铁电体,具有高的 P_{max} 和 P_r , 低的 E_b , 从而导致较差的储能性能。因此,将 T_m 和 T_B 的温度区域调至室温是一种非常好的策略为了实现优异的储能性能。

Ye 等^[83]通过引入 Bi(Mg_{2/3}Nb_{1/3})O₃ 将 T_m 和 T_B 的温度区域调至室温,获得了拥有较低 P_r 的细小电滞回线。因此,0.9NaNbO₃-0.1Bi(Mg_{2/3}Nb_{1/3})O₃ 陶瓷在 300 kV/cm 的电场下实现了 3.4 J/cm³ 的储能密度及 82% 的储能效率。在 0.78NaNbO₃-0.22Bi(Mg_{2/3}Ta_{1/3})O₃ 陶瓷中, T_m 和 T_B 的温度区域也被调至室温。因此,在 0.78NaNbO₃-0.22Bi(Mg_{2/3}Ta_{1/3})O₃ 陶瓷中和 627 kV/cm 的电场下高的储能密度 5.01 J/cm³

(b) Domain structure and P - E hysteresis loops of typical relaxor ferroelectrics图 7 基于神经网络的弛豫铁电体原理图^[2]Fig. 7 Schematic diagram of NN-based relaxor ferroelectrics^[2]表 6 二元 NaNbO_3 -(A, B) O_3 (A 为+3、B 为+3) 陶瓷的烧结温度及储能性能Table 6 Sintering temperature and energy storage performance of binary NaNbO_3 -(A, B) O_3 (A is +3, B is +3) ceramics

Composition	$E_b/(\text{kV} \cdot \text{cm}^{-1})$	$W_{\text{rec}}/(\text{J} \cdot \text{cm}^{-3})$	$\eta/\%$	ϵ' (at 1 kHz)	(Sintering Temperature/ $^{\circ}\text{C}$)/(Time/h)	Sample thickness/ μm	Electrode area/ mm^2	Reference
0.9NaNbO ₃ -0.1Bi(Mg _{2/3} Nb _{1/3})O ₃	300	3.400	82.00	750	1 100-1 270/2.0	200		[83]
0.78NaNbO ₃ -0.22Bi(Mg _{2/3} Ta _{1/3})O ₃	627	5.010	86.10	340	1 200-1 330/2.0	150	3.140	[84]
0.85NN-0.15Bi(Ni _{0.67} Ta _{0.33})O ₃	575	5.530	82.00	500	1 180-1 280/3.0	180	3.140	[85]
0.85NaNbO ₃ -0.15Bi(Zn _{2/3} Nb _{1/3})O ₃	220	1.660	73.50	900	1 050-1 200/2.0	200	7.065	[86]
0.85NaNbO ₃ -0.15Bi(Ni _{2/3} Nb _{1/3})O ₃	440	3.300	80.90	570	1 200-1 260/2.0	150	3.140	[87]
0.85NaNbO ₃ -0.1Bi(Ni _{2/3} Nb _{1/3})O ₃	1 050	11.200	90.50	831	1 145/3.0	50	0.785	[88]
0.85NaNbO ₃ -0.15Bi(Mg _{2/3} Sb _{1/3})O ₃	580	4.650	77.00	400	1 170-1 250/2.0			[89]
0.86NaNbO ₃ -0.14Bi(Ni _{2/3} Nb _{1/6} Ta _{1/6})O ₃	420	3.430	83.30	590	1 150-1 180/2.0			[90]
0.85NaNbO ₃ -0.15Bi(Ni _{2/3} Sb _{1/3})O ₃	460	3.700	77.00	450	1 120-1 180/2.0	150	3.140	[91]
0.91NaNbO ₃ -0.09Bi(Zn _{0.5} Ti _{0.5})O ₃	250	2.200	62.70	1 000	1 030/1.0	200		[30]
0.93NaNbO ₃ -0.07Bi(Mg _{0.5} Zr _{0.5})O ₃	255	2.310	80.20	1 200	1 230-1 280/3.5			[92]
0.92NaNbO ₃ -0.08Bi(Mg _{0.5} Ti _{0.5})O ₃	300	3.120	74.00	1 300	1 190-1 260/2.0	300	0.785	[33]
0.88NaNbO ₃ -0.12Bi(Zn _{0.5} Zr _{0.5})O ₃	340	3.140	84.50	1 000	1 285-1 350/2.0	150	3.140	[93]
0.91NaNbO ₃ -0.09Bi(Zn _{0.5} Ti _{0.5})O ₃	200	2.100	76.00	1 900	1 180-1 250/2.0			[94]
0.8NaNbO ₃ -0.2Bi(Mg _{0.5} Hf _{0.5})O ₃	370	3.510	93.77	320	1 190-1 250/2.0	160	0.785	[95]
0.88NaNbO ₃ -0.12Bi(Ni _{0.5} Zr _{0.5})O ₃	500	4.900	70.00	550	1 245-1 300/2.0	150	3.140	[96]
0.88NaNbO ₃ -0.12Bi(Sn _{0.5} Ni _{0.5})O ₃	310	2.010	80.30	400	1 130-1 250	200	3.140	[97]
0.91NaNbO ₃ -0.09Bi(Mg _{0.5} Sn _{0.5})O ₃	570	4.930	81.50	700	1 180-1 250/3.0	150	3.140	[98]
0.9NaNbO ₃ -0.1Bi(Ni _{0.5} Sn _{0.5})O ₃	633	5.000	67.80	700	1 190-1 300/2.0	130	3.140	[99]
0.9NaNbO ₃ -0.1Bi(Zn _{0.5} Sn _{0.5})O ₃	350	3.140	83.30	900	1200-1300/2.0	100	3.140	[100]
0.8NaNbO ₃ -0.2Bi(Mg _{0.5} Hf _{0.5})O ₃	550	5.900	89.90	320	1 190-1 250/2.0			[101]
0.85NaNbO ₃ -0.15Bi(Mg _{0.5} Hf _{0.5})O ₃	405	3.150	83.10	400	1 220/3.0	110		[102]
0.95NaNbO ₃ -0.05La(Mn _{0.5} Ni _{0.5})O ₃	200	1.770	77.00	200	1 325/6.0	200	7.065	[103]
0.88NaNbO ₃ -0.12Bi(Fe _{0.5} Sc _{0.5})O ₃	740	4.320	85.00	400	1 130-1 150/3.0	100	0.785	[104]
0.88La _{0.03} Na _{0.91} NbO ₃ -0.12Bi(Li _{0.5} Nb _{0.5})O ₃	300	2.020	80.00	1 900	1 050/2.0	200		[105]
0.9NaNbO ₃ -0.1BiFeO ₃	995	18.500	78.70	800	1 100-1 200/3.0	60-80	0.785	[106]
0.88NaNbO ₃ -0.12(Bi _{0.8} Sr _{0.2})(Fe _{0.9} Nb _{0.1})O ₃	983	16.500	83.30	600	1 140-1 200/3.0	60-80	0.785	[107]
0.88NaNbO ₃ -0.12(0.55BiFeO ₃ -0.45SrTiO ₃)	970	16.200	82.30	900	1 180-1 220/3.0	50	0.785	[108]
0.88NaNbO ₃ -0.12(Bi _{0.9} Na _{0.1})(Fe _{0.8} Ti _{0.2})O ₃	873	12.700	82.50	800	1 150-1 250			[109]
0.9NaNbO ₃ -0.1(Bi _{0.5} La _{0.5})(Mg _{2/3} Ta _{1/3})O ₃	440	3.690	78.00	800	1 200-1 300/4.0			[110]
0.88Na _{0.98} NbO ₃ -0.12Bi(Al _{0.5} Y _{0.5})O ₃	223	4.640	85.98	1 000	1 150-1 250/4.0	150-250		[111]
0.96NaMg _{0.12} Nb _{0.952} O ₃ -0.04BiYbO ₃	170	0.998	70.00	900	1 150-1 300/3.0			[112]

和储能效率 86.1% 被同时获得了^[84]。Pang 等^[85]以 $(1-x)\text{NaNbO}_3-x\text{Bi}(\text{Ni}_{0.67}\text{Ta}_{0.33})\text{O}_3$ 为研究对象, 通过引入 $\text{Bi}(\text{Ni}_{0.67}\text{Ta}_{0.33})\text{O}_3$ 可以降低 P_r 获得细小的电滞回线, 当掺杂含量为 0.15 时(摩尔分数), 在 575 kV/cm 的电场下获得了 5.53 J/cm^3 的储能密度和 82% 储能效率。同时在 20~140 °C 拥有良好的温度稳定性及在 2~90 Hz 下优良的频率稳定性。

2) 三元体系

对于二元陶瓷体系, 通过化学改性的方式虽然降低了剩余极化强度, 提高了储能密度及储能效率, 但是大部分的陶瓷材料的储能密度仍小于 5 J/cm^3 。因此, 科研人员在二元体系的基础上加入第三组分, 以期获得更高的储能密度($>5 \text{ J/cm}^3$)及储能效率($>85\%$)。Zhang 等^[113]在 $0.86 \text{ NaNbO}_3-0.14\text{CaTiO}_3$ 的基础上引入第三组分 $\text{Bi}(\text{Mg}_{2/3}\text{Nb}_{1/3})\text{O}_3$,

通过稳定反铁电相、产生 PNRs 及降低晶粒尺寸综合优化策略来提高储能性能。当掺杂含量为 8% 时(摩尔分数), 储能密度高达 5.41 J/cm^3 、储能效率达到 86.7%, 同时在 25~150 °C 的温度、1~600 Hz 的频率及 $1\sim 10^4$ 的疲劳测试下仍然具有优异的性能。Dong 等^[114]以 $(1-x)[0.90\text{NN}-0.10\text{Bi}(\text{Mg}_{2/3}\text{Nb}_{1/3})\text{O}_3]-x(\text{Bi}_{0.5}\text{Na}_{0.5})_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ 为研究对象, 通过第一性原理、相场模拟、TEM 等表征方式证明该体系中存在核壳结构, 晶粒中极性相和弱极性相的共存增大了极化差值, 最终获得了 7.72 J/cm^3 的储能密度、83.78% 的储能效率及 -40~200 °C 温度范围内良好的稳定性, 这进一步打破了储能密度和储能效率之间的制约关系。Kang 等^[115]通过稳定反铁电 R 相、细化晶粒尺寸及产生 PNRs 获得了极高的储能效率 (92.3%), 同时储能密度也高达 5.82 J/cm^3 。

表 7 三元 $\text{NaNbO}_3-(\text{A}, \text{B})\text{O}_3$ (A 为 +3、B 为 +3) 陶瓷的烧结温度及储能性能

Table 7 Sintering temperature and energy storage performance of ternary $\text{NaNbO}_3-(\text{A}, \text{B})\text{O}_3$ (A is +3, B is +3) ceramics

Composition	$E_b/$ ($\text{kV}\cdot\text{cm}^{-1}$)	$W_{\text{rec}}/$ ($\text{J}\cdot\text{cm}^{-3}$)	$\eta/\%$	ϵ' (at 1 kHz)	(Sintering Temperature/ °C)/(Time/h)	Sample thickness/ μm	Electrode area/ mm^2	Reference
$0.83\text{NaNbO}_3-0.12\text{Bi}(\text{Mg}_{2/3}\text{Nb}_{1/3})\text{O}_3-0.05\text{CaZrO}_3$	640	5.90	85.00	400	1 190–1 210/ 2.0	80–100		[113]
$0.6[0.90\text{NN}-0.10\text{Bi}(\text{Mg}_{2/3}\text{Nb}_{1/3})\text{O}_3]-0.4(\text{Bi}_{0.5}\text{Na}_{0.5})_{0.7}\text{Sr}_{0.3}\text{TiO}_3$	595	7.72	83.78	600	1 180–1 200/ 2.0	100	3.140 0	[114]
$0.96(0.8\text{NaNbO}_3-0.2\text{SrTiO}_3)-0.04\text{Bi}(\text{Zn}_{0.5}\text{Sn}_{0.5})\text{O}_3$	573	5.82	92.30	700	1 250–1 350/ 2.0	100	3.140 0	[115]
$0.75[0.90\text{NaNbO}_3-0.10\text{Bi}(\text{Mg}_{0.5}\text{Ta}_{0.5})\text{O}_3]-0.25(\text{Bi}_{0.5}\text{Na}_{0.5})_{0.7}\text{Sr}_{0.3}\text{TiO}_3$	800	8.00	90.40	600	1 180–1 280/ 2.0	150	3.140 0	[116]
$0.8(0.92\text{NaNbO}_3-0.08\text{BiNi}_{0.67}\text{Ta}_{0.33})\text{O}_3-0.2\text{CaTiO}_3$	646	7.10	90.00	400	1 250–1 290/ 3.0	50–70	0.799 2	[117]
$0.78\text{NaNbO}_3-0.14\text{CaTiO}_3-0.08\text{Bi}(\text{Mg}_{2/3}\text{Nb}_{1/3})\text{O}_3$	482	5.41	86.70	1 000	1 280–1 320/ 0.5	80–120	3.140 0	[118]
$0.6(0.9\text{NaNbO}_3-0.1\text{Bi}(\text{Ni}_{0.5}\text{Zr}_{0.5})\text{O}_3)-0.4(\text{Bi}_{0.5}\text{Na}_{0.5})_{0.7}\text{Sr}_{0.3}\text{TiO}_3$	530	6.43	82.00	600	1 220–1 260/ 2.0	150	3.140 0	[119]
$0.88(0.95\text{NaNbO}_3-0.05\text{Bi}(\text{Mg}_{0.5}\text{Sn}_{0.5})\text{O}_3)-0.12\text{CaTiO}_3$	646	6.35	80.00	700	1 170–1 260/ 2.0	150	3.140 0	[120]
$0.90(0.88\text{NaNbO}_3-0.12\text{Bi}(\text{Ni}_{0.5}\text{Zr}_{0.5})\text{O}_3)-0.10\text{CaTiO}_3$	575	5.10	83.00	380	1 260/2.0	100	3.140 0	[121]
$0.88(0.85\text{NaNbO}_3-0.15\text{Sr}_{0.7}\text{Bi}_{0.2}\text{TiO}_3)-0.12\text{Bi}(\text{Mg}_{0.5}\text{Zr}_{0.5})\text{O}_3$	640	7.59	81.30	600	1 120/2.0	100	0.785 0	[122]

4 总结和展望

为了应对日益严重的全球环境污染和对人类健康的潜在威胁, 环境友好型储能陶瓷在过去的十年中引起了广泛的关注。但是, 相比于铁电体而言, 反铁电材料受到较少的关注。一方面, 对它的基础物理性能仍然缺乏系统的认识。另一方面, 拥有反铁电-铁电之间可逆相转变的反铁电材料体系是非常有限的。因此, 发展新型 NN 基反铁电材料是非常有意义的, 并且为进一步理解反铁电性质提供了

新的机会。

本文介绍了 NN 基储能陶瓷的最新研究进展, 重点综述了提高储能性能的方法。在成分调节方面, 通过离子掺杂可以提高致密度, 优化微观形貌, 减少缺陷, 进而提高击穿场强。在 A 位掺杂离子半径小于 Na^+ , B 位离子半径大于 Nb^{5+} 时, 有利于降低容差因子, 保持反转对称性, 增强反铁电稳定性, 降低剩余极化, 提高储能性能。通过复合离子掺杂也需要进一步降低容差因子, 稳定 NN 基陶瓷的反铁电性, 提高 ΔP , 减少储能损耗; 此外,

通过合适的离子掺杂提高 NN 基陶瓷的弛豫反铁电特性, 可以大幅度增加储能密度, 储能效率有待进一步提高。

未来 NN 基储能陶瓷的发展趋势: 1) 原料制备方面: 采用湿化学法(如水热法、溶胶凝胶法、自蔓延法等)和高能球磨法降低粉体粒度来进一步提高电学性能。2) 烧结工艺方面: 采用先进的制备工艺(如 SPS、闪烧、冷烧结、热压烧结等)以期提高储能性能的同时大幅度的降低能耗。3) 成型工艺方面: 采用轧膜、流延、冷等静压等工艺进一步优化微观结构, 进而提高储能性能。4) 理论研究方面: 结合先进的微区原位表征技术(如原位高分辨 TEM、微区红外等)和理论计算(如第一性原理、相场模拟等)进一步探究工艺-结构-性能之间的关联, 提出新理论和新机制。5) 器件制备方面: 综合考虑力、热和电性能, 推进提高储能性能和高稳定性电介质材料的器件研制。

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Research Progress on NaNbO₃-Based Ceramics for Capacitive Energy Storage

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Extended Abstract

Dielectric capacitors are one of the most important components in electrical equipment and electronic devices, and have attracted recent attention in the fields of new energy vehicles, advanced propulsion weapons, renewable energy storage, high-voltage transmission, and medical defibrillators. Dielectric capacitors have ultra-short charge and discharge time, ultra-high power density and high operational safety, compared with electrochemical capacitors such as batteries, fuel cells and supercapacitors. However, the low energy storage density of dielectric capacitors limits their wide application. Therefore, it is necessary to develop dielectric capacitors with a high temperature and a high energy density.

NaNbO₃(NN)-based ceramic material is considered as one of the most potential dielectric energy storage materials because of its wide band gap, lower cost and high polarization. However, there are still some problems in the application of NN-based ceramic materials, such as low energy storage density and energy storage efficiency, and poor temperature stability. In order to optimize the energy storage performance of NN-based ceramics, phase structure regulation, micro-morphology optimization, doping modification (for A-site, B-site, A/ B-site co-doping) are used to improve the energy storage density, efficiency, and frequency/temperature stability. These optimization strategies provide opportunities for the application of NN-based ceramics.

NN-based ceramics have a complex phase structure, and pure NN cannot obtain double hysteresis loops at room temperature, which is attributed to the irreversible transition between the antiferroelectric P (AFE P) and ferroelectric Q (FE Q) phases. The AFE P phase can be stabilized, and the double hysteresis loop with a reversible phase transition can be obtained, improving the energy storage density and energy storage efficiency *via* reducing the tolerance factor. In terms of microstructure optimization, advanced sintering process, suitable sintering additives and preparation process can further improve the energy storage performance of NN-based ceramics. The advanced sintering process can optimize the microstructure, adjust the grain size and oxygen vacancy concentration to improve the energy storage performance. For instance, compared with Na_{0.7}Bi_{0.1}Nb_{0.9}Ta_{0.1}O₃ ceramic prepared *via* conventional sintering, the energy storage efficiency of the ceramic sample prepared *via* spark plasma sintering (SPS) increases from 81.1% to 90.5%. Adding suitable sintering additives can form a liquid phase, and then improve the densification process of ceramics. Also, the addition of sintering additives can reduce the sintering temperature and play the role of refining the grains, which is conducive to increasing the resistance of the ceramics and thus increasing the breakdown field. For MnO₂-doped 0.95NaNbO₃–0.05SrSnO₃ (NN5SS) ceramic, the energy storage density can be increased by nearly 14 times, compared to undoped NN5SS. The advanced preparation process can improve the density and electrical uniformity, thus improving the energy storage performance. The viscous polymer processing (VPP) can increase the energy storage density of 0.84 NaNbO₃–0.06 BiFeO₃–0.1 SrTiO₃ ceramics from 2.7 J/cm³ to 5.29 J/cm³, compared to conventional solid phase sintering.

The energy storage performance of NN-based ceramic can be improved *via* doping modification. Doping modification can introduce relaxation antiferroelectric properties, showing that long-range ordered antiferroelectric domains are broken to form micron-sized or nano-sized domains, which have a rapid response to the applied electric field, reduce the polarization lag between applied or discharged electric fields, and thus obtain a superior energy storage performance. Also, the solution of the second or third component can introduce relaxation characteristics, and the T_B and T_m temperature regions with nanodomains and polar nanoregions can be adjusted to room temperature in the NN-based system, showing the relaxation characteristics and improving the energy storage performance.

Summary and prospects The energy storage performance can be improved to a certain extent by means of phase structure regulation, micro-morphology optimization, doping modification, *etc.*. However, the harsher application environment requires a higher energy storage performance (*i.e.*, $W_{rec} > 10 \text{ J/cm}^3$, $\eta > 90\%$). The future development aspects of NN-based energy storage ceramics involve 1) raw material preparation, *i.e.*, wet chemical method (such as hydrothermal method, sol–gel method, self-spreading method, *etc.*) and high-energy ball milling method are used to reduce the particle size of the powder to further improve the electrical performance; 2) sintering process, *i.e.*, advanced preparation processes (such as SPS, flash sintering, cold sintering, hot press sintering, *etc.*) are used to improve the energy storage performance while greatly reducing energy consumption; 3) molding process, *i.e.*, the process of rolling film, casting and cold isostatic pressing are used to further optimize the microstructure and improve the energy storage performance; 4) theoretical research, *i.e.*, combined with advanced *in-situ* characterization techniques (such as *in-situ* high resolution TEM, micro-infrared, *etc.*) and theoretical calculations (such as first-principles, phase field simulation, *etc.*), a relationship between process-structure-performance is further explored, and new theories and mechanisms are proposed; and 5) device preparation, *i.e.*, the device with superior energy storage performance and high stability dielectric materials needs to be developed.

Keywords lead-free antiferroelectric ceramics; sodium niobate; doping modification; dielectric energy storage