

烧结气氛对反铁电陶瓷储能性能的影响

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摘 要: 贱金属内电极多层陶瓷电容器由于低成本优势受到广泛关注, 为了防止贱金属内电极(Ni 或 Cu)在高温下氧化, 需在低氧或还原气氛下烧结。本工作研究了低氧气氛烧结环境对 $\text{Pb}_{0.95}\text{La}_{0.02}\text{Sr}_{0.02}(\text{Zr}_{0.50}\text{Sn}_{0.40}\text{Ti}_{0.10})\text{O}_3$ (PLSZST)反铁电陶瓷电学性能的影响。氧含量降低, 反铁电陶瓷的绝缘特性和储能特性有所降低, 在 5.3×10^{-10} atm (1 atm=101 324.997 Pa)氧含量下, 陶瓷体可恢复储能密度为 $2.76 \text{ J} \cdot \text{cm}^{-3}$, 低于空气烧结样品的可恢复储能密度($3.56 \text{ J} \cdot \text{cm}^{-3}$), 放电储能密度为 $2.21 \text{ J} \cdot \text{cm}^{-3}$, 放电电流为 28.6 A。该工作为 PLSZST 反铁电陶瓷抗还原特性研究提供帮助, 进一步推动贱金属内电极 PLSZST 反铁电多层陶瓷电容器研发及生产。

关键词: 反铁电陶瓷; 贱金属内电极; 低氧烧结气氛; 多层陶瓷电容器; 储能

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近年来, 随着我国新能源汽车、5G 通讯和高功率脉冲等技术的发展, 对于高压高功率多层陶瓷电容器(MLCC)的需求日益旺盛^[1-2], 因此对电容器的设计及研发提出了相应的要求, 即能满足高压、高功率的应用需求。与 BaTiCO_3 (BT)基铁电材料相比, PbLaZrSnTiO_3 (PLZST)基反铁电材料在电场诱导反铁电铁电体(AFE-FE)相变电场附近具有极大的电流吞吐能力, 同样体积的反铁电 MLCC 的最大放电电流可以比铁电电容器大 50% 以上; 或者从电容量随电场变化的曲线中可知, 反铁电的电压系数为正, 而铁电体的电压系数为负^[3]。传统的 BT 基铁电陶瓷电容器, 其电容量随电压呈现大幅度衰减, 这会严重影响性能释放。而 PLZST 基反铁电陶瓷电容器在一定电压范围内, 电容量会随电压的增加而增大。目前, 铁电 MLCC 极差的偏压特性已经成为电路系统的重大障碍。薄膜电容虽然电容量保持平稳, 但其体积较大、使用温度范围窄, 在许多场合无法适用。因此, 在高压和高功率的应用环境中, PLZST 基反铁电 MLCC 具有极大的优势。

烧结气氛是成功制备 MLCC 的关键所在。为了得到性能优异的 MLCC 产品, 在烧结过程中需严格控制 MLCC 内电极与陶瓷体间烧结气氛相匹配。MLCC 内电极所用材料主要为贵金属 Ag/Pd 或 Au 和贱金属 Ni 或 Cu, 由于贵金属材料的价格逐年攀升, 贱金属材料更具价格优势^[4]。为了防止贱金属 Ni 或 Cu 在高温下氧化, 需在低氧或还原气氛下烧结。

当前关于 PLZST 基反铁电材料在低氧气氛或还原气氛烧结的文章或工作鲜有报道, 主要集中在 PbZrTiO_3 (PZT)基或 PbLaZrTiO_3 (PLZT)基材料^[5-11]。Hong 等^[10]报道了在 900 °C 的还原气氛条件下烧结的 PZT-PZNN, 陶瓷体的电容量从 23.16 nF 降到 12.26 nF, 电阻值从 0.2 Ω 增加至 0.8 Ω ; Shimakawa 等^[6]研究了 PZT 在 4% H_2 (体积分数)、500 °C 气氛下退火, 发现有明显的 Pb 金属被析出; Jeong 等^[11]将 PMNZT 先在 900 °C 空气下烧结, 随后在 400 °C 的 N_2/H_2 还原气氛下退火实现了 PMNZT 与铜共烧, 在 1×10^8 个电循环后有效机电耦合系数和动态压电常数明显降低; Kondo 等^[7]为了制备

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PLZT 材料的 FeRAM 器件, 将电极材料 SrRuO_3 与 PLZT 在 $\text{Ar}+3\%\text{H}_2$ (体积分数) 的还原气氛下共烧结, 发现 SrRuO_3 与 PLZT 两者会发生化学反应形成焦绿石相, 但没有析出金属 Pb; Schaab 等^[8]发现 PLZST 在低氧环境下退火会导致陶瓷体产生更多的缺陷, 如氧空位或氧空穴。由此可知, 在还原性气氛或低氧气氛环境下, 陶瓷体的晶体结构和电学性能会发生明显下降, 主要原因是金属铅的析出会破坏晶格结构, 或者产生晶格缺陷, 例如氧空位、自由电子等导致材料性能衰退^[8]。日本的 TDK 公司已推出基于 Cu 内电极的 PLZT 基反铁电 MLCC 的高端产品, 并且实现商业化。国内仅个别企业有 Ag/Pd 内电极的反铁电 MLCC, 而 Cu 内电极的反铁电 MLCC 的还未有相关产品。因此, 为了实现 Cu 内电极与 PLZST 共烧结, PLSZST 反铁电陶瓷在低氧烧结气氛环境下的性能研究具有重要意义。

基于以上背景, 本工作将 PLZST 基反铁电陶瓷放置在 4 种低氧气氛烧结环境下烧结, 研究了低氧气氛烧结环境下, PLZST 基反铁电陶瓷的晶体结构、微观形貌及电学性能。结果表明, 氧含量降低, 反铁电陶瓷的绝缘特性和储能特性有所降低, 但未发现 Pb^{2+} 被还原成金属 Pb。

1 实验

1.1 样品制备

选用 Pb_3O_4 (95%, 沪试)、 La_2O_3 (99.99%, Acros)、 ZrO_2 (99%, 阿拉丁)、 SnO_2 (99.8%, 沃凯)、 TiO_2 (98%, 沃凯)、 SrCO_3 (99%, 沪试) 为原料, 使用固相法制备 $\text{Pb}_{0.95}\text{La}_{0.02}\text{Sr}_{0.02}(\text{Zr}_{0.50}\text{Sn}_{0.40}\text{Ti}_{0.10})\text{O}_3$ (PLSZST) 反铁电陶瓷。首先根据化学计量比称量 500 g 原料, 使用乙醇作为溶剂, 一次球磨 12 h 后在 70 °C 烘干。

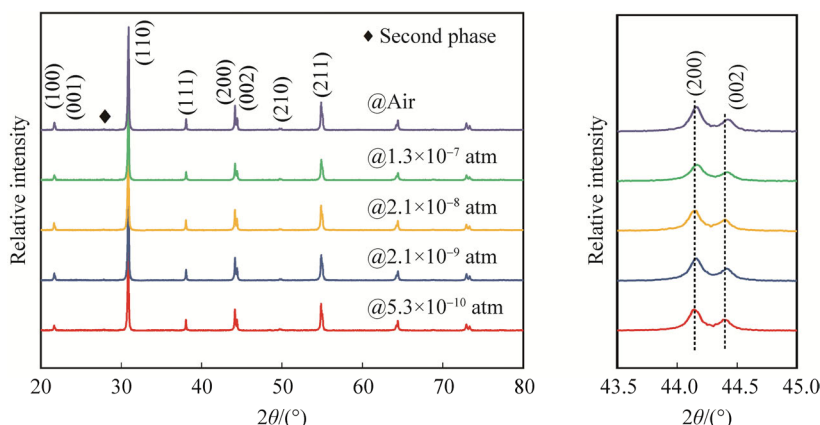
将混合好的原料在密闭坩埚中于 850 °C 煅烧 2 h, 得到煅烧粉。然后, 将 0.6% (质量分数) 的 $\text{BaCO}_3\text{-B}_2\text{O}_3\text{-SiO}_2\text{-K}_2\text{CO}_3$ (BBSK) 玻璃加入煅烧粉中, 二次球磨 12 h 后烘干, 得到合成粉。用 5% (质量分数) 的聚乙烯醇(PVA)作为黏合剂, 在 20 MPa 的压力下将合成粉压成厚 2 mm, 直径 10 mm 的陶瓷生坯。最后, 将陶瓷生坯在 1020 °C 的烧结温度和 5.3×10^{-10} 、 2.1×10^{-9} 、 2.1×10^{-8} 、 1.3×10^{-7} atm (1 atm=101 324.997 Pa) 的低氧含量气氛和空气气氛下烧结。

1.2 样品表征

本工作使用 D/Max-2400 型(Rigaku Corporation) X 射线衍射仪分析了烧结样品的相结构; 使用 Quanta F250 型(FEI Quanta)扫描电子显微镜分析了样品热腐蚀表面的微观形貌及晶粒尺寸; 使用 E4980A 型(Keysight)LCR 测试设备测试了样品的介电常数及损耗随温度变化特性; 使用 TF analyzer 2000 型(aixACCT)铁电分析仪测试了样品的电滞回线及漏电流密度曲线; 使用实验室自建的充放电测试系统对样品的充放电性能进行了研究^[12], Pearson 6585 (Pearson Electronics) 电流线圈、P6015A (Tektronix) 高压探头和 DPO4104B (Tektronix) 高速示波器分别记录放电电流、电压和放电波形。

2 结果与讨论

为研究烧结气氛对 PLSZST-0.6%BBSK (质量分数) 反铁电材料的晶体结构的影响, 进行了 XRD 测试, 如图 1 所示。由图 1 可见, 在所有气氛烧结环境中, 所有样品都形成钙钛矿结构, 有少量第二相产生, 这可能是 Pb 在高温时挥发产生的焦绿石相^[13]。从 44.2°附近的分裂峰可知, 低氧气氛条件下 2 个分裂峰的强度及角度并未发生改变, 这



1 atm=101 324.997 Pa.

图 1 PLSZST-0.6%BBSK (质量分数) 在不同烧结气氛下的 XRD 谱

Fig. 1 XRD patterns of PLSZST-0.6%BBSK (in mass) ceramic sintered at different atmosphere

说明陶瓷体四方结构特性并未改变^[14-16]。随着氧含量的降低, (200)和(002)峰向低角度方向移动, 说明低氧气氛导致了材料的晶格扭曲, 根据 Bragg 公式可知, 陶瓷体的晶胞体积在增大。低氧条件下, 氧空位增多导致电子数量增多, 导致 Ti^{4+} 还原成低价的 Ti 离子, Ti^{4+} 、 Ti^{3+} 的离子半径分别为 0.605、0.670 Å^[13]。

将 PLSZST-0.6%BBSK 反铁电材料在低氧气氛下和空气烧结的陶瓷样品进行抛光并在各自烧结气氛条件下热腐蚀, 表面 SEM 结果如图 2 所示。由图 2 可见, 所有样品的晶粒与晶界分布明显, 在表面处未看到有第二相生成, 这说明低氧环境下,

陶瓷体未有金属铅或者其他物质析出; 其次, 在低氧环境烧结的样品晶粒之间产生更多的孔洞, 表明低氧气氛烧结的陶瓷体致密度低, 该现象与有关报道一致^[17-18]; 随着烧结气氛中氧含量的增加, 陶瓷体的晶粒有逐渐长大趋势。PLSZST-0.6%BBSK 反铁电材料在不同气氛下烧结样品的平均晶粒尺寸分布如图 2f 所示。从晶粒尺寸的分布图上可看出在 5.3×10^{-10} atm 的氧含量下, 平均晶粒尺寸为 0.96 μm , 随着氧含量增加, 陶瓷体晶粒逐渐长大, 在 1.3×10^{-7} atm 的氧含量下, 平均晶粒尺寸为 1.12 μm , 此气氛烧结下的晶粒尺寸已接近空气下的样品晶粒尺寸(1.15 μm)。

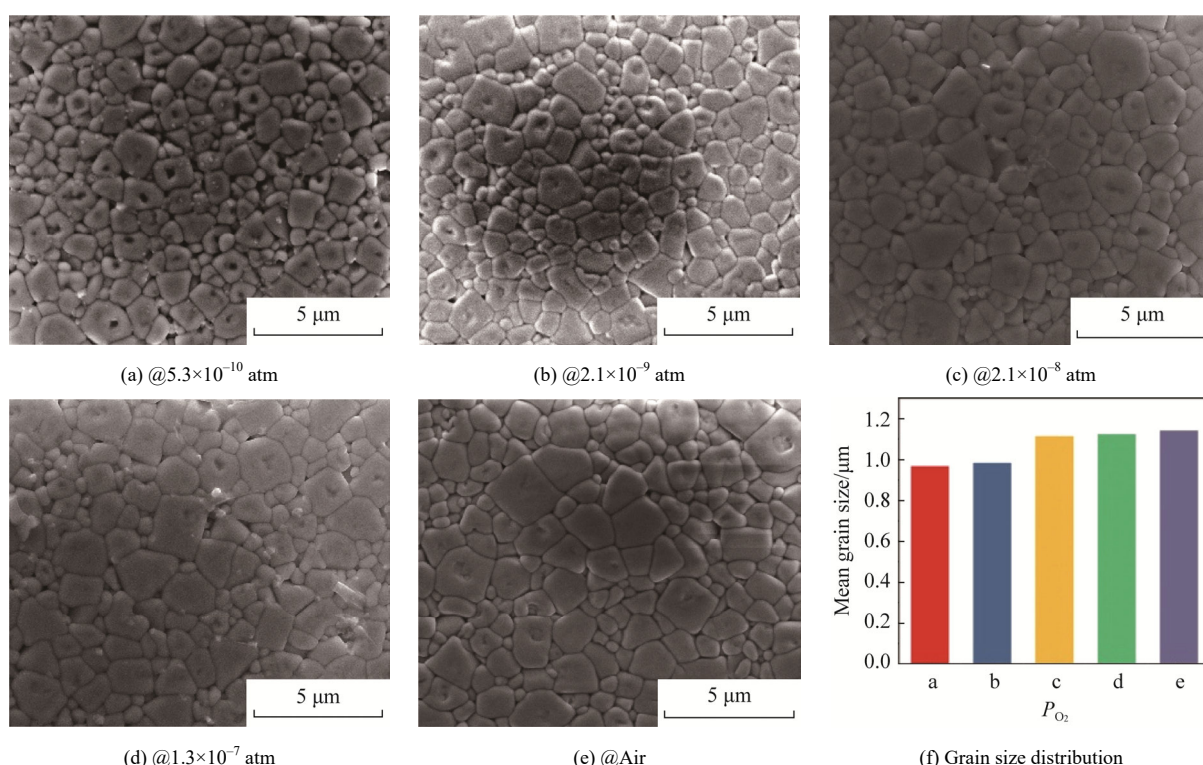


图 2 PLSZST-0.6%BBSK 在不同烧结气氛下的热腐蚀表面 SEM 照片

Fig. 2 SEM images of hot corrosion surface of PLSZST-0.6%BBSK under different sintering atmospheres

图 3 为 PLSZST-0.6%BBSK 陶瓷样品在测试频率为 1、10、100、1000 kHz 下的介电温谱。由图 3 可见, 所有陶瓷样品的介电温谱都显示了相同的变化特征, 随着温度的升高, 介电常数先增大到最大值然后缓慢下降, 这个介电异常峰是由四方反铁电相转变为顺电相引起的^[19-23]。随着频率的增加, 介电常数与介电异常峰值并未发生明显变化, 这说明陶瓷体发生的是弥散型相变^[24-25], 而且也未随氧含量的变化而变化, 这表明氧含量未改变反铁电体的相变特征。另外, 在整个温度范围内, 都有较小的介电损耗(<0.04), 随频率的增加, 介电损耗也有增

长趋势, 其峰值有向高频移动的趋势, 这表明该反铁电体出现类弛豫特征^[21]。从图 3 可以明显看出低氧含量下的陶瓷样品具有更高的介电常数, 在约 150 $^{\circ}\text{C}$ 的最大介电常数比空气下的样品高约 15%, 这种现象与先前有关文献报道一致^[17, 26-27]。

图 4a 为 PLSZST-0.6%BBSK 在氧含量分别为 5.3×10^{-10} 、 2.1×10^{-9} 、 2.1×10^{-8} 、 1.3×10^{-7} atm 和空气气氛下的电滞回线图。由图 4a 可见, 在所有气氛条件下, 陶瓷体都具有典型的双电滞回线特征, 表明低氧气氛条件未改变陶瓷体的反铁电结构, 与 XRD 测试结果一致; 另外, 随着氧含量的增加, 陶瓷体

的最大耐击穿场强和最大极化强度也逐渐增加, 最大极化强度的增加是来源于耐击穿场强的提升, 这是因为在外电场强度增加, 电场诱导的电位移增加, 产生更大的极化强度, 但是当电场强度达到一定值后, 反铁电畴全部转为铁电畴, 电位移增加微小, 导致极化强度逐渐饱和^[28]。在 5.3×10^{-10} atm 氧含量烧结的陶瓷样品, 可以看出极化强度未达到饱和就已经击穿, 与陶瓷体具有低的致密度和较多的孔洞

有关。不同烧结气氛下样品的储能密度和效率如图 4b 所示。随着氧含量的降低, 陶瓷体的击穿场强和最大极化强度减小, 导致陶瓷体的饱和储能密度和可恢复储能密度逐渐减小, 在 5.3×10^{-10} atm 氧含量烧结的陶瓷样品可恢复储能密度为 $2.76 \text{ J} \cdot \text{cm}^{-3}$, 低于空气下烧结样品的可恢复储能密度($3.56 \text{ J} \cdot \text{cm}^{-3}$), 而储能效率未有明显降低, 即氧含量的增加未引起转换场和剩余极化强度的变化。

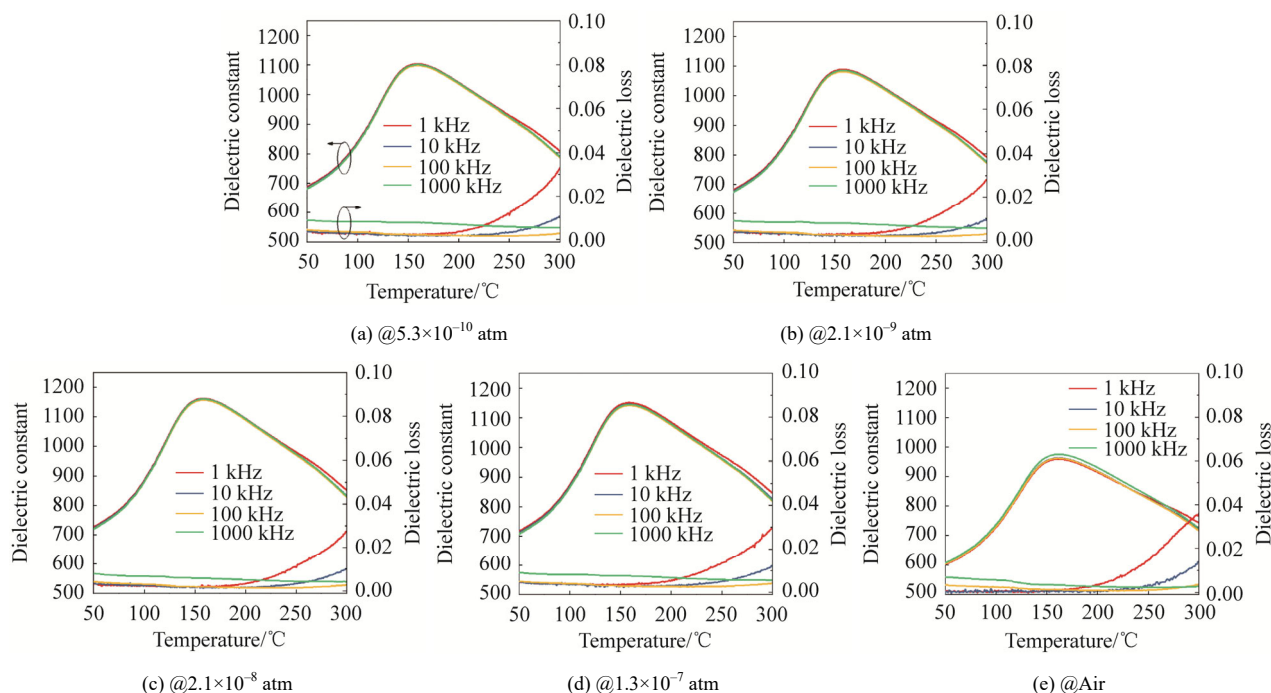


图 3 气氛下烧结样品在不同频率下的介电温谱

Fig. 3 Dielectric temperature spectra of sintered samples under different frequencies in atmosphere

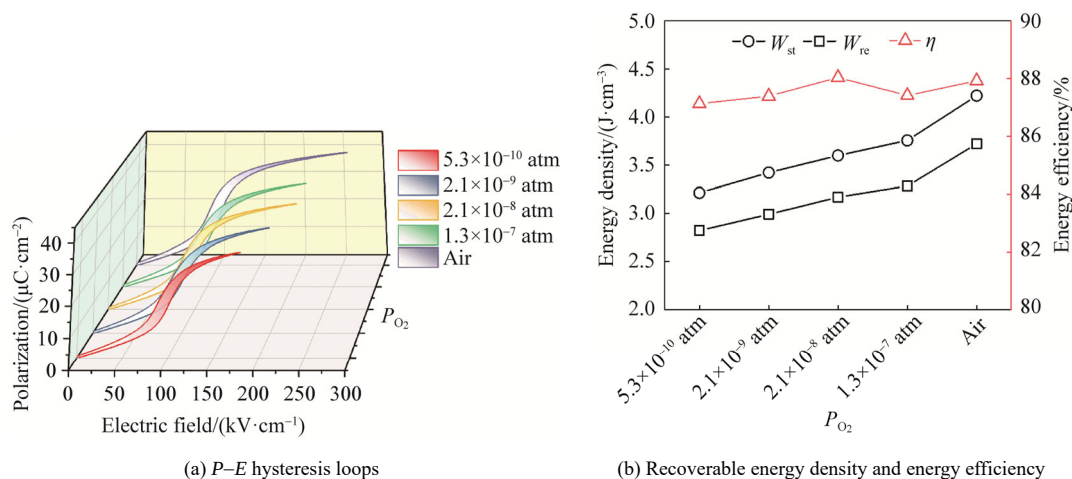


图 4 不同气氛下烧结样品的电滞回线图与储能密度和效率

Fig. 4 Hysteresis curves, energy storage density and efficiency of sintered samples under different atmospheres

利用铁电分析仪测试了不同气氛烧结的 PLSZST-0.6%BBSK 样品漏电流密度随外加电场变

化的特性, 测试频率为 10 Hz, 每个测试点停留 30 s, 以降低漏电流中极化电流的影响, 测试结果如图 5

所示。由图 5 可见, 样品的漏电流密度随着施加电场的增高而增大, 当到达转换场时材料的漏电流密度出现极大值。在氧含量为 5.3×10^{-10} atm 气氛条件下, 在外加电场为 $100 \text{ kV} \cdot \text{cm}^{-1}$ 下陶瓷体最大漏电流密度约为 $0.25 \mu\text{A} \cdot \text{cm}^{-2}$; 随着氧含量进一步增加, 漏电流密度变化微小。主要因为, 当氧含量为 5.3×10^{-10} atm, 陶瓷体的密度较低并且具有较多的孔洞, 导致自由电子更容易通过, 随着氧含量逐渐提升, 陶瓷致密度也相应提升, 漏电流开始逐渐减小。根据漏电流密度曲线, 根据 $100 \text{ kV} \cdot \text{cm}^{-1}$ 测试电场下的漏电流密度值计算出绝缘电阻率。低氧条件下绝缘电阻率在 $10^{11} \Omega \cdot \text{cm}$ 数量级, 随着氧含量增加, 绝缘电阻率有所增加; 在空气下的样品, 绝缘电阻率在 $10^{12} \Omega \cdot \text{cm}$ 数量级, 表明低氧气氛烧结导致绝缘电阻率下降, 样品在低氧气氛条件下, 产生了过多的载流子。陶瓷在高温烧结时, 发生式(1)~式(3)缺陷反应, 低氧条件下, 缺陷反应向右移动, 缺陷载流子数量增多, 导致陶瓷体绝缘特性降低, 即漏电流增加^[14]。

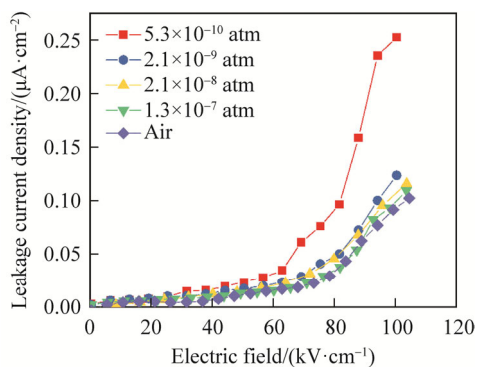
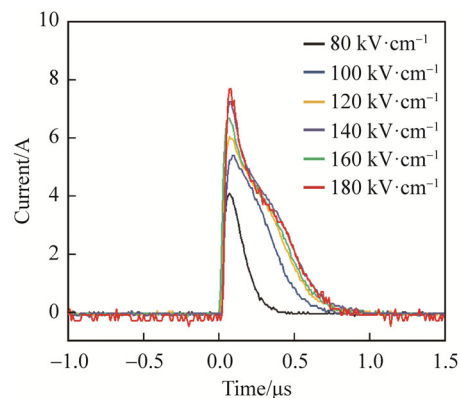


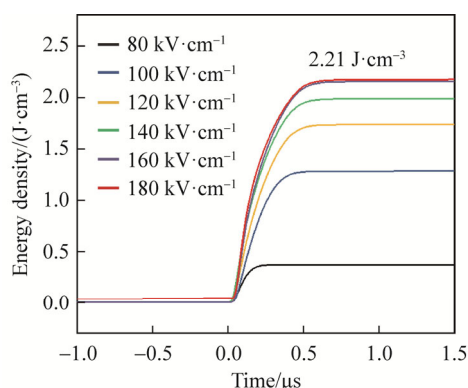
图 5 不同气氛下烧结 PLSZST-0.6%BBSK 样品漏电流随外加电场变化的曲线

Fig. 5 Curves of leakage current of sintered PLSZST-0.6%BBSK samples under different atmospheres as a function of external electric field

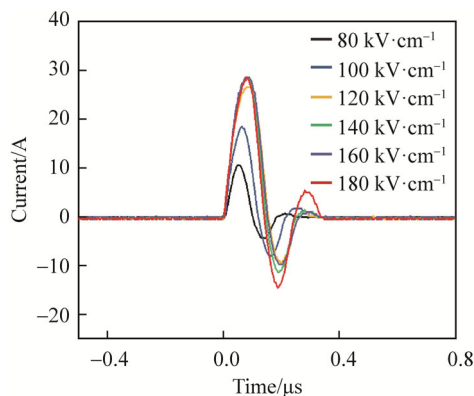
为了进一步评估 5.3×10^{-10} atm 气氛条件下样品的性能, 进行了充放电测试, 其中过阻尼下放电性能如图 6a~图 6b 所示。图 6a 为放电电流波形随充电电场的变化。由图 6a 可见, 当充电电场小于正向转换场时, 在 $80 \text{ kV} \cdot \text{cm}^{-1}$, 放电时间约为 $0.2 \mu\text{s}$, 而当充电电场大于正向转换场时, 放电时间增长缓慢, 并且还出现一个较斜平台, 是因为在放电阶段



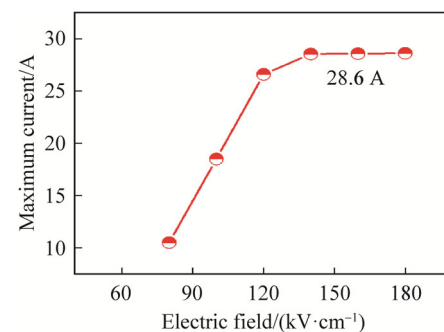
(a) Discharge current waveforms of overdamped circuit



(b) Energy density of overdamped circuit



(c) Discharge current waveforms of underdamped circuit



(d) Maximum current of overdamped circuit

图 6 PLSZST-0.6%BBSK 样品在 5.3×10^{-10} atm 氧含量气氛条件下的充放电特性

Fig. 6 Charge and discharge characteristics of PLSZST-0.6%BBSK sample under 5.3×10^{-10} atm oxygen content atmosphere conditions

对应的是铁电到反铁电相转变阶段(FE-AFE), 当充电电场小于正向转换场时, 反铁电畴未能全部转换为铁电畴, 在放电时, 只有部分铁电畴又重新转变为反铁电畴; 当充电电场大于正向转换场, 反铁电畴全部转变为铁电畴, 在放电时, 铁电畴需要全部转变为反铁电畴, 放电时间增大, 继续增大电场, 只会使偶极子发生位移极化, 放电时间增长缓慢, 平台基本不变^[29]。图 6b 为放电储能密度随充电电场变化。由图 6b 可见, 与放电电流对应, 随电场增加, 放电储能密度先迅速增长, 然后缓慢增长, 在 $160 \text{ kV} \cdot \text{cm}^{-1}$ 时, 放电储能密度为 $2.21 \text{ J} \cdot \text{cm}^{-3}$, 继续增加电场, 放电储能密度只有微小的增大。图 6c 展示了欠阻尼下的放电电流波形。随充电电场的增加, 放电电流峰值由迅速增长变为缓慢增长, 并且放电周期也具有相同增长趋势, 这种现象与过阻尼下放电特征一致。将放电电流的峰值汇总于图 6d, 结果显示, 在充电电场为 $160 \text{ kV} \cdot \text{cm}^{-1}$ 时放电电流已接近饱和, 为 28.6 A 。

3 结论

通过传统固相法制备了 PLSZST 反铁电陶瓷, 在 1020°C 烧结温度和 5.3×10^{-10} 、 2.1×10^{-9} 、 2.1×10^{-8} 、 $1.3 \times 10^{-7} \text{ atm}$ 的低氧含量气氛和空气气氛下烧结。结果表明, 低氧气氛烧结环境下, 陶瓷体具有四方钙钛矿结构, 且未发现金属 Pb 析出; 随着氧含量的降低, 陶瓷体的绝缘特性和储能特性有所降低, 在 $5.3 \times 10^{-10} \text{ atm}$ 氧含量下, 陶瓷体可恢复储能密度为 $2.76 \text{ J} \cdot \text{cm}^{-3}$, 低于空气下烧结样品的可恢复储能密度 ($3.56 \text{ J} \cdot \text{cm}^{-3}$), 放电储能密度为 $2.21 \text{ J} \cdot \text{cm}^{-3}$, 放电电流为 28.6 A 。

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Influences of Sintering Atmosphere on the Energy Storage Properties of Antiferroelectric

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Extended Abstract

Introduction In recent years, the high-voltage and high-power multi-layer ceramic capacitors (MLCCs) have attracted extensive attention with the development of new energy vehicles, 5G communication and high-power pulse technologies. At present, the materials used in the MLCC inner electrode are mainly precious metal (Ag/Pd or Au) and base metal (Ni or Cu). Base metal materials have more cost advantages compared with the precious metal materials. In order to prevent the oxidation of the base metal Ni or Cu at high temperatures, it is necessary to sintering in a low oxygen or reducing atmosphere. In order to obtain MLCC products with excellent performance, it is necessary to strictly control the matching of the sintering atmosphere between the inner electrode and the ceramic body during the sintering process. The crystal structure and electrical properties of the ceramic will be significantly reduced in the reducing atmosphere or low oxygen atmosphere environment, mainly because the precipitation of metal lead will destroy the lattice structure, or produce lattice defects. Therefore, it is of great significance to study the properties of PbLaZrSnTiO₃-based (PLZST-based) antiferroelectric ceramics in low oxygen sintering atmosphere. In this paper, PLZST-based antiferroelectric ceramics were sintered in four kinds of low oxygen sintering atmosphere. The crystal structure, microstructure and electrical properties of PLZST-based antiferroelectric ceramics were studied. Moreover, the energy storage properties of all samples were studied.

Methods Pb_{0.95}La_{0.02}Sr_{0.02}(Zr_{0.50}Sn_{0.40}Ti_{0.10})O₃ (PLSZST) antiferroelectric ceramics doped with were prepared using the traditional solid-state method. High quality raw materials, namely Pb₃O₄(95%, Sinopharm), La₂O₃(99.99%, Acros), ZrO₂(99%, Aladdin), SnO₂(99.8%, Sinopharm), TiO₂ (99.8%, Sinopharm) and SrCO₃(99%, Sinopharm), were weighted 500 g according to stoichiometric and ball milling for 12 h with ethyl alcohol as a solvent and dried at 70 °C. These raw materials were calcined at 850 °C for 2 h in a closed crucible. Then, 0.6% BaCO₃-B₂O₃-SiO₂-K₂CO₃(BBSK, in mass) was added to the mixed powder according to the solid weight ratio as the calcination powder. After ball milling for 12 h, the powder was dried. Next, the powder was pressed into pellets at 20 MPa with 5% Polyvinyl Alcohol (PVA, in mass) as the binding agent 2 mm thick and 10 mm in diameter. Finally, the green ceramics with BBSK addition were sintered at 1020 °C and low oxygen sintering atmosphere (5.3×10⁻¹⁰, 2.1×10⁻⁹, 2.1×10⁻⁸, 1.3×10⁻⁷ atm) and air for 2 h in closed crucibles filled with the calcination powder.

Results and discussion In order to study the effect of sintering atmosphere on the crystal structure of PLSZST-0.6% BBSK (in mass) antiferroelectric material, XRD were conducted as shown in Fig. 1. It can be seen that all samples have perovskite structure, and a small amount of second phase is generated, which may be pyrocholate phase produced by Pb volatilization at high temperature. From the splitting peak near 44.2°, it can be seen that the intensity and Angle of the two splitting peaks do not change under the condition of low oxygen atmosphere, which indicates that the tetragonal structure of the ceramic body does not change. The peaks of (200) and (002) move to the lower Angle at lower oxygen content, indicating that the low oxygen atmosphere leads to the lattice distortion of the material. Then, the microstructure was studied. As can be seen in the surface micrograph, there are no metal lead or other substances precipitated from the ceramic body as observed in those samples treated at low oxygen sintering atmosphere. It can be seen from the f dielectric temperature spectra that all samples show the same variation characteristics. With the increase of temperature, the dielectric constant first increases to the maximum value and then slowly decreases. This dielectric anomaly peak is caused by the transformation of tetragonal antiferroelectric phase into paraelectric phase. With the increase of frequency, the dielectric constant and the peak value of dielectric anomaly do not change significantly, which indicates that the ceramics are a diffuse phase transition, and does not change with the change of oxygen content, which indicates that the oxygen content does not change the phase

transition characteristics of antiferroelectric. With the decrease of oxygen content, the breakdown field strength and maximum polarization strength of the ceramic decrease, resulting in the gradual decrease of the saturated energy storage density and recoverable energy storage density of the ceramic body. The ceramic sintered at 5.3×10^{-10} atm has a recoverable energy storage density of $2.76 \text{ J} \cdot \text{cm}^{-3}$ which is lower than that of the ceramic sintered at air ($3.56 \text{ J} \cdot \text{cm}^{-3}$), showing a discharge energy density of $2.21 \text{ J} \cdot \text{cm}^{-3}$.

Conclusions Multi-layer ceramic capacitors with base metal inner electrodes have been widely concerned because of its lower cost advantages. In order to prevent the oxidation of the base metal inner electrodes (Ni or Cu) at high temperatures, it needs to be sintered in low oxygen or reducing atmosphere. The effect of low oxygen atmosphere on the electrical properties of PLSZST antiferroelectric ceramics was studied. With the decrease of oxygen content, the insulation characteristics and energy storage characteristics of antiferroelectric ceramics were reduced. Under the oxygen content of 5.3×10^{-10} atm, the ceramic has a recoverable energy storage density of $2.76 \text{ J} \cdot \text{cm}^{-3}$, which is lower than that of sintered sample under air ($3.56 \text{ J} \cdot \text{cm}^{-3}$), has a discharge energy storage density of $2.21 \text{ J} \cdot \text{cm}^{-3}$, and has a discharge current of 28.6 A. This work provides understanding of anti-reduction characteristics of PLZST-based antiferroelectric ceramics, and further promotes the development and production of PLZST-based antiferroelectric multilayer ceramic capacitors with internal electrodes in base metals.

Keywords antiferroelectric ceramics; base metal inner electrodes; low oxygen atmosphere; multilayer ceramic capacitors; energy storage