

锆锡钛酸镧铅反铁电体陶瓷的低温烧结和储能特性

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摘 要: 随着风电、光电等绿色能源的利用和对大功率电力电子装备需求的增加, 大功率储能器件受到了广泛的关注, 而具有高储能密度和高储能效率的(Pb, La)(Zr, Sn, Ti)O₃ (PLZST)反铁电体陶瓷用于超级介电储能电容器具有明显的优势。但是, 受到陶瓷本身高温烧结温度(1 200~1 300 °C)的限制, 难以适应贱金属内电极多层陶瓷电容器的应用。为了适应贱金属铜(Cu)内电极的烧结, 将玻璃粉 MgO-Al₂O₃-ZnO-B₂O₃-SiO₂(MAZBS)添加到(Pb_{0.97}La_{0.02})(Zr_{0.55}Sn_{0.41}Ti_{0.04})O₃(PLZST)反铁电体陶瓷中, 使烧结温度低于铜内电极的熔点。研究结果表明: 当添加了玻璃粉 MAZBS 的质量分数为 0.75%时, PLZST 陶瓷在较低的温度(930 °C)下可以实现致密烧结, 且陶瓷在室温和外加电场 300 kV/cm 下具有较高的放电储能密度(6.08 J/cm³), 和储能效率(77%)。

关键词: 锆锡钛酸镧铅; 反铁电陶瓷; 低温烧结; 储能密度; 储能效率

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近年来, 全球面临环境污染、能源短缺和气候变暖等严峻问题, 促使人们积极探索低碳新能源解决方案。尽管各种新能源器件不断涌现, 但其功率密度相对较低, 而且存在较大的安全隐患。另一方面, 电介质储能电容器因其高功率密度、快速充放电速率和长寿命等特性备受关注, 被视为解决新能源高功率问题的关键技术之一^[1]。该技术在民用领域广泛应用, 包括太阳能、风能和氢能等新能源发电系统, 以及混合动力交通工具逆变系统中的关键组成部分。在军用方面, 电介质储能电容器也被广泛应用于电磁炮、激光武器、航母飞机弹射装置等大功率设备。然而, 尽管电介质储能电容器在各个领域取得显著进展, 其体积依然较大。以应用于混合动力汽车的电介质储能电容器为例, 其体积占据整个逆变设备总体积的约 40%^[2-3]。为解决这一问题, 多层陶瓷电容器(MLCC)因其小巧、可靠、易于

集成等特点成为备受关注的解决途径。

目前, 高储能密度的介电材料研究已成为材料领域内一项备受关注的课题^[4]。高储能密度的介电材料主要分为线性介电体、正常铁电体、弛豫型铁电体和反铁电体。大量的研究表明, 反铁电体由于存在电场诱导的反铁电-铁电相变, 通常具有较大的储能密度^[5-6]。上述材料的储能密度和效率可以通过电滞回线(P - E 曲线)对极化强度积分来进行计算, 具体公式为:

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

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

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

其中: W_{tot} 、 W_{rec} 和 η 分别为总储能密度、放电储能密度和储能效率; P_{max} 、 P_r 和 E 分别为最大极化强

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度、剩余极化强度、和外加电场强度^[7]。

然而, 尽管可以通过离子掺杂来调整材料的反铁电性和储能性能, 但仍然面临一个挑战, 即这些材料通常具有较高的烧结温度(超过 1 200 °C)。最近几年, 贵金属内电极的价格一直在上涨。为了降低元器件成本, 多层陶瓷电容器(MLCC)逐渐采用贱金属(如 Ni、Cu 等)内电极^[8]替代贵金属内电极, 如 Pt、Ag、Pd^[9]等。虽然铜作为反铁电体多层陶瓷电容器的内电极是一个相对合理的选择, 但铅基反铁电陶瓷的烧结温度(1 200~1 300 °C)与铜的烧结温度(熔点 1 084 °C)存在不匹配的问题。因此, 降低反铁电体陶瓷的烧结温度是解决这个问题的关键策略。降低陶瓷烧结温度的方法大致分为以下几类: 1) 在预烧后粉末中加入一定量的低软化点玻璃相, 以产生液相并促进低温烧结过程。例如: Chen 等^[10]在陶瓷中添加了质量分数为 3% PbO–Bi₂O₃–SiO₂, 并在 1 250 °C 烧结, 获得的储能密度为 2.3 J/cm³ 和储能效率为 76.8%。Sun 等^[11]在陶瓷中掺杂质量分数为 0.8% Al₂O₃, 并在 1 040 °C 烧结, 获得了储能密度 3.2 J/cm³ 和良好的储能效率 90%; 2) 在预烧后的粉末中加入一定量的金属氧化物。如 Li 等^[12]在陶瓷中掺杂了质量分数为 0.05% CuO 和质量分数为 0.15% Bi₂O₃, 并在 1 000 °C 获得了最佳储能性能; 3) 改进烧结工艺, 如 Chen 等^[13]通过氧化层与陶瓷颗粒形成共晶的核–壳结构, 将烧结温度降至 1 100 °C。

相比于(Pb,La)(ZrTi)O₃(PLZT)、Pb(ZrTi)O₃(PZT)陶瓷, (Pb_{0.97}La_{0.02})(Zr_{0.55}Sn_{0.41}Ti_{0.04})O₃(PLZST)有良好的储能密度和储能效率^[14–16], 因此, 在本工作中设计了 PLZST–x% (MgO–Al₂O₃–ZnO–B₂O₃–SiO₂) (MAZBS, 其中 x%为质量分数)陶瓷体系, 对其介电特性、极化性能以及储能密度等方面进行了较系统的研究。采用传统固相烧结法制备的 PLZST–x% MAZBS(x=0.00, 0.25, 0.50, 0.75, 1.00, 1.25)陶瓷为研究对象, 系统地研究其晶体结构、微观形貌以及介电、铁电及储能性能随成分的变化。

1 实验

1.1 实验方法

采用传统的固相方法制备 PLZST–x%MAZBS (其中 x=0.00, 0.25, 0.50, 0.75, 1.00, 1.25)反铁电体陶瓷样品。本工作中使用阿拉丁提供的原材料, 即 PbO(99.0%, 质量分数, 下同)、La₂O₃(99.5%)、ZrO₂(99.5%)、SnO₂(99.8%)和 TiO₂(99.8%)。按照摩尔比称量, 以无水乙醇为溶剂球磨 18 h, 然后在

100 °C干燥 12 h。干燥的粉料放在密闭的坩埚中, 然后在马弗炉中于 900 °C煅烧 2 h。玻璃粉 MAZBS 通过水淬得到, 然后将玻璃粉按照固体质量比加入到陶瓷粉料中, 经过 24 h 的高能球磨, 然后在 80 °C干燥 10 h。接下来, 粉末用质量分数为 5%的乙烯醇缩丁醛(PVB)作为粘合剂, 混合后在 20 MPa 下压制成厚度为 1 mm, 直径为 12 mm 的生片。最后, 将添加了 MAZBS 玻璃相的陶瓷生坯在 930~1 000 °C烧结 4 h。作为对比, x=0 的样品是在 1 200~1 300 °C烧结。为了性能测试, 样品经过抛磨, 并在两面镀上了金电极。各个样品的电极尺寸(直径)和样品厚度分别为: x=0, (3.00±0.11), (0.055±0.007) mm; x=0.25, (0.82±0.19), (0.072±0.07) mm; x=0.50, (1.68±0.04), (0.076±0.007) mm; x=0.75, (2.28±0.33), (0.055±0.004) mm; x=1.00, (0.87±0.30), (0.066±0.003) mm; x=1.25, (1.90±0.44), (0.062±0.005) mm。

1.2 结构表征与性能测试

通过 X 射线衍射仪(XRD, 日本理学公司 Rigaku, Ultima-IV)表征晶相结构。使用热重–差示扫描量热仪(TG–DSC, 德国耐驰 NETZSCH, STA449F5)测量 MAZBS 玻璃粉末的热行为。使用 Fourier 红外光谱仪(美国赛默飞世尔, Nicolet 6700)测试玻璃粉末的分子团的振动和转动。通过扫描电子显微镜(SEM, 日本株式会社日立高新技术公司, S3400-N、SU8010)表征陶瓷的表面形貌。使用阻抗分析仪(LCR, 上海同果科技, HCT1821)测试陶瓷的介电性能。使用多铁性综合测试系统(美国 Radiant Technologies INC, Multiferroic II 40 KV)测试陶瓷的电滞回线。

2 结果与讨论

2.1 微观结构表征

图 1a 为 MAZBS 玻璃粉的红外光谱。由图 1a 可见, 在 400~600 cm⁻¹ 范围内, 吸收峰对应[ZnO₄]四面体单元中 Zn–O 的拉伸振动波段^[17]。在 600~700 cm⁻¹ 光谱范围内, 吸收峰是[AlO₃]三角形单元中 Al–O–Al 键的弯曲振动波段。在 800~1 000 cm⁻¹ 光谱范围内, 吸收峰是 Si–O–B 的拉伸振动与[BO₄]四面体型的 B–O 拉伸振动重叠波段^[18]。1 200~1 300 cm⁻¹ 的红外吸收峰对应[BO₃]三元单元的桥接氧 B–O 的拉伸振动的典型波段, 而 1 300~1 400 cm⁻¹ 的吸收峰是[MgO₄]四面体和[BO₃]三角单元中非桥接氧 B–O 的不对称拉伸振动波段^[17–20]。这些结果表明 Al³⁺、Zn²⁺和 Mg²⁺已经被

引入到玻璃网络中并形成非桥氧(NBO)。图 1b 中的 TG-DSC 曲线揭示了 MAZBS 玻璃的热变化。显然, MAZBS 的玻璃化转变温度(T_g)约为 450 °C, 这有助于避免有机粘结剂在排胶过程中燃烧不充分而被陶瓷里的玻璃吸附形成积碳^[21]。值得注意的是, 在 700 °C 和 900 °C 处存在吸热和放热峰, 分

别对应于 MAZBS 玻璃的结晶温度(T_c)和软化温度(T_f)。较低的 T_g 和 T_f 值可以归因于 Al^{3+} 、 Zn^{2+} 和 Mg^{2+} 引入引起的 NBO 的形成, 使得 $[BO_3]$ 玻璃网络不稳定^[22-23]。因此, 通过添加这种低软化点玻璃, 可以在相对低的温度下形成液相烧结, 从而降低陶瓷的烧结温度。

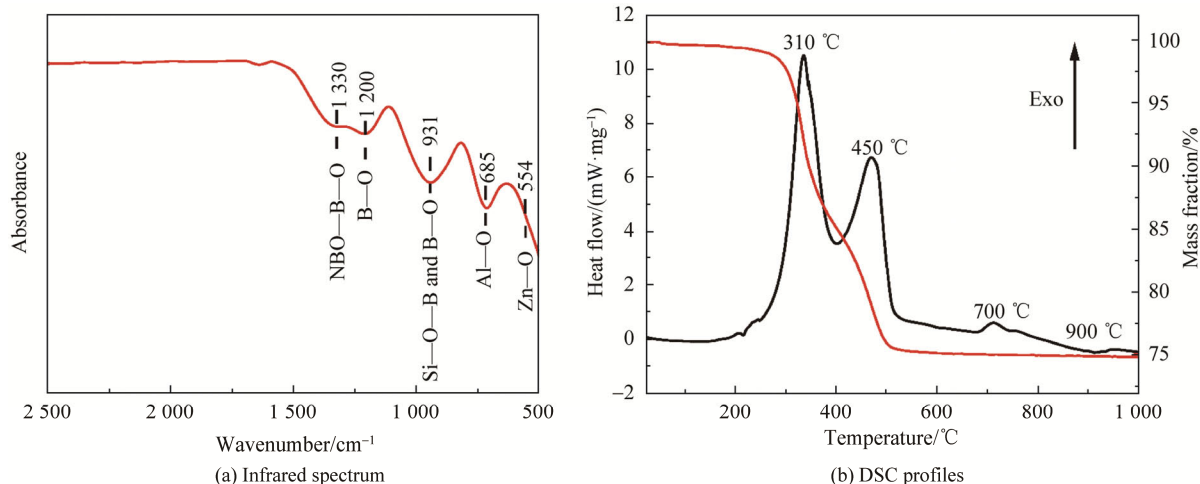


图 1 MAZBS 玻璃粉的 Fourier 变换红外和热重/差示扫描量热图谱
Fig. 1 FTIR and TG/DSC profiles for $MgO-Al_2O_3-ZnO-B_2O_3-SiO_2$ (MAZBS) glass powders

图 2 为 PLZST- $x\%$ MAZBS 陶瓷在 20°~80°范围内的 XRD 谱。由图 2 可见, 所有陶瓷的衍射峰都较为尖锐, 且没有明显的杂质衍射峰, 呈现出典型的钙钛矿结构^[24]。将(200)峰的谱放大, 在 44.2°附近的衍射峰放大谱中, 可以清晰地观察到随着玻璃相掺入量的增加, (200)特征峰向左移动。根据 Bragg 衍射方程:

$$2d\sin\theta = n\lambda \quad (4)$$

其中: d 为晶面间距; θ 为入射 X 射线与相应晶面的夹角; λ 为 X 射线波长; n 为衍射级数; d 与 θ 在测试范围内成反比。由于玻璃相中半径较大的 Mg^{2+} (0.69 Å) 取代了 Ti^{4+} (0.60 Å), 导致晶面间距 d 增大, θ 减小, 从而(200)衍射峰向左移动^[25]。

图 3 为各陶瓷样品的 SEM 照片。在没有掺入玻璃相的情况下, 晶粒多呈球形且较为均匀。而一旦掺入了玻璃相, 晶粒的形状变得不规则, 数量增加, 但陶瓷的致密程度仍然较高。通过 ImageJ 软件对照片上的晶粒尺寸进行统计, 得到的结果图 4 所示。未掺杂玻璃相时, PLZST 的平均粒度为 2.14 μm , 而玻璃相含量为 0.75% 时, 平均粒度急剧下降至 0.32 μm 。随着玻璃相含量的进一步增加, 平均粒度略微上升。这一现象可以解释为 2 个方面的影响。首先, 过量的 MAZBS 玻璃引入的液相增多, 提高了陶瓷颗粒在成核时相互碰撞的概率, 促使晶粒生长^[26]。其次, 当玻璃相液化后, 陶瓷晶粒被分散成相互独立的个体, 但晶粒之间的传质受到玻璃相的阻碍, 从而减缓了晶粒的生长速率。因此, 随着玻璃相掺杂量的增加, 陶瓷的平均晶粒尺寸仅略微增大^[27]。

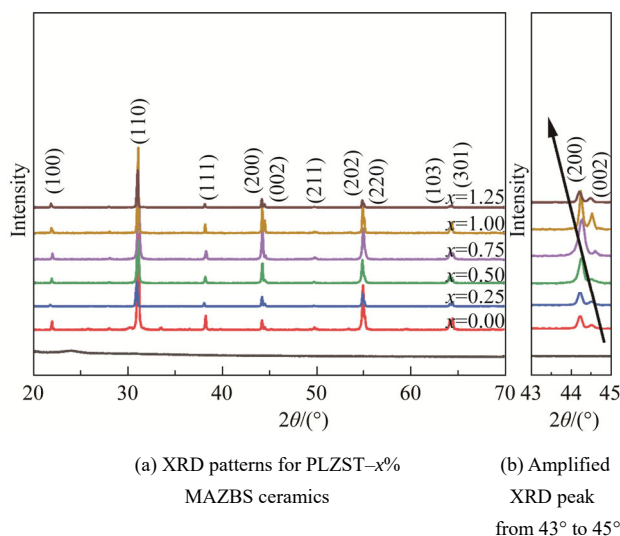
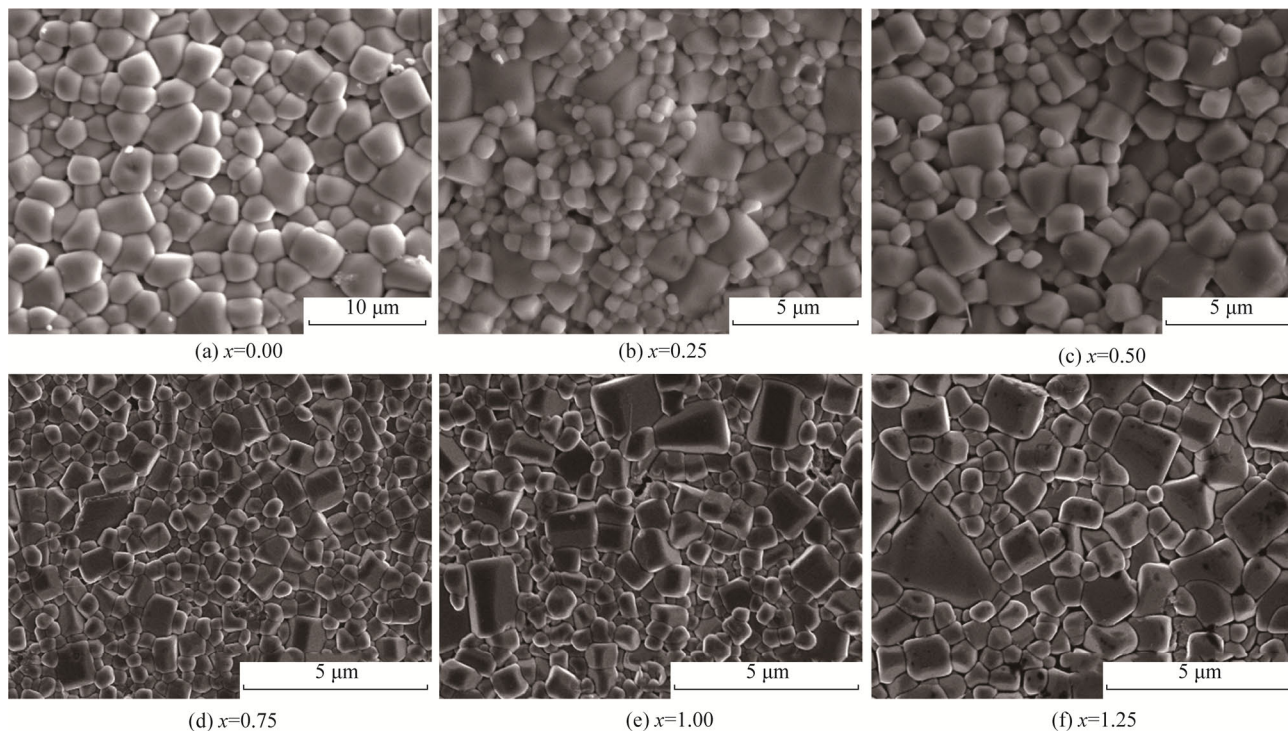
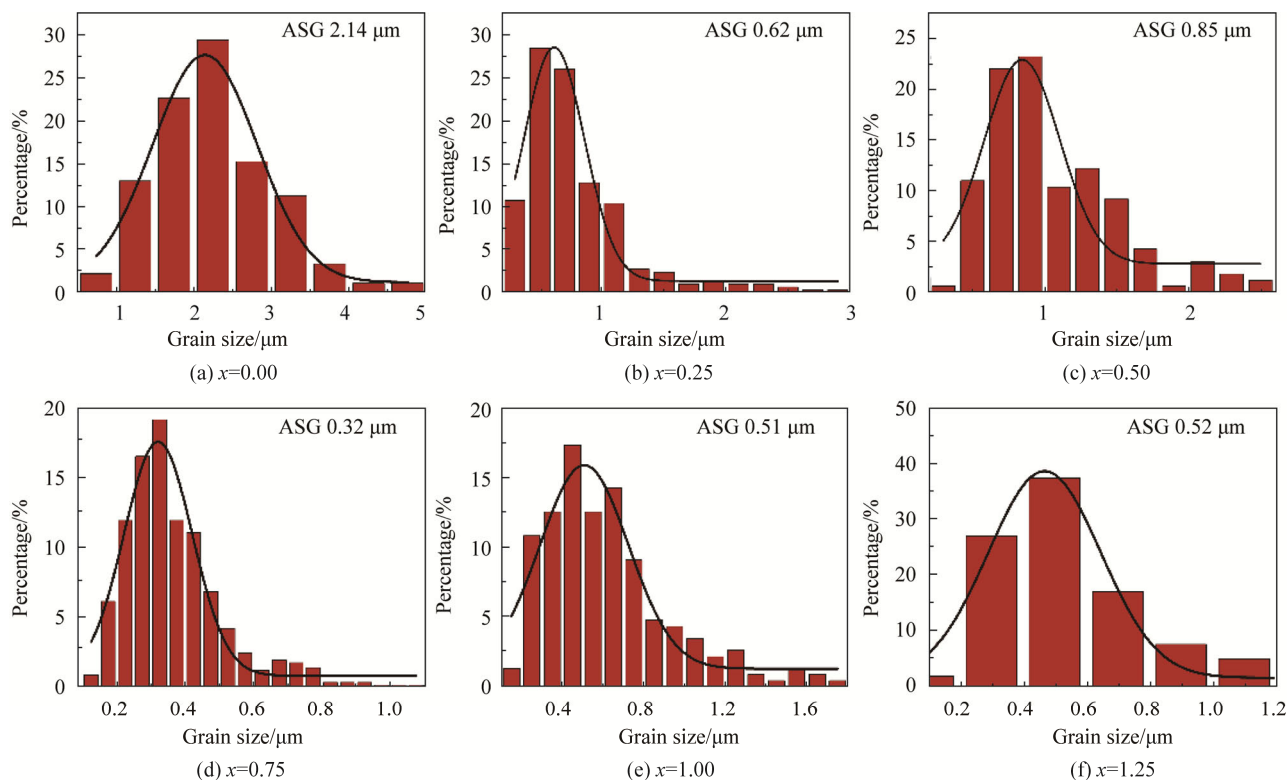


图 2 PLZST- $x\%$ MAZBS 陶瓷的 XRD 衍射谱及(200)/(002) 放大衍射峰

Fig. 2 XRD patterns and amplified (200)/(002) peak for $(Pb_{0.97}La_{0.02})(Zr_{0.55}Sn_{0.41}Ti_{0.04})O_3-x\%$ MAZBS ceramics

图3 PLZST- $x\%$ MAZBS 陶瓷表面形貌的 SEM 照片Fig. 3 SEM images of surface morphologies of PLZST- $x\%$ MAZBS ceramics

ASG is average grain size.

图4 PLZST- $x\%$ MAZBS 陶瓷表面形貌的晶粒尺寸分布Fig. 4 Grain size distributions of surface morphologies of PLZST- $x\%$ MAZBS ceramics

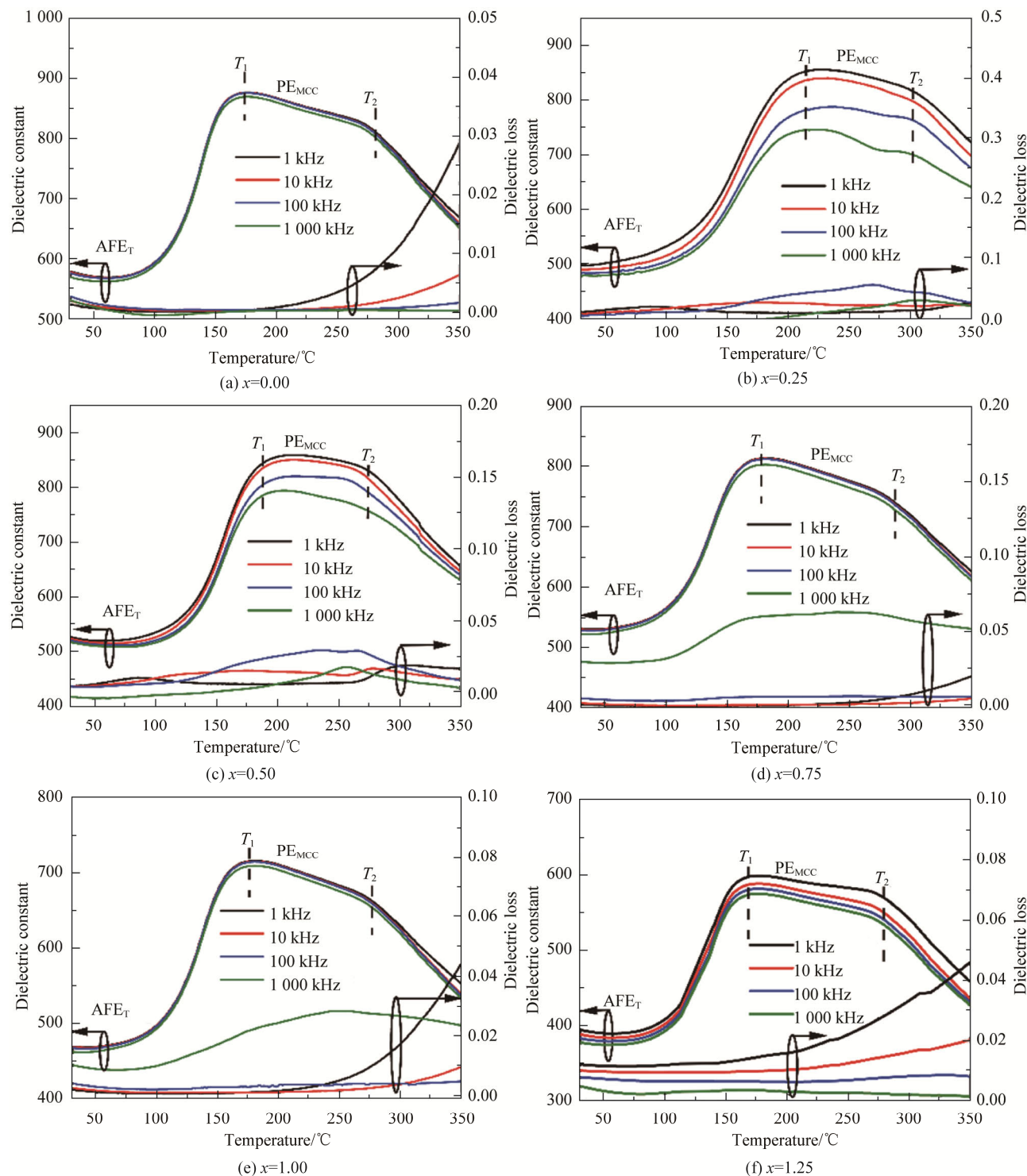
2.2 性能分析

图 5 为在 35~350 °C 范围内, 所有组分在不同频

率下的介电温谱。观察到所有样品的介电损耗均在 5% 以下, 表明陶瓷致密度较高, 具有良好的绝缘性能。

随着温度的升高, 所有样品均呈现从四方反铁电相(AFE_T)向顺电相(PE)的转变, 并在介电温谱中观察到宽化的介电峰, 即存在 1 个宽广的介电平台。这可能是因为, 在 T_1 温度处发生了反铁电相(AFE)到多胞立方顺电相(MCC)的转变, 而在 T_2 温度处发生了多胞立方顺电相(MCC)到顺电相(PE)转变。类似的现象在其它

多离子掺杂的 PbZrO_3 基固溶体中也有报道, 特别是在富锡体系中^[28-29]。此外, 随着玻璃相含量的增加, 陶瓷的最大介电常数降低, 即从 916 ($x=0$)下降到 600 ($x=1.25$), 而 Curie 温度基本保持不变($T_C \sim 160^\circ\text{C}$)。在 200°C 以上, 介电损耗随着温度的升高而增大, 这可能是由于高温时氧缺位激发形成离子电导所致^[30]。



AFE_T is tetragonal anti ferroelectric; PE is paraelectric; MMC is multicell cubic.

图 5 PLZST- $x\%$ MAZBS 陶瓷不同频率的介电温谱

Fig. 5 Temperature dependence of dielectric constant and dielectric loss at different frequencies for PLZST- $x\%$ MAZBS ceramics

图 6 为 PLZST- $x\%$ MAZBS 陶瓷的 P - E 电滞回线。所有样品均表现出反铁电-铁电[AFE-FE(I)]相变。随着玻璃相含量的增加,样品的最大极化强度先增加后减少。样品的 W_{rec} 和 η 随玻璃相含量的变化如图 7a 所示。由图 7a 可见, W_{rec} 呈现先增加后减小的趋势, η 随着玻璃含量的增加而下降,其中,

W_{rec} 由 4.60 J/cm^3 ($x=0.00$)最大可增大到 6.08 J/cm^3 ($x=0.75$), η 由 88% ($x=0.00$)最大值减小到 76% ($x=1.25$),并在 300 kV/cm 的电场下, PLZST- 0.75% MAZBS 获得储能密度 6.08 J/cm^3 和储能效率(η) 77% 。这可能是由于玻璃相含量的增加,填充了陶瓷晶界,使陶瓷样品更为致密,有利于获得更高的

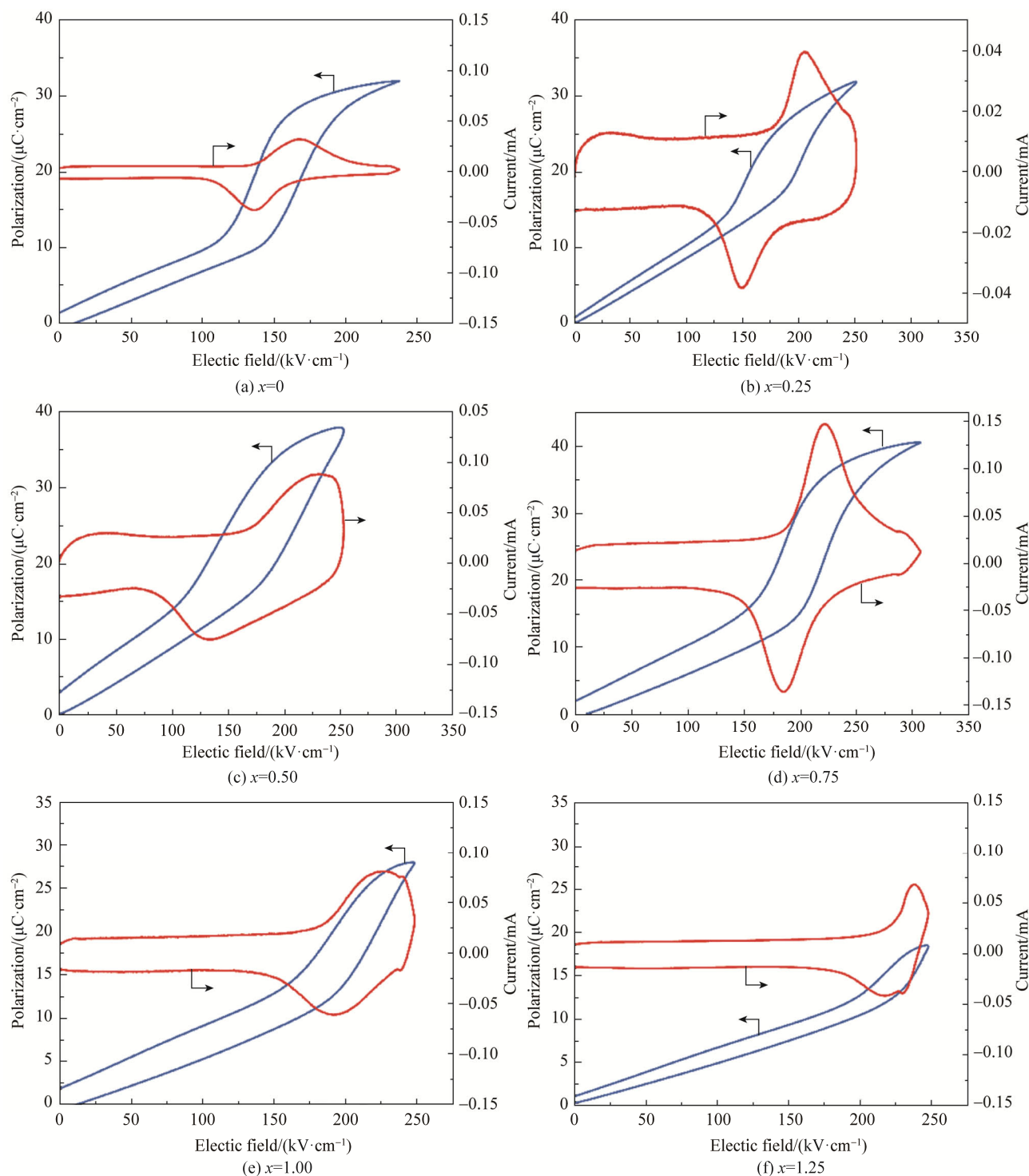


图 6 PLZST- $x\%$ MAZBS 陶瓷 10 Hz 下的 P - E 电滞回线
Fig. 6 P - E hysteresis loops at 10 Hz for PLZST- $x\%$ MAZBS ceramics

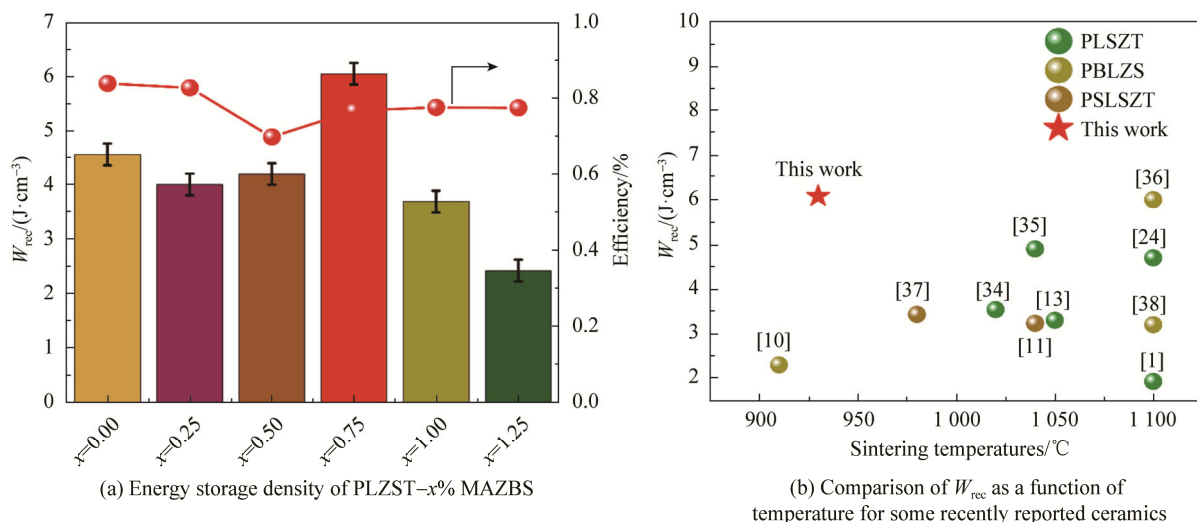
耐击穿电场强度。但是,随着玻璃相含量的进一步增加,部分玻璃相里面的离子进入陶瓷晶格使得陶瓷相中产生缺陷,导致样品的耐击穿电场强度下降^[31]。随着玻璃相含量的增加,相转变电场略为增大,这可能一方面是由于玻璃相含量的增加,导致体系的反铁电相-玻璃相的串联结构,玻璃相产生分压作用,因而需要更高的电场来施加在陶瓷样品上来驱动反向排列的电偶极子翻转成同向排列^[32-33];另一方面是由于 Mg^{2+} (0.69 Å) 取代了 Ti^{4+} (0.60 Å) 所导致的。根据容差因子(t)公式:

$$t = \frac{R_A + R_O}{\sqrt{2}(R_B + R_O)} \quad (5)$$

式中: R_A 为 A 位离子的半径; R_B 为 B 位离子的半径; R_O 为氧离子的半径。 t 减小时,更有利于反铁电相的稳定性。 Mg^{2+} 在 B 位离子的取代将减小 t ,

从而增加反铁电相的稳定性,这也预示着 AFE-FE 相变电场强度将增加,与实验结果一致。图 7b 为最近报道的各类介质陶瓷的储能性能对比图,包括 PLZST、PBLZST、PLSZST 等铅基反铁电(AFE)陶瓷^[1, 10-12, 24, 34-38]。相比之下,PLZST-MAZBS 陶瓷具有较高的储能密度和较低的烧结温度。综合考虑烧结温度和储能密度,PLZST-0.75% MAZBS 是应用于低温共烧铜贱金属电极多层储能电容器的较理想材料。

图 8a 为不同测试频率下 PLZST-0.75% MAZBS 的 $P-E$ 电滞回线。在实际应用中,介质电容器的频率稳定性被视为一个关键参数。本工作探讨了频率对 PLZST-0.75%MAZBS 陶瓷极化行为的影响,施加电场为 250 kV/cm。如图 8a 所示,测试频率分别为 5、10、20、50 Hz 和 100 Hz 时,对应的极化强



PBLZST is $(\text{PbBaLa})(\text{ZrSnTi})\text{O}_3$; PSLZST is $(\text{PbSrLa})(\text{SnZrTi})\text{O}_3$.

图 7 PLZST-x% MAZBS 陶瓷的储能密度与文献结果的对比

Fig. 7 Energy storage comparison of PLZST-x% MAZBS ceramics with those in literatures

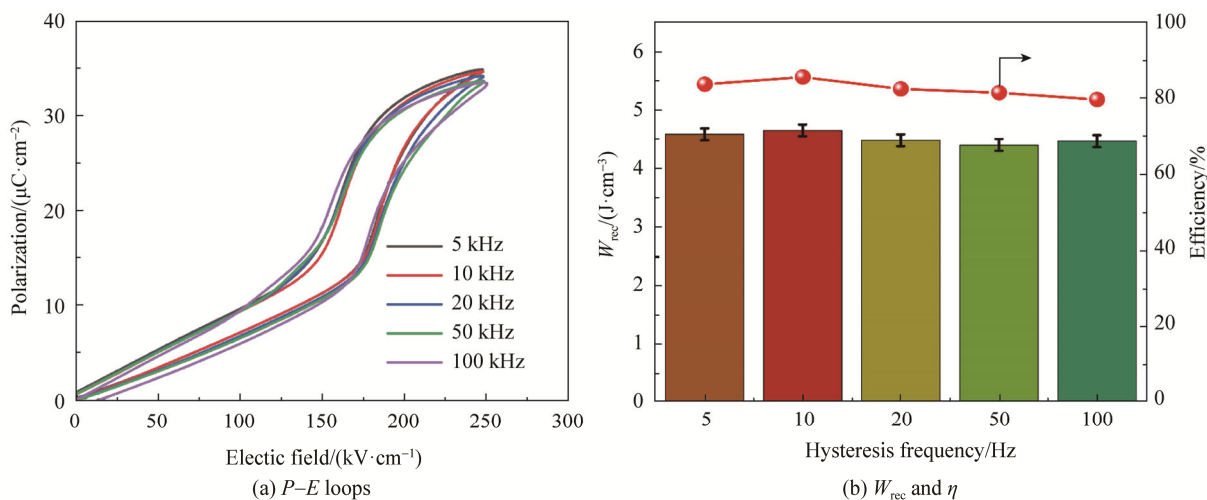


图 8 PLZST-0.75% MAZBS 陶瓷的变频电滞回线, 以及对应的储能密度和效率

Fig. 8 $P-E$ loops and recoverable energy density and efficiency as a function of frequency for PLZST-0.75% MAZBS ceramic

度分别为 34.8、34.6、34.1、33.6 $\mu\text{C}/\text{cm}^2$ 和 33.3 $\mu\text{C}/\text{cm}^2$ 。随着测试频率的升高, 最大极化强度稍有下降, 而反铁电-铁电相转变电场基本保持不变。这是因为随着测试频率增大, 电偶极子翻转对电场的响应程度降低, 导致单位体积内电偶极矩的矢量和减小, 即极化强度降低^[39–40]。图 8b 为不同频率下的储能特性。随着频率的升高, 储能密度和效率变化均相对较小, 这说明频率的变化对该陶瓷的极化强度影响相对较小。

3 结论

系统地研究了 MAZBS 玻璃相掺杂对 PLZST 陶瓷储能性能的影响。研究表明, 适量的 MAZBS 玻璃相掺入可将 PLZST 陶瓷的烧结温度由 1 200 $^{\circ}\text{C}$ 降低至 930 $^{\circ}\text{C}$ 。通过红外光谱表征, 观察到 Al^{3+} 、 Zn^{2+} 和 Mg^{2+} 掺入导致非桥氧键形成。热分析结果显示了 MAZBS 的玻璃化转变温度和软化温度。X 射线衍射进一步证实 PLZST- $x\%$ MAZBS 陶瓷呈现钙钛矿结构。介电温谱分析表明样品随着温度的升高呈现出四方反铁电体-顺电体相变, 并且随着玻璃相含量的增加, 最大介电常数值逐渐降低。 P - E 电滞回线结果显示陶瓷的电场诱导反铁电体-铁电体相变特性, 得到在玻璃相掺量为 0.75% 时获得最大极化强度。PLZST-0.75% MAZBS 陶瓷表现出在外加电场强度为 300 kV/cm 时, 陶瓷的最大储能密度为 6.08 J/cm^3 , 储能效率为 77%。本工作对开发高储能密度铜贱金属内电极反铁电体多层陶瓷电容器具有一定的指导意义。

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Low-Temperature Sintering and Energy Storage Properties of Lead Lanthanum Zirconate Stannate–Titanate Antiferroelectric Ceramics

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Extended Abstract

Introduction There exist severe problems in the society, *i.e.*, environmental pollution, energy shortage, and climate change. These problems directly affect the living environment and have significant threats to globally sustainable development. In the past decades, some low-carbon new energy solutions are developed to address the continuously growing energy demand and mitigate the adverse impacts of climate change. Despite of the continuous emergence of new energy devices, it is still important to face the challenges, *i.e.*, relatively low power density, safety, large volume, *etc.*.

In this paper, the dielectric materials for multilayer energy storage capacitors (MLCC) were prepared by a solid-state reaction method at a lower sintering temperature with low-cost base metal electrodes (*e.g.*, Cu). In addition, the energy storage properties of the MLCC were also characterized.

Methods $(\text{Pb}_{0.97}\text{La}_{0.02})(\text{Zr}_{0.55}\text{Sn}_{0.41}\text{Ti}_{0.04})\text{O}_3$ (PLZST)– $x\%$ $\text{MgO--Al}_2\text{O}_3\text{--ZnO--B}_2\text{O}_3\text{--SiO}_2$ (MAZBS, $x=0.00, 0.25, 0.50, 0.75, 1.00, 1.25$) ceramics were synthesized by a conventional solid-state reaction method. The fabricated ceramics were characterized by Fourier transformation infrared spectroscopy (FTIR), thermal analysis, X-ray diffraction (XRD), and scanning electron microscopy (SEM). The dielectric, ferroelectric, and energy storage properties were examined by a LCR impedance analyzer and a polarization–electric field ($P\text{--}E$) hysteresis loop analyzer.

PbO (purity: 99.0% in mass fraction, the same below), La_2O_3 (99.5%), ZrO_2 (99.5%), SnO_2 (99.8%), and TiO_2 (99.8%) were used as raw materials to synthesize PLZST. MAZBS glass powders were prepared by a water quench method. Afterwards, they were

mixed with the oxides powders in a designed mass ratio, ground by high-energy ball milling for 24 h, dried at 80 °C for 10 h, and then sintered to form PLZST- $x\%$ MAZBS ($x=0.00, 0.25, 0.50, 0.75, 1.00, 1.25$) antiferroelectric ceramics. The calcined powders with 5% polyvinyl butyral (PVB) as a binder were pressed into discs with 12 mm in diameter and 1 mm in thickness at 20 MPa. Finally, the green bodies with added MAZBS glass phase were sintered at 930–1 000 °C for 4 h, while the sample without x was sintered at 1 200–1 300 °C for 2 h. For the properties test, the ceramics were firstly polished, and gold electrodes were then deposited on the both surfaces. The electrode diameter and thickness for each sample were (3.00±0.11) mm and (0.055±0.007) mm as $x=0.00$, (0.82±0.19) mm and (0.072±0.07) mm as $x=0.25$, (1.68±0.04) mm and (0.076±0.007) mm as $x=0.50$, (2.28±0.33) mm and (0.055±0.004) mm as $x=0.75$, (0.87±0.30) mm and (0.066±0.003) mm as $x=1.00$, (1.90±0.44) mm and (0.062±0.005) mm as $x=1.25$.

Results and discussion The XRD patterns of PLZST- $x\%$ MAZBS ($x=0.00, 0.25, 0.50, 0.75, 1.00, 1.25$) antiferroelectric ceramics reveal a shift towards low angles for a peak (200) at 43°–45° when the glass content increases. This shift indicates a possible substitution of Ti^{4+} (with the radius of 0.60 Å) by Mg^{2+} (with the radius of 0.69 Å). Concurrently, the dielectric constant decreases with increasing the glass content due to the lower dielectric constant of glass. The P - E hysteresis loop results demonstrate that PLZST- $x\%$ MAZBS ceramics exhibit an optimum energy storage performance when $x=0.75$, and a good performance at different frequencies. However, a further increase in glass content leads to the entrance of metallic ions from the glass phase into the ceramic lattice, causing the defects and reduction of the dielectric breakdown strength of the ceramics.

Conclusions The impact of MAZBS glass content on the energy storage properties of PLZST ceramics was investigated. It was indicated that an appropriate content of MAZBS glass phase could reduce the sintering temperature of PLZST ceramics from 1 200 °C to 930 °C. The XRD patterns confirmed a perovskite structure of PLZST- $x\%$ MAZBS ceramics. The FTIR spectroscopy revealed the formation of non-bridging oxygen bonds due to the doping of Al^{3+} , Zn^{2+} , and Mg^{2+} . The glass transition temperature and softening temperature of MAZBS glass were examined via the TG/DSC analysis. The dielectric analysis indicated a tetragonal antiferroelectric-ferroelectric phase transition with increasing the temperature, and the dielectric constant peak gradually decreased with the increase of glass content. The results of P - E hysteresis loop illustrated the electric field-induced antiferroelectric-ferroelectric phase transition characteristics of ceramics, with the maximum polarization achieved at the glass phase content of 0.75%. The PLZST-0.75% MAZBS ceramics had a maximum energy storage density of 6.08 J/cm³ and an efficiency of 77% at 300 kV/cm. This result indicated that PLZST-MAZBS ceramics could be developed into high-energy density ceramic capacitors with cost-effective copper inner electrodes.

Keywords lead lanthanum zirconate stannate-titanate; antiferroelectrics ceramics; low-temperature sintering; energy storage density; energy storage efficiency