

$(\text{Pb}_{0.97}\text{La}_{0.02})(\text{Zr}_{0.6}\text{Sn}_{0.4})\text{O}_3$ 反铁电陶瓷的介电储能性能

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摘 要: 电介质电容器具有超高的功率密度和超快的充放电速率, 因而在脉冲功率技术中具有应用前景。利用固相法制备了 $(\text{Pb}_{0.97}\text{La}_{0.02})(\text{Zr}_{0.6}\text{Sn}_{0.4})\text{O}_3$ (PLZS) 反铁电陶瓷, 研究了不同烧结温度下 PLZS 陶瓷的晶体结构、微观形貌、介电性能、反铁电及储能性能。结果表明, 不同温度烧结的样品均具有正交钙钛矿结构, 且随着烧结温度的升高, 陶瓷的致密度逐渐提高、晶粒尺寸也逐渐增大。因此, 最佳温度下 (1 225 °C) 烧结的陶瓷具有最佳的储能性能, 可回收能量密度约 13.3 J/cm³, 储能效率约 83.6%。

关键词: 固相法; 反铁电陶瓷; 介电性能; 储能性能

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电介质电容器作为脉冲功率设备中的关键电子元件, 在混合动力汽车、智能电网、核物理与技术等领域具有广泛的应用。相对于电化学储能单元如锂电池、固体燃料电池等, 电介质电容器能通过电介质材料在电场作用时的极化和去极化实现能量的存储和释放, 因而具有超高的功率密度 ($\sim 10^8$ W/kg)、超快的充放电速率 ($< 1 \mu\text{s}$)^[1-2]。然而, 电介质电容器的能量密度相对较低, 不利于脉冲功率器件的小型化、轻型化和集成化的发展。

可回收能量密度 (W_{rec}) 和储能效率 (η) 是衡量电介质电容器储能性能的重要指标, 通过利用电介质材料的电滞回线 (P - E loops) 间接计算获得^[1-3]:

$$W_{\text{rec}} = \int_{P_r}^{P_{\text{max}}} E dP \quad (1)$$

$$W_{\text{total}} = \int_0^{P_{\text{max}}} E dP \quad (2)$$

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

其中: P_{max} 、 P_r 分别为最大极化强度和剩余极化强度; W_{total} 为总能量密度。显然, 提高 P_{max} 、减小 P_r 和增大击穿电场强度 E_b 是实现优异储能性能的主要途径^[1-3]。

在众多的电介质材料中, 电介质陶瓷由于温度稳定性好、机械性能优异等特点而受到广泛关注和研究。电介质陶瓷主要包括顺电体、铁电体、弛豫铁电体和反铁电体^[1-2]。其中, 反铁电陶瓷中的反铁电相在电场作用下转变为铁电相, 极化强度迅速增大, 表现出较高的 P_{max} 。当撤除电场作用时, 电场诱导的铁电相又转变为反铁电相, 因而呈现出较低的 P_r 。因此, 反铁电陶瓷通常具有双电滞回线和超高的 W_{rec} , 在介电储能领域展现出广阔的应用前景^[3-5]。

锆酸铅 (PbZrO_3) 是一种典型的反铁电材料, 但由于陶瓷的相变电场强度较高, 难以观察到反铁电材料的双电滞回线^[4, 6]。通常情况下, 在 A 位掺杂离子半径较大的离子 (例如 Ba^{2+})、或者 B 位掺杂离子半径较小的离子 (例如 Ti^{4+}) 有利于破坏反铁电有序性, 稳定铁电相并减小相变电场。反之则有助于稳定反铁电相、提高相变电场^[3, 6-7]。因此, 成分优化是调控 PbZrO_3 基反铁电陶瓷储能性能的重要手段。目前, 大多数 PbZrO_3 基反铁电陶瓷均含有 Ti 元素, 然而, Ti 元素含量一旦超过 10%, 反铁电陶瓷转变为铁电陶瓷, 也就是反铁电体存在的成分区间较窄。由于 Zr/Sn 比例在较大范围内的

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可调性以及电场诱导的多级相变现象, $\text{Pb}(\text{Zr}, \text{Sn})\text{O}_3$ 反铁电陶瓷近年来逐渐受到关注^[6, 8-9]。本论文选取 $(\text{Pb}_{0.97}\text{La}_{0.02})(\text{Zr}_{0.6}\text{Sn}_{0.4})\text{O}_3$ (PLZS) 反铁电陶瓷为研究对象, 研究了不同烧结温度下陶瓷的晶体结构、微观形貌、介电性能、反铁电及储能性能。

1 实验

1.1 样品制备

采用固相反应法制备 PLZS 陶瓷。首先, 将原料 PbO (>99.9%, aladdin)、 La_2O_3 (>99.99%, aladdin)、 ZrO_2 (>99%, aladdin) 和 SnO_2 (>99%, aladdin) 根据化学计量比进行称量, 其中, PbO 过量 1% (摩尔分数)。随后将称量好的粉体放入球磨罐中, 同时放入一定比例的球磨珠和无水乙醇, 球磨 12 h。结束后将混合溶液倒入培养皿中, 并置于 80 °C 的烘箱中烘干。然后, 将粉体研磨后放入带盖的氧化铝坩埚中, 一并放入马弗炉中, 在 900 °C 煅烧 3 h。煅烧完成后, 将粉体再次球磨 12 h, 并烘干。随后, 在粉体中加入 7% (质量分数) 的聚乙烯醇水溶液(PVA)进行造粒, 并在 10 MPa 压力下制成直径约 10 mm, 厚度约 1 mm 的陶瓷生坯。然后, 将陶瓷生坯放入马弗炉中, 以 2 °C/min 升温至 600 °C, 保温 3 h, 从而将 PVA 排除。随后, 利用冷等静压机在 180 MPa 压力下将密封好的陶瓷生坯进一步压制, 保压时间为 30 min。最后, 将陶瓷生坯用同组分的粉体掩埋后放入马弗炉中, 以 5 °C/min 升温至 1200、1225 °C 和 1250 °C 烧结 2 h。利用阿基米德法测得不同温度时, 陶瓷的密度分别为 8.42、8.46 g/cm³ 和 8.47 g/cm³。

1.2 表征方法

将陶瓷表面抛光后采用 X 射线衍射仪(Bruker D8 Advance, 德国)表征其晶体结构。采用扫描电子显微镜(TESCAN mira4, 捷克)表征陶瓷的微观形貌。

采用丝网印刷的方式在陶瓷表面涂抹银浆, 并

放入马弗炉中, 升温至 550 °C 保温 10 min, 将银浆烘干。随后, 采用高温介电测试系统(哈尔滨巨浪科技有限公司)表征其介电性能, 测试的温度范围为室温至 450 °C。采用铁电分析仪(Radiant, 美国)在硅油中测试陶瓷的电滞回线($P-E$ loops), 测试频率为 10 Hz, 测试样品的厚度为 80 μm , 电极面积为 0.785 mm²。

2 结果与讨论

2.1 物相分析

图 1a 为不同烧结温度时, PLZS 陶瓷的 X 射线衍射(XRD)图像。由图 1a 可见, 所有样品的主要衍射峰与钙钛矿结构一一对应, 说明 PLZS 的烧结温度范围较宽, 且没有杂相生成。此外, 还能观察到许多较弱的衍射峰, 这是由于相邻 Pb^{2+} 的反平行位移导致的超晶格衍射峰, 通常被认为是反铁电陶瓷的特征衍射峰^[10]。图 1b 为(200)衍射峰的放大图像。由图 1b 可见, 该衍射峰的右侧存在一个鼓包, 说明 PLZS 陶瓷为正交相结构, 与文献报道一致^[10]。

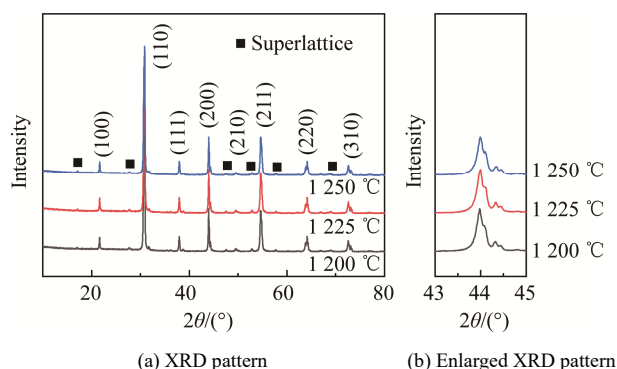


图 1 不同烧结温度制备的 PLZS 陶瓷的 XRD 图像
Fig. 1 XRD patterns for PLZS ceramics

2.2 微观形貌分析

图 2a~图 2c 为不同烧结温度制备的 PLZS 陶瓷的扫描电子显微镜(SEM)照片。由图 2a~图 2c 可见,

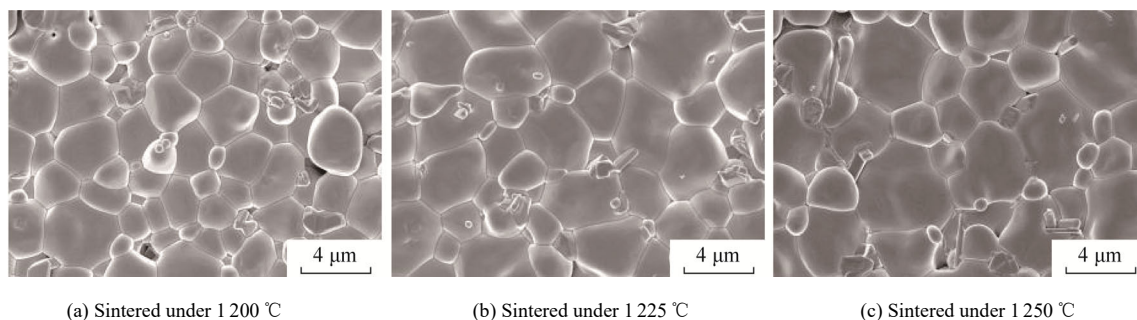
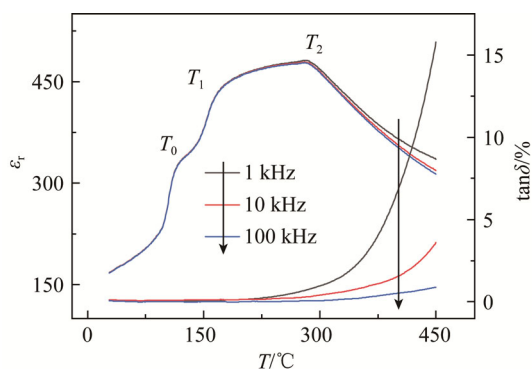


图 2 不同烧结温度制备的 PLZS 陶瓷的 SEM 照片及相应的晶粒尺寸分布
Fig. 2 SEM morphologies and related grain size distribution for PLZS ceramics

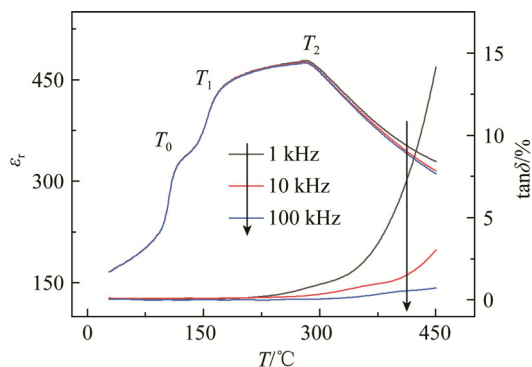
1 200 °C 下烧结的样品中存在少量的孔洞,但随着烧结温度升高,孔洞几乎不可见,呈现出致密的微观结构,有利于提高陶瓷的击穿电场强度(E_b)。同时,烧结温度对陶瓷的晶粒尺寸的影响较大,因此,随着烧结温度的提高,晶粒尺寸逐渐增大^[11]。根据晶粒尺寸分布情况,不同温度制备的陶瓷的平均晶粒尺寸分别为 2.03、2.73 μm 和 2.91 μm 。

2.3 介电性能分析

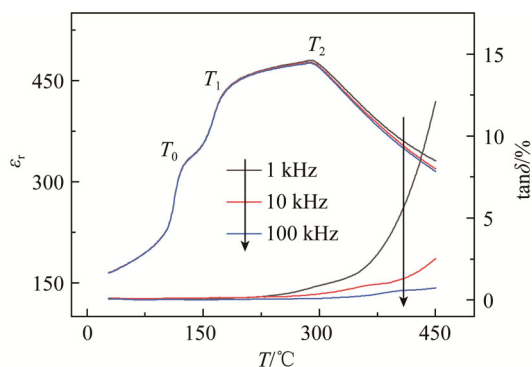
图 3 为不同烧结温度制备的 PLZS 陶瓷的介电常数(ϵ_r)和介电损耗($\tan\delta$)随温度的变化。所有样品



(a) Sintered under 1 200 °C



(b) Sintered under 1 225 °C



(c) Sintered under 1 250 °C

ϵ_r is dielectric constant; T is temperature.

图 3 不同烧结温度制备的 PLZS 陶瓷的介电常数和介电损耗随温度的变化

Fig. 3 Temperature-dependent ϵ_r and $\tan\delta$ for PLZS ceramics

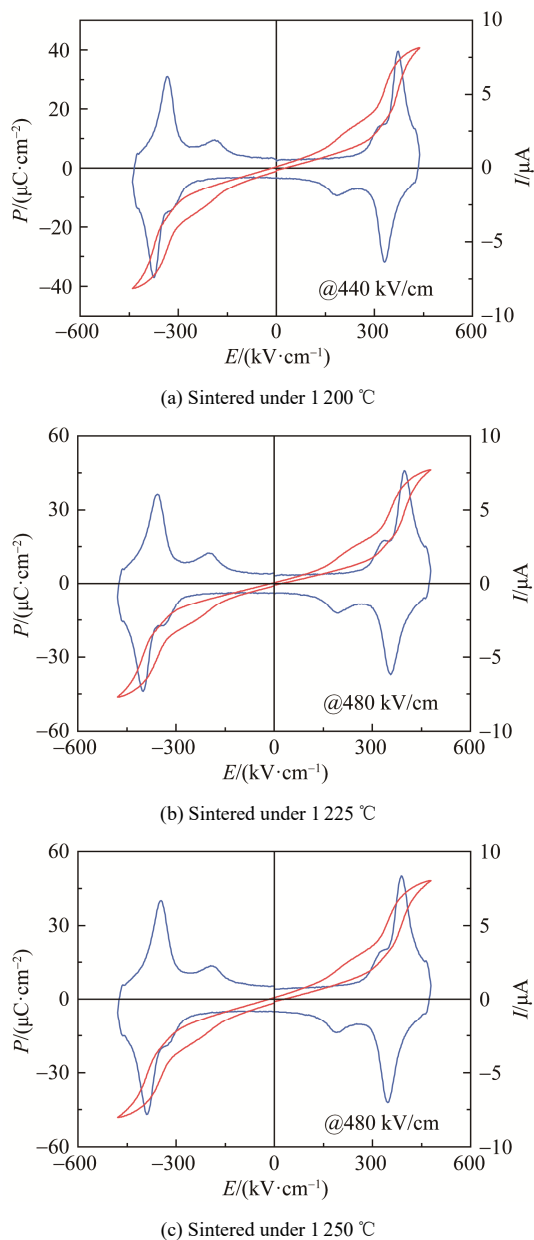
的 ϵ_r 随温度的升高呈现出先增大后减小的趋势,且在这一过程中出现 3 个异常介电峰,说明这一过程中连续出现相变现象。根据文献报道^[6, 8],温度点 T_0 时的介电峰来源于正交反铁电相(AFE_O)转变为四方反铁电相(AFE_T),随着温度进一步升高,四方反铁电相又转变为立方顺电相(PE_C),此时对应的温度点为 T_1 。温度 T_1 和 T_2 之间的 ϵ_r 变化较小,这是因为此时形成了多重晶胞立方相的中间态。此外,所有样品的 $\tan\delta$ 在低温时数值非常小($<0.2\%$),有利于提高陶瓷的 E_b ;而当温度达到某一数值后, $\tan\delta$ 逐渐增大,特别是低频时,这是由于高温诱导的缺陷参与导电引起的^[12]。

2.4 反铁电及储能性能分析

图 4 为不同烧结温度制备的 PLZS 陶瓷的 P - E 及 I - E 回线,测试电场为样品所能承受的最大电场强度,对应的 $P_{\max}$ 、 P_r 、 E 、 W_{rec} 、 W_{total} 和 η 见表 1。首先,1 225 °C 和 1 250 °C 制备的 PLZS 陶瓷的 E_b 较高,可能是因为该温度时制备的陶瓷样品更加致密、较小的厚度和电极面积、中等的介电常数和低介电损耗^[2]。 $P_{\max}$ 随烧结温度的提高逐渐增大,但 P_r 先增大后减小,可能是因为 1 250 °C 烧结时, Pb 的挥发更为严重,导致样品中存在较多的缺陷。其次,所有样品均具有双 P - E 回线,表现出典型的反铁电性能。同时,每个样品的极化强度在低电场时缓慢增加,随后快速增加,最后在高电场时迅速增加,这是由于 PLZS 陶瓷在电场作用时先产生了反铁电-铁电相转变,随后又出现了铁电-铁电相转变,即电场诱导的多级相变行为^[8]。 I - E 曲线中不同强度的极化电流峰进一步证明了电场诱导的多级相变现象。最后,由表 1 可知,1 225 °C 制备的 PLZS 陶瓷的储能性能最为优异,其 W_{rec} 和 η 分别为 13.3 J/cm^3 和 83.6%,在介电储能领域具有应用潜力。

为了进一步探讨电场诱导的相变过程,不同电场时、1 225 °C 制备的 PLZS 陶瓷的 P - E 及相应的 I - E 回线如图 5a 和图 5b 所示。当电场强度较低时, P - E 回线呈线性, I - E 回线也观察不到电流峰,说明此时未发生极化翻转现象。当电场强度逐渐增大,例如 350 kV/cm 时,极化的滞后性开始增加,相应的 I - E 回线出现 4 个电流峰,说明反铁电相转变为铁电相。当电场强度进一步提高,极化强度在高电场时迅速增加, I - E 回线出现 8 个极化电流峰,说明 PLZS 陶瓷在电场强度持续增大的过程中,出现了反铁电相转变为铁电相,随后又转变为另一铁电相,即电场诱导的多级相变。图 5c 为 1 225 °C 制备

的 PLZS 陶瓷的 W_{rec} 、 W_{total} 和 η 随外加电场强度的变化。由于电场诱导的相变，能量密度迅速增大，但同时损耗增大，导致能量效率减小。



P is polarization; I is polarization current; E is applied electric field.

图4 不同烧结温度制备的 PLZS 陶瓷的 P - E 和 I - E 回线
Fig. 4 P - E loops and I - E curves for PLZS ceramics

表1 不同烧结温度制备的 PLZS 陶瓷的 P_{max} 、 P_r 、 E 、 W_{rec} 、 W_{total} 和 η 值

Table 1 P_{max} , P_r , E , W_{rec} , W_{total} and η for PLZS ceramics

$T/^\circ\text{C}$	$P_{\text{max}}/(\mu\text{C}\cdot\text{cm}^{-2})$	$P_r/(\mu\text{C}\cdot\text{cm}^{-2})$	$E/(\text{kV}\cdot\text{cm}^{-1})$	$W_{\text{rec}}/(\text{J}\cdot\text{cm}^{-3})$	$W_{\text{total}}/(\text{J}\cdot\text{cm}^{-3})$	$\eta/\%$
1200	40.7	0.5	440	10.8	12.9	83.7
1225	46.3	0.3	480	13.3	15.9	83.6
1250	48.2	0.6	480	13.4	16.2	82.7

P_{max} is maximum polarization; P_r is remanent polarization; W_{rec} is recoverable energy density; W_{total} is total energy density; η is efficiency.

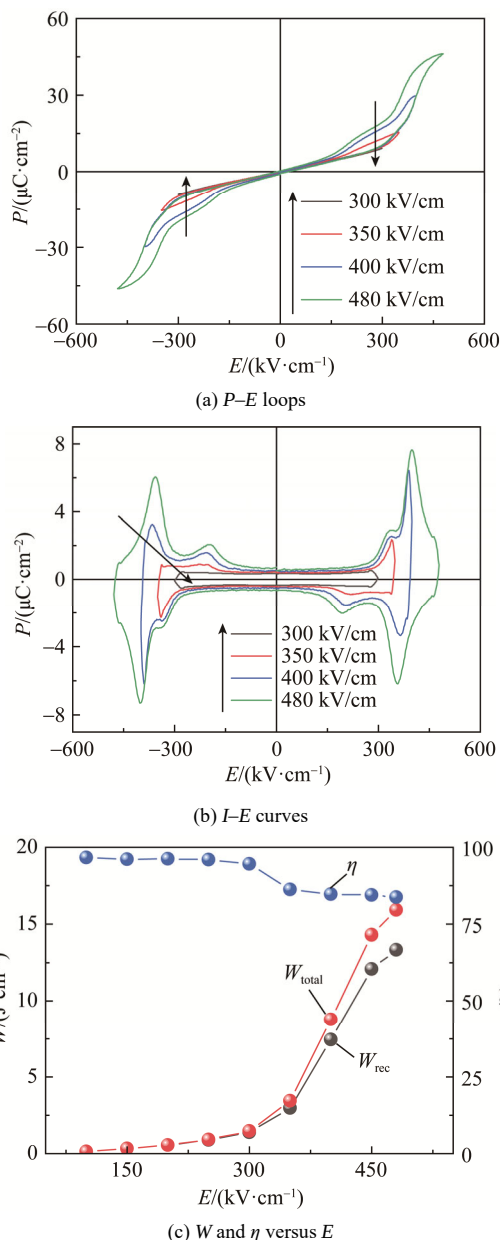


图5 1225 °C 制备的 PLZS 陶瓷的(a) P - E 、(b) I - E 回线以及(c) W_{rec} 、 W_{total} 和 η 随外加电场的变化

Fig. 5 Electric-field dependent (a) P - E loops, (b) I - E curves, (c) W_{rec} , W_{total} and η for PLZS ceramics sintered under 1225 °C

3 结论

利用传统的固相烧结法制备了 $(\text{Pb}_{0.97}\text{La}_{0.02})(\text{Zr}_{0.6}\text{Sn}_{0.4})\text{O}_3$ 反铁电陶瓷，通过烧结温度的优化，获得了具有优异储能性能的 PLZS 陶瓷。研究发现，所有样品均具有正交钙钛矿结构。同时，随着烧结温度升高，陶瓷致密度提高、晶粒尺寸增大。此外，介电随温度的变化中观察到一系列的相变过程。最终，所有样品均观察到双电滞回线，呈现出典型的反铁电行为，其中，1225 °C 时烧结的样

品获得最优的介电储能性能: $W_{\text{rec}}=13.3 \text{ J/cm}^3$, $\eta=83.6\%$ 。

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Energy Storage Properties of $(\text{Pb}_{0.97}\text{La}_{0.02})(\text{Zr}_{0.6}\text{Sn}_{0.4})\text{O}_3$ Antiferroelectric Ceramics

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Extended Abstract

Introduction As one of the important electronic components in pulsed power devices, dielectric capacitors have wide applications in hybrid vehicles, and distributed power system. However, a relatively low energy density affects their application in portable and light-weight devices. The dielectric capacitors store and release energy in form of electrostatic polarization and depolarization of dielectric materials. Hence, achieving the maximum polarization (P_{max}), small remanent polarization (P_r) and large electric breakdown strength (E_b) in dielectric materials is an effective approach to improve the energy storage properties. The antiferroelectric ceramics are one of the most prospect materials for energy storage due to their unique antiferroelectric-ferroelectric (AFE-FE) phase transition during charging and discharging process. As one of the classic antiferroelectric ceramics, $\text{Pb}(\text{Zr,Ti})\text{O}_3$ antiferroelectric ceramics are widely investigated. However, the content of Ti should be lower than 10% to stabilize the antiferroelectric phase, leading to the narrow windows for compositional regulation. In recent years, $\text{Pb}(\text{Zr,Sn})\text{O}_3$ antiferroelectric ceramics become popular because of the electric field induced multistage phase transition. In this paper, $(\text{Pb}_{0.97}\text{La}_{0.02})(\text{Zr}_{0.6}\text{Sn}_{0.4})\text{O}_3$ (PLZS) antiferroelectric ceramic was synthesized *via* solid-state sintering at different temperatures. In addition, the crystal structures, microstructures, dielectric properties and energy storage properties of the ceramic were also investigated.

Methods PbO , La_2O_3 , ZrO_2 and SnO_2 were used as raw materials, and weighted and mixed according to the stoichiometry. The mixed materials with alcohol were ground in a ball mill for 12 h. Afterwards, the suspension was dried, the powders were calcined at 900°C for 3 h, and then ground with alcohol for another 12 h. The dried powders with polyvinyl alcohol were pressed into disks with the diameter of 10 mm and the thickness of 1 mm. Finally, the green disks were sintered at $1\,200\text{--}1\,250^\circ\text{C}$ for 2 h to obtain the densified ceramics.

The crystal structures of ceramics were determined by X-ray diffraction (XRD). The surface microstructure of ceramics was characterized by scanning electron microscopy (SEM). For the measurement of dielectric properties, the ceramics were polished and covered with a silver paste, which was dried at 550°C for 10 min. The dielectric properties were analyzed by a dielectric test system at room temperature to 450°C , and the $P\text{--}E$ loops of ceramics were determined by a ferroelectric analyzer.

Results and discussion All the prepared ceramics show an orthorhombic perovskite structure without secondary phase. Moreover, some weak diffractions appear due to an antiparallel aligned adjacent Pb^{2+} in antiferroelectric ceramics. The microstructure of

ceramics becomes denser with decreasing holes and increasing grain size as sintering temperature increases, which is beneficial to enhancing E_b . All the samples show three dielectric anomalies in a temperature-dependent dielectric constant (ϵ_r), indicating a successive phase transition between orthorhombic antiferroelectric phase (AFE_O), tetragonal antiferroelectric phase (AFE_T), multicell cubic phase (MCC) and cubic paraelectric phase (PE_C) as the temperature increases. In addition, the dielectric loss ($\tan\delta$) for all the samples is quite low ($<0.2\%$) at a low temperature, which is also helpful to enhance E_b . All the samples sintered at different temperatures show double P – E loops and I – E curves, having the typical antiferroelectric properties. Furthermore, the polarization increases slowly at a relatively low electric field, and increases quickly at a moderate electric field due to the electric field induced AFE–FE phase transition., the polarization increases more quickly with further increasing electric field because of the electric field induced FE–FE phase transition. Hence, the corresponding I – E curves exhibit electric field induced current peaks. As a result, the PLZS ceramic sintered at 1 225 °C has the optimal energy storage properties (*i.e.*, W_{rec} of 13.3 J/cm³ and η of 83.6%) at 480 kV/cm, indicating great potential applications in pulsed power devices. Note that a large E_b plays an important role in achieving superior energy storage properties, and a large E_b can be attributed to dense microstructure, small thickness and electrode area, moderate ϵ_r and low $\tan\delta$.

Conclusions PLZS antiferroelectric ceramics were fabricated *via* solid–state reaction. The crystal structure, microstructure morphologies, antiferroelectric properties and energy storage behavior of PLZS ceramics sintered at different temperatures were investigated. All the samples exhibited an orthorhombic antiferroelectric phase. Also, the density of prepared ceramics improved, and grain size increased with increasing sintering temperature. Therefore, the sample sintered at 1 225 °C achieved the optimum energy storage properties (*i.e.*, recoverable energy density of 13.3 J/cm³ and efficiency of 83.6%).

Keywords solid–state reaction; antiferroelectric ceramics; dielectric properties; energy storage properties