

BiScO₃–PbTiO₃–Bi(Zn_{2/3}Nb_{1/3})O₃ 高温钙钛矿陶瓷的微结构与性能

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摘 要: 开发兼具高压电系数(d_{33})和高退极化温度(T_d)的钙钛矿陶瓷是构建先进高温压电器件的关键。本工作将小容差因子、强铁电活性离子的 Bi(Zn_{2/3}Nb_{1/3})O₃ (BZN)基元引入至具有高温应用潜力的 BiScO₃–PbTiO₃ (BS–PT)高温钙钛矿压电体中, 制备并研究了(0.995– x)BS– x PT–0.005BZN 三元系高温压电陶瓷的微结构与压电性能。结果表明, 所有陶瓷均具有三方相和四方相共存的特征且结构致密; $x=0.62$ 组成位于准同型相界, 综合高温性能最佳; T_d 高达 409 °C 并兼具优异的高温 d_{33} (709 pC·N⁻¹)。研究表明, BS– x PT–BZN 有望用于制作在恶劣高温环境下服役的压电器件。

关键词: 铋酸铋–钛酸铅; 压电陶瓷; 微结构; 高温压电性; 退极化温度

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压电陶瓷可实现机械能与电能互换, 被广泛用于制作压电传感器、压电能量采集器、压电换能器等功能器件, 在国民经济发展中发挥着重要作用^[1]。近年来, 蓬勃发展的航天航空、智能驾驶、核工业等先进领域亟需可在恶劣高温环境下服役的压电器件^[2]。构建此类高温压电器件的关键在于开发兼具大高温压电系数(d_{33})和高退极化温度(T_d)的压电陶瓷材料^[3-4]。

钙钛矿压电家族以其优异的压电性能而被熟知和广泛应用, 其中, BiScO₃–PbTiO₃ (BS–PT)以其高 Curie 温度和优异的压电性成为高温压电基体候选者^[3-5]。为调控 BS–PT 基体的高温压电品质, 引入第三组元被认为是非常行之有效的方法, 此方法将二元基体拓展成三元体系, 提升了组分、结构与性能的可调性^[4, 6]。Talanov 等^[7]将 Pb(Mg_{1/3}Nb_{2/3})TiO₃ 弛豫体引入 BS–PT 基体进行相结构优化, 获得了较高的室温压电系数 ($d_{33}=509$ pC·N⁻¹); 但由于 Pb(Mg_{1/3}Nb_{2/3})TiO₃ 显著高于 BS 的容差因子, 陶瓷 Curie 温度显著降低至 156 °C, 难以实现高温应用。董亚珠等^[8]通过引入 Bi(Sn_{1/3}Nb_{2/3})O₃ 对 BS–PT 基体的四方结构畸变和畴热稳定进行调制与优化, 使陶

瓷高温 d_{33} 及其劣化温度均得到不同程度的改善。此后, 含强铁电活性 Bi 和 Zn 离子的 Bi(Zn_{1/2}Ti_{1/2})O₃ 被引入至 BS–PT 基体中, 使 A/B–O 键的结合力得到增强, 进而改性后陶瓷展示出可观的高温压电系数(d_{33} 约为 525 pC·N⁻¹)和退极化温度($T_d=410$ °C)^[9]。目前, 利用引入第三组元策略已取得许多重要进展, 但获取兼具大高温 d_{33} 和高 T_d 的高温压电陶瓷仍是一项关键挑战。

近期工作中, 含强铁电活性 Zn 离子的 PZN 弛豫体被引入至 BS–PT 基体中, 构建了 BS–PT–PZN 陶瓷, 其 d_{33} 高达 497 pC·N⁻¹, 但 T_d 仅为 250 °C, 远低于 BS–PT 基体($T_d=327$ °C)^[10], 这主要应与 PZN ($t=0.986$)具有比 BS($t=0.907$)更高的容差因子(t)有关^[11]。此外, 第一性原理计算表明, 同为铁电活性离子的 Pb 和 Bi 均具有 6s 孤电子对, 但后者 6s 与 O 离子 2p 之间的杂化能力更强, 更有助于增强压电性^[12]。因此, 本工作将 t 与 BS 相近且含有强铁电活性 Bi 和 Zn 离子的 Bi(Zn_{2/3}Nb_{1/3})O₃ (BZN; $t=0.916$)^[11, 13]引入至 BS–PT 基体中, 制备并研究了(0.995– x)BS– x PT–0.005BZN 三元系高温压电陶瓷的微结构与电学性能及其关联机制。通过组分优化与微结构调控, 位

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于准同型相界的 $x=0.62$ 陶瓷组成展现出大高温 d_{33} (709 pC·N⁻¹) 和高 T_d (409 °C), 有望应用于制作先进高温压电器件。

1 实验

1.1 样品制备

采用传统高温固相反应法制备了三元系压电陶瓷 (0.995- x)BiScO₃- x PbTiO₃-0.005Bi(Zn_{2/3}Nb_{1/3})O₃ (简称为 BS- x PT-BZN; $0.60 \leq x \leq 0.63$, x 为摩尔)。所用化学原料纯度(质量分数)为 Bi₂O₃(99.00%)、Pb₃O₄(99.00%)、Sc₂O₃(99.99%)、TiO₂(99.00%)、ZnO(99.00%)和 Nb₂O₅(99.99%)。主要制备过程如下: 首先按化学计量比称量烘干后的原料, 以无水乙醇为球磨介质, 将其卧式球磨 24 h。浆料烘干后, 放入高纯氧化铝密封坩埚于 850 °C 煅烧 2 h, 将煅烧后的产物放入卧式球磨罐并加入无水乙醇, 进行 24 h 二次球磨, 浆料烘干后得到 BS- x PT-BZN 粉体。在粉体中滴加 PVA[5%(质量分数)]黏结剂, 以单轴压力 7 MPa 干压成直径为 11.5 mm 的陶瓷素坯体圆片。素坯体经排胶后放置于密闭氧化铝坩埚(在其周围撒上相同组分的粉体以在高温下形成保护气氛), 于 1140 °C 烧结 2 h 后随炉冷却, 得到 BS- x PT-BZN 陶瓷。

1.2 样品表征

用 D8-Advance 型 X 射线衍射仪分析陶瓷相组成, 测试条件: Cu 靶(室温), Pt 靶(高温), 管电压 40 kV, 管电流 30 mA, 升温速率 5 °C/min。用 Sigma-300 型扫描电子显微镜观测经热蚀(900 °C 保温 30 min)处理后陶瓷断面的晶粒形貌, 加速电压 20 kV, 并用 Nano Measurer 软件统计分析陶瓷的晶粒尺寸。用 Premier II 型铁电测试仪表征陶瓷的铁电性能, 测试条件: 温度为室温, 电场为 50 kV/cm, 频率为 1 Hz。变温介电和压电性能测试前, 上下表面被覆银电极的陶瓷需放置于 120 °C 硅油中并施加 50 kV/cm DC 电场进行人工极化 30 min, 极化后在室温静置 24 h。用 TZDM-RT-1000 型高温介电温谱测试系统分析极化后陶瓷的介电性能, 升温速率为 2 °C/min。用 ZJ-6A 型准静态 d_{33} 仪测试极化后陶瓷的室温压电系数 d_{33} 。用 TZFD-600 型高温准静态 d_{33} 测试系统表征极化后陶瓷的原位变温 d_{33} 。

2 结果与讨论

图 1 为 BS- x PT-BZN 陶瓷断面的 SEM 照片和平均晶粒直径(d_{AGS})分布图。由图 1 可见, 所有陶瓷

样品的晶粒发育良好, 结构致密, 这有利于其耐受外加电场进行人工极化。随着 x PT 含量的增加, 陶瓷的晶粒逐渐长大, 于 $x=0.61$ 时达到最大, 平均晶粒尺寸为 3.91 μm , 随后又有所降低。这是因为随着 PT 含量增加, 陶瓷原料中氧化铅含量相应增加, 氧化铅对陶瓷烧结行为具有助烧作用, 而 PT 本身的高四方度则不利于陶瓷烧结。随着 x PT 含量增加, 2 种作用相互博弈, 最终得到了上述实验结果。类似现象在其它 BS-PT 基陶瓷中也有观测到^[10, 14]。晶粒尺寸统计结果显示, 与 BS-PT 基体平均晶粒尺寸 ($d_{AGS}=2.17\sim 2.65 \mu\text{m}$)^[14]相比, 本工作中相同 PT 含量下的 $x=0.60\sim 0.63$ 陶瓷, 其平均晶粒尺寸($d_{AGS}=2.29\sim 3.91 \mu\text{m}$)均有所增加, 这可能与引入含具有助烧作用 Zn 元素的 BZN 有关^[15-16]。

图 2 为 BS- x PT-BZN 陶瓷的 XRD 谱及其局部特征衍射峰。由图 2a 可以看出, 所有样品都表现出典型的钙钛矿结构特征; 但在 2θ 约 28.2°和 28.8°处有 2 个微弱的杂峰, 前者对应于 K_β 的(110)峰, 后者为 PbO 物相(PDF 85-0711)的衍射峰。类似的现象在其它 BS-PT 基三元压电体系中也有观察到, 并且已有研究表明, 这对陶瓷性能的影响可以忽略^[17-18]。随着陶瓷组成中 PT 含量增加, BS- x PT-BZN 陶瓷在 45°处的(002)和(200)特征峰劈裂现象愈加明显, 这意味着陶瓷相结构随组分变化而发生了演化。据此, 本工作采用 Gauss-Lorentz 函数对 BS- x PT-BZN 陶瓷在 43°~46°范围内的 XRD 数据进行了拟合, 如图 2b 所示。拟合结果显示, 除 $x=0.60$ 陶瓷样品外, 所有陶瓷样品均显示出 3 个明显的拟合峰, 分别为四方相(T)的(002)_T与(200)_T峰和三方相(R)的(200)_R峰。根据拟合峰的强度(I)结合式(1)^[14, 17]计算了不同陶瓷样品中的四方相含量(x_T), 如图 2b 中的 x_T 值。

$$x_T = \frac{I(002)_T + I(200)_T}{I(002)_T + I(200)_R + I(200)_T} \times 100\% \quad (1)$$

由式(1)可以看出, 随着陶瓷中四方 PT 铁电体含量增加, T 含量由 29% ($x=0.60$)逐渐增长至 89% ($x=0.63$)。上述结果表明, 本工作中所有 BS- x PT-BZN ($x=0.60\sim 0.63$)陶瓷均含有三方相和四方相, 这种多相共存态为准同型相界的形成提供了必要条件。

高 Curie 温度是高温压电器件用压电陶瓷的必备条件, 一般不低于 400 °C^[2-5]。图 3 为 BS- x PT-BZN 陶瓷的介电曲线和 Curie 温度。由图 3a 可见, 所有陶瓷样品在整个测试温度区间内均表现出 1 个明显的介电常数异常峰和介电损耗异常峰, 其对应的测试温度位于 400~450 °C。通常, 将压电陶瓷介电常

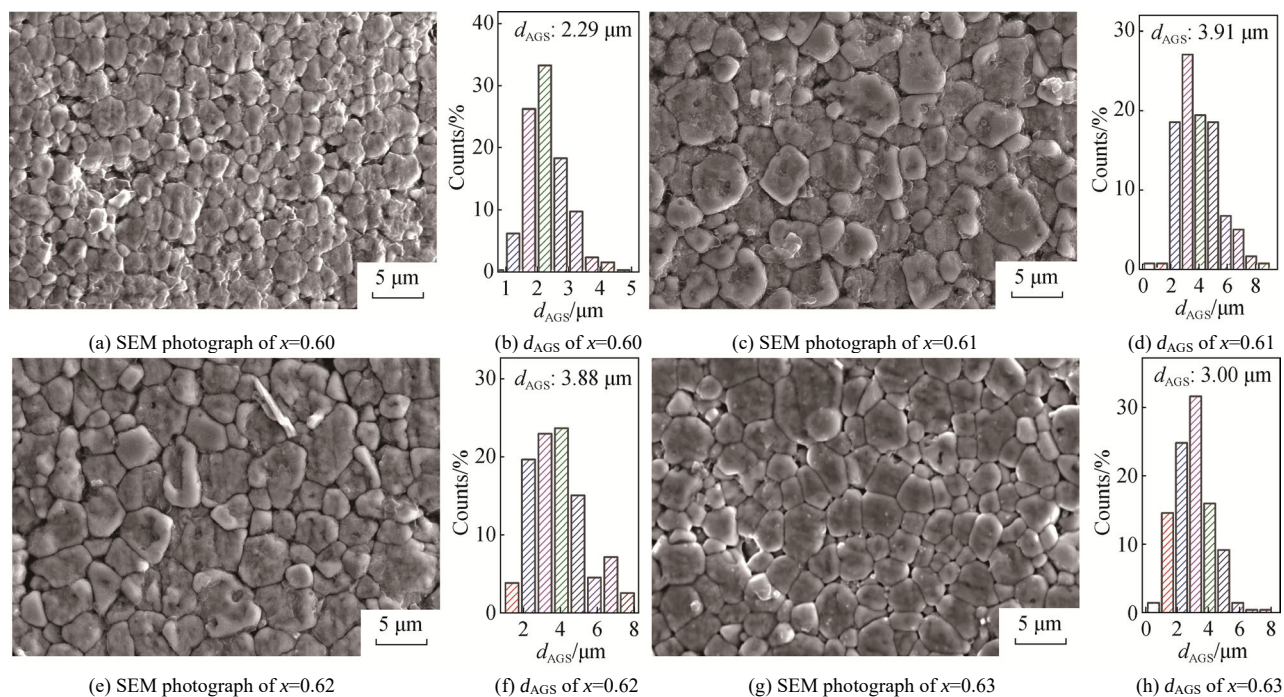
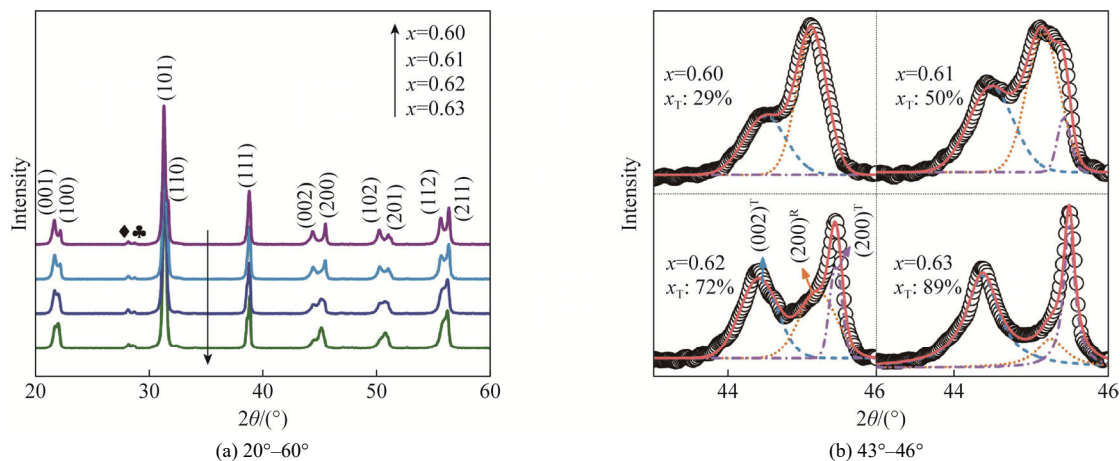
图 1 BS-xPT-BZN 陶瓷断面的 SEM 照片和平均晶粒尺寸(d_{AGS})分布Fig. 1 SEM photographs of the cross-section and average grain size (d_{AGS}) distributions of BS-xPT-BZN ceramics

图 2 BS-xPT-BZN 陶瓷 XRD 谱及特征峰

Fig. 2 XRD patterns and characteristic peaks of BS-xPT-BZN ceramics

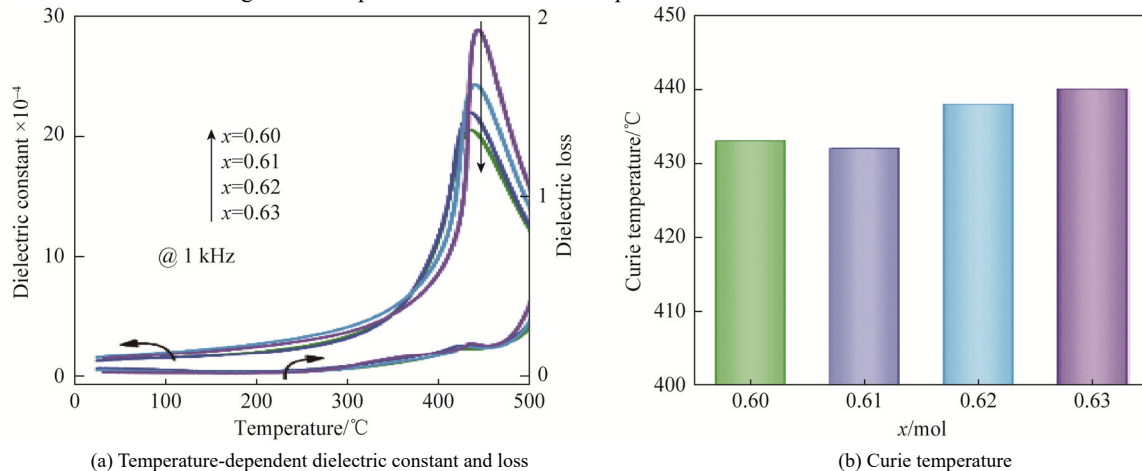


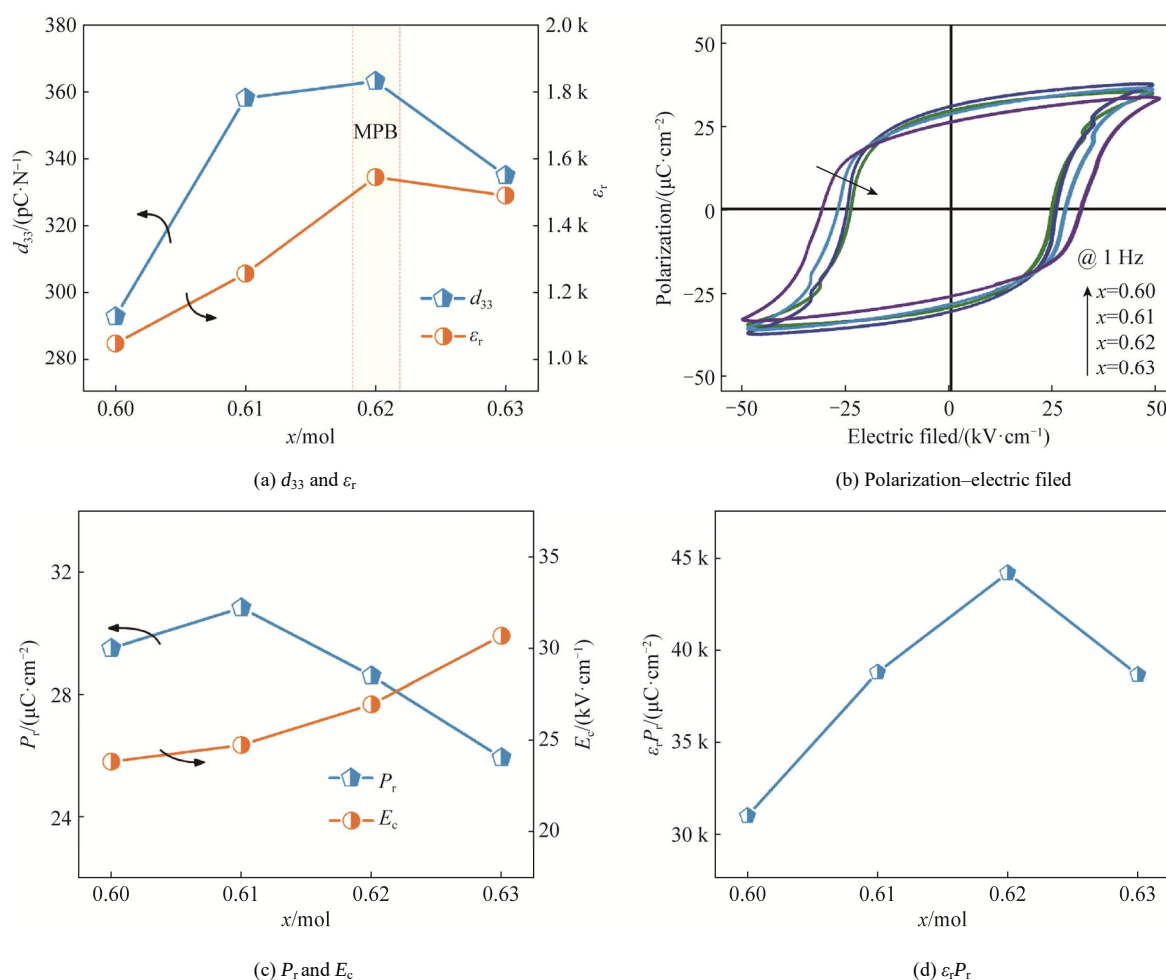
图 3 BS-xPT-BZN 陶瓷的介电性能和 Curie 温度

Fig. 3 Dielectric properties and Curie temperature of BS-xPT-BZN ceramics

数异常峰峰值所对应的温度记为 Curie 温度(T_C)。由图 3b 可见, Curie 温度值随陶瓷组成中 PT 含量增加而增大, 这主要归因于四方铁电体 PT 的高 Curie 温度($T_C=490\text{ }^\circ\text{C}$)^[11]。局部样品(如 $x=0.61$)的 T_C 值未随 PT 含量增加呈现出线性增加的行为, 这与该体系中多样离子半径、化合价、外层电子结构的多种离子共存所产生的随机场效应有关^[3-4]。此外, 本工作中所有陶瓷样品的 Curie 温度值均高于 $430\text{ }^\circ\text{C}$, 与 BS-PT 基体的 Curie 温度相近^[11, 14], 这主要是因为 BZN 与 BS 具有相似的容差因子^[11]。高 Curie 温度为其高温应用奠定了必要的基础。

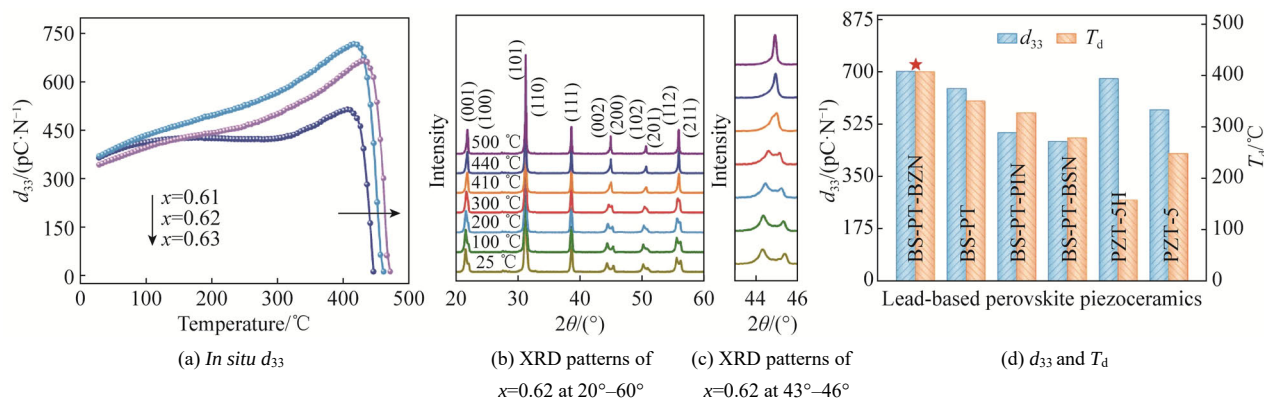
图 4 为 BS- x PT-BZN 陶瓷的室温压电、介电和铁电性能。由图 4a 可以看出, 随 PT 含量增加, 陶瓷 d_{33} 和 ε_r 先增大后减小, 在 $x=0.62$ 处均达到最大值, 分别为 $363\text{ pC}\cdot\text{N}^{-1}$ 和 1545 。此外, $x=0.62$ 样品的机电耦合系数(k_p)为 0.49 , 可与经典的型号为 PIC152 商业 PZT 陶瓷($k_p=0.48$)相媲美, 这将有利于

高温下其压电性能的发挥。对于多元系钙钛矿压电陶瓷, 室温压电系数 d_{33} 最大值通常在准同型相界 (MPB) 处获得^[19]。结合 XRD 显示的多相共存特征, $x=0.62$ 应为本工作中 BS- x PT-BZN 体系的 MPB 组成。由图 4b 可见, 所有陶瓷样品均表现出近似矩形的电滞回线, 表明它们均具有良好的铁电极化行为。自电滞回线上提取各样品的剩余极化强度(P_r)和矫顽场(E_c)如图 4c 所示。由图 4c 可见, 位于准同型相界的 $x=0.62$ 陶瓷并未具有最大的 P_r 值, 这可能是源于其较高的 E_c 所致。而 $x=0.62$ 陶瓷高 E_c 应该与其含有较高的四方相含量有关(图 2d), 因为四方相中铁电畴的翻转相对比较困难^[20]。压电陶瓷的 d_{33} 正比于 $\varepsilon_r P_r$ ^[19]。由图 4d 可见, $\varepsilon_r P_r$ 值随 PT 含量增加也呈现出先增加后降低的趋势, 在 $x=0.62$ 处达到最大值, 与 d_{33} 随 PT 含量变化的趋势相似, 这说明 $x=0.62$ 陶瓷的高压电系数主要源于高介电常数的贡献。



d_{33} is Piezoelectric coefficient; ε_r is dielectric constant; P_r is remanent polarization; E_c is coercive field.

图 4 BS- x PT-BZN 陶瓷的电学性能
Fig. 4 Electric properties of BS- x PT-BZN ceramics



T_d is depolarization temperature.

图5 BS- x PT-BZN 陶瓷的高温压电性能和 XRD 谱

Fig. 5 High-temperature piezoelectric properties and XRD patterns of BS- x PT-BZN ceramics

图 5 为 BS- x PT-BZN 陶瓷的变温压电性能和 XRD 谱。由图 5a 可以看出,随着温度升高,所有陶瓷样品的 d_{33} 值首先呈现出逐渐增大的趋势,这主要归因于与压电系数增强相关的体系 Gibbs 自由能曲面在温度驱动下逐渐平坦化^[21–22];当温度高于某一值时,陶瓷样品的 d_{33} 迅速劣化甚至消失,这主要归因于压电陶瓷的热退极化行为所引发的铁电态被摧毁所致^[21–22]。将压电陶瓷原位 d_{33} 值随温度变化时拐点处所对应的温度记为退极化温度(T_d)^[22]。由图 5a 还可以看出, $x=0.61$ 、 $x=0.62$ 和 $x=0.63$ 陶瓷的 T_d 逐渐增大,这主要是与它们所含四方相含量逐渐增多有关(图 2b),因为四方铁电相一般比三方铁电相具有更强的抗温度刺激的能力^[21–23]。与 $x=0.61$ 和 $x=0.63$ 陶瓷相比,具有较高四方相含量且位于准同型相界的 $x=0.62$ 表现出综合性最佳的高温压电品质,即较高的退极化温度($T_d=409$ °C)并伴随着大的高温压电系数($d_{33}=709$ pC·N⁻¹)。由图 5b~图 5c 可见,从 43°~46°的局部放大图中观察 45°附近特征峰,可以看出,与高于退极化温度(约为 410 °C)的 440 °C 和 500 °C 的尖锐单峰相比,在不超过 410 °C 时,(002)和(200)特征峰表现为驼峰,表明其保持着多相共存的 MPB 特征,这主要与 BS-PT 基体优良的“类垂直”准同型相界有关^[4],也是其在高温下表现出优异压电性的关键性因素。图 5d 进一步显示了本工作中最佳 BS- x PT-BZN ($x=0.62$)压电陶瓷与其它代表性 BS-PT 基压电陶瓷和商业 PZT 压电陶瓷的最大高温 d_{33} 和退极化温度 T_d ^[4, 22, 24],BS- x PT-BZN 兼具大高温压电系数和高退极化温度,在高温应用方面更具竞争力。

3 结论

采用传统高温固相反应法制备了 BS- x PT-BZN

($x=0.60\sim0.63$)三元系高温压电陶瓷。结果表明,陶瓷样品晶粒发育良好,结构致密。位于准同型相界的 $x=0.62$ 陶瓷具有最佳综合高温品质: Curie 温度为 438 °C,退极化温度为 409 °C,最大原位高温准静态压电系数为 709 pC·N⁻¹。优异的高温压电性能主要与其在宽温区内保持多相共存的 MPB 特征有关。大的高温压电性能和高退极化温度表明,BS- x PT-BZN 压电陶瓷材料是一种非常有望用于制作更先进高温压电器件的候选者。

对于实际应用,压电系数的温度稳定性也是一项关键性技术指标。目前提高压电系数温度稳定性的方法主要有多重 MPB 设计、晶格畸变调制和组分梯度陶瓷构建等。对于 BS-PT-BZN 三元压电体系,它比 BS-PT 二元系具有更多的 MPB 组分点,因此,基于 BS-PT 和 BZN-PT 的 MPB 组成点连线对材料组分调控,以获取兼具高压电性、优异温度稳定性和高退极化温度的研究值得期待。

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Microstructure and Properties of BiScO₃-PbTiO₃-Bi(Zn_{2/3}Nb_{1/3})O₃ High-Temperature Perovskite Ceramics

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Extended Abstract

Introduction Piezoelectric ceramics for the exchange of mechanical energy and electric energy are widely used in the production of piezoelectric sensors, piezoelectric energy harvesters, piezoelectric transducers and other functional devices. Among the piezoelectric ceramics, Pb(Zr, Ti)O₃ (PZT) based perovskite piezoelectric ceramic with high piezoelectric properties is popular. However, the serious thermal depolarization behavior of PZT at a high temperature makes it difficult to meet the application requirements of high-temperature piezoelectric applications in aerospace, nuclear industry and other fields. The Curie temperature of BiScO₃-PbTiO₃ (BS-PT) perovskite piezoelectric ceramic, located at the morphotropic phase boundary (MPB), is nearly 100 °C higher than that of PZT-based piezoelectric ceramics when their piezoelectric coefficient (*d*₃₃) values are similar. Therefore, BS-PT piezoelectric system is considered as a matrix with a great potential for high-temperature piezoelectric applications. Obtaining BS-PT-based high-temperature piezoelectric ceramics with both high temperature (*d*₃₃) and high thermal depolarization temperature (*T_d*) remains a key challenge. For perovskite-type piezoelectric ceramics, the Curie temperature is like-inversely proportional to the tolerance factor, and ferroelectric active ions are usually attributed to promoting the polarization coupling. These indicate that introducing the small tolerance factor and ferroelectric active ions into BS-PT matrix could break through the bottleneck above. In this paper, Bi(Zn_{2/3}Nb_{1/3})O₃ (BZN), with ferroelectric active Bi/Zn ions and a tolerance factor similar to BS was introduced into BS-PT matrix, and the related microstructure, electrical properties and their correlation mechanism were investigated.

Materials and method For the preparation of BS-*x*PT-BZN (0.60 ≤ *x* ≤ 0.63) piezoelectric ceramics by a high-temperature

solid-state reaction method, the raw materials were mixed and ground in a ball mill, and then sintered at 850 °C for 2 h. Afterwards, the sintered materials were pressed, and further sintered at 1 140 °C for 2 h. The BS- x PT-BZN piezoelectric ceramic with silver electrodes was placed in a silicone oil bath at 120 °C and loaded in a DC electric field of 50 kV/cm for 30 min for artificial polarization. The phase composition, grain morphology, ferroelectric, piezoelectric and dielectric properties of the BS- x PT-BZN ceramics were characterized by a model D8-Advance type X-ray diffractometer, a model Sigma-300 type field emission scanning electron microscope, a model ZJ-6A type quasi-static d_{33} meter, and a model TZDM-RT-1000 high-temperature dielectric temperature spectrum test system.

Results and discussion All the BS- x PT-BZN ceramic samples have a dense microstructure, and the average grain sizes are 2.29–3.91 μm . Meanwhile, the BS- x PT-BZN piezoelectric ceramics sintered have a perovskite phase structure. The tetragonal phase content gradually increases and all the ceramic samples maintain the characteristics of two phases coexist as the PT content increases. As a result, the composition with a high Curie temperature and located at the morphotropic phase boundary (MPB) is obtained. Among all the compositions studied, the ceramic sample with x of 0.62 has a maximum room temperature d_{33} value, and thus is considered as MPB composition. This is because the maximum d_{33} value is usually obtained in the MPB composition with a flatter Gibbs free energy profile. In addition, the Curie temperature of the MPB is as high as 438 °C, which is conducive to the acquisition of T_d and high-temperature application. Also, the *in-situ* variable temperature d_{33} test results show that the depolarization temperature of MPB sample with x of 0.62 is up to 409 °C and accompanied by a large high temperature d_{33} (709 $\text{pC}\cdot\text{N}^{-1}$), which is much better than that of reported Pb-based perovskite piezoelectric ceramics. The excellent high-temperature piezoelectric performance is due to the vertical MPB phase boundary characteristics of BS-PT matrix itself, and the increase of tetragonal phase content of BS-PT matrix results from the introduction of BZN, which has a small tolerance factor and contains ferroelectric active ions. This study demonstrates that BS- x PT-BZN piezoelectric ceramics are advanced high-temperature piezoelectric materials suitable for electromechanical applications at elevated temperatures.

Conclusions BS- x PT-BZN ($0.60 \leq x \leq 0.63$) ternary system high-temperature piezoelectric ceramics were prepared by a high-temperature solid-phase reaction method. The results showed that the ceramic samples had a good grain development and compact structure. The ceramics with x of 0.62 located at the morphotropic phase boundary had the optimal comprehensive high-temperature performance (*i.e.*, the Curie temperature T_C of 438 °C, thermal depolarization temperature T_d of 409 °C, and the maximum *in-situ* high-temperature quasi-static piezoelectric coefficient d_{33} of 709 $\text{pC}\cdot\text{N}^{-1}$). The excellent high temperature piezoelectric properties could be mainly related to the MPB characteristics that maintained multi-phase coexistence in a wide temperature region. The large high-temperature piezoelectric properties and high thermal depolarization temperature indicate that BS- x PT-BZN piezoelectric ceramics could be a promising candidate for the preparation of advanced high-temperature piezoelectric devices.

Keywords bismuth scandate-lead titanate; piezoelectric ceramic; microstructure; high-temperature piezoelectricity; depolarization temperature