

(Ba_{0.85}Ca_{0.15})(Ti_{0.9}Zr_{0.1-x}Sn_x)O₃ 无铅压电陶瓷的 相结构与压电性能

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摘要: 钙锆共掺钛酸钡陶瓷(BCZT)具有优异的介电性能和压电性能, 是一类具有发展潜力的无铅压电陶瓷, 但其压电性能仍无法与铅基陶瓷媲美。为提高压电性能, 本研究对陶瓷材料进行 Sn 元素掺杂改性((Ba_{0.85}Ca_{0.15})(Ti_{0.9}Zr_{0.1-x}Sn_x)O₃, $x=0.02\sim 0.07$)。晶体结构分析证实所有组分的陶瓷无杂相, 处于正交相与四方相两相共存状态, 并具有较大的 c/a ; 显微结构分析发现所有陶瓷都很致密, 且平均晶粒尺寸随着 Sn 含量的增加而增大。当 $x=0.04$ 时, 陶瓷最致密, 且室温处于准同型相界附近, 因此拥有最佳的电学性能: $d_{33}=590\text{ pC}\cdot\text{N}^{-1}$, $k_p=52.2\%$, $\tan\delta=0.016$, $\epsilon_{33}^T=5372$, $d_{33}^*=734\text{ pm}\cdot\text{V}^{-1}$, $IR=57.8\text{ G}\Omega\cdot\text{cm}$ 。本研究表明: Sn 掺杂的 BCZT 基无铅压电陶瓷具有优异的压电性能, 有望在换能器、机电传感器和驱动器等方面得到应用。

关键词: (Ba,Ca)(Ti,Zr)O₃ 基无铅压电陶瓷; Sn 掺杂; 准同型相界; 晶粒尺寸效应

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Phase Structure and Piezoelectric Property of (Ba_{0.85}Ca_{0.15})(Ti_{0.9}Zr_{0.1-x}Sn_x)O₃ Lead-free Piezoceramics

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Abstract: Zr and Ca co-doped brium titanate (BCTZ) based ceramics have attracted much attention due to their excellent dielectric and piezoelectric properties, which are potential candidates for lead-free piezoelectric materials. However, the piezoelectric property of BCTZ-based ceramics are still lower than that of commercial lead-based ceramics. Therefore, Sn elements are doped in (Ba_{0.85}Ca_{0.15})(Ti_{0.9}Zr_{0.1-x}Sn_x)O₃ ($x = 0.02\sim 0.07$) ceramics to improve their piezoelectric property in this work. First, all ceramics exhibit a pure perovskite structure without any secondary phase. Furthermore, orthorhombic and tetragonal phases coexist at room temperature for all counterparts. Second, all ceramics display a dense microstructure. And the grain size gradually increases with Sn content increasing. The crystal structure of $x=0.04$ ceramic locates in morphotropic phase boundary. Meanwhile, the $x=0.04$ ceramic exhibits the most dense microstructure. Hence, $x=0.04$ ceramic has the best piezoelectric property with $d_{33} = 590\text{ pC}\cdot\text{N}^{-1}$, $k_p = 52.2\%$, $\tan\delta = 0.016$,

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$\epsilon_{33}^T = 5372$, $d_{33}^* = 734 \text{ pm}\cdot\text{V}^{-1}$, and $\text{IR} = 57.8 \text{ G}\Omega\cdot\text{cm}$. This work demonstrates that the Sn-doped BCZT based lead-free piezoelectric ceramics could be applied in transducers, electromechanical sensors and actuators.

Key words: (Ba,Ca)(Ti,Zr)O₃ based lead-free piezoceramics; Sn doping; morphotropic phase boundary; grain size effect

锆钛酸铅基压电陶瓷^[1-2]以其优异的压电性能已在传感器^[3]、换能器和致动器等领域得到广泛应用,但铅元素会威胁环境和人体健康,寻找具有高压电性能的铅基陶瓷替代品成为科学家们关注的研究方向。BaTiO₃ (BT)^[4-5]、(K,Na)NbO₃ (KNN)^[6-7]、(Bi,Na)TiO₃ (BNT)^[8-9]等诸多无铅压电陶瓷已走进科学家们的视野,其中 BaTiO₃ 以优异的介电性能^[10]和高机电耦合系数^[11]等优点而备受青睐。

掺杂改性^[12-15]是一种常见的提升陶瓷压电性能的方法,在 ABO₃ 钙钛矿结构的 A 位或者 B 位中掺入等价或不等价的离子,可以调控陶瓷的压电、介电和铁电等性能。Favarim 等^[16-19]研究了 Zr⁴⁺、Ca²⁺ 离子掺杂对于 BaTiO₃ 体系的影响,实验结果表明 Zr 和 Ca 均能使陶瓷的准同型相界(MPB)向低温方向移动,掺杂过量的 Zr 则会大幅降低陶瓷的居里温度,适当的掺杂有助于改良 BaTiO₃ 陶瓷的压电性能。任晓兵教授^[20]在 2009 年制备了一种具有高压电性能的 BaZr_{0.2}Ti_{0.8-x}Ba_{0.7}Ca_{0.3}TiO₃(BZT-xBCT)无铅压电陶瓷,该体系的高压电性能源自具有三重临界点的准同型相界,这为科学家提升 BaTiO₃ 陶瓷的压电性能提供了一个崭新的思路,此后大量科研人员对此进行了探究。国外学者 Wanwisa 等^[21]通过构建三元掺杂体系 BaTiO₃-CaTiO₃-BaSnO₃ 调控正交相-四方相(O-T)相变至室温最终实现了高压电常数($d_{33}=515 \text{ pC}\cdot\text{N}^{-1}$)和大压电响应($d_{33}^*=1293 \text{ pm}\cdot\text{V}^{-1}$)。四川师范大学赁敦敏课题组^[22]制备了(1-x)BaTiO_{3-x}CaZrO₃(BT-xCZ)体系无铅压电陶瓷,调节相变温度至室温,构建菱方相、正交相与四方相多相共存的相结构,并进一步调控电畴结构,最终获得了优异的压电性能($d_{33}=(445\pm 20) \text{ pC}\cdot\text{N}^{-1}$)和机电耦合系数($k_p=55\%$)。众多研究表明,通过掺杂元素来调控相界是一种有效提升压电性能的方法。

本工作通过对 BaTiO₃ 基无铅压电陶瓷掺杂适量的 Ca²⁺与 Zr⁴⁺,并调控 Sn⁴⁺的掺杂量来获得最佳的准同型相界与合适的晶粒尺寸^[23-24]。通过传统固相法制备了(Ba_{0.85}Ca_{0.15})(Ti_{0.9}Zr_{0.1-x}Sn_x)O₃($x=0.02, 0.03, 0.04, 0.05, 0.06, 0.07$)无铅压电陶瓷(简称为 BCZTSn),该组分的陶瓷在室温下恰好位于正交相与四方相的转变点附近,探究了不同掺杂量对于相结构与相界转变的影响。掺杂 Sn 还影响了晶粒的生

长,通过调控获得了合适的晶粒尺寸。通过调控陶瓷的相结构和微观结构,优化其介电、铁电以及压电性能,最终在 Sn 掺杂量为 0.04 时,获得了优异的电学性能: $d_{33}=590 \text{ pC}\cdot\text{N}^{-1}$, $k_p=52.2\%$, $\tan\delta=0.016$, $\epsilon_{33}^T=5372$, $d_{33}^*=734 \text{ pm}\cdot\text{V}^{-1}$, $\text{IR}=57.8 \text{ G}\Omega\cdot\text{cm}$ 。为 BaTiO₃ 基无铅压电陶瓷在换能器、机电传感器、驱动器等方面的应用提供了广阔的前景和多种可能。

1 实验方法

1.1 样品制备

实验中以分析纯度的 BaCO₃(麦克林生物, 99.0%), CaCO₃(国药集团, 99.0%), TiO₂(福晨化学, 99.0%), BaZrO₃(阿法埃莎, 99.0%)和 SnO₂(阿拉丁, 99.5%)为原料,采用传统固相法制备了(Ba_{0.85}Ca_{0.15})(Ti_{0.9}Zr_{0.1-x}Sn_x)O₃($x=0.02, 0.03, 0.04, 0.05, 0.06, 0.07$)无铅压电陶瓷(简称为 BCZTSn)。具体步骤如下: 首先将原料按照化学计量比称量后放入球磨罐中,以无水乙醇为介质,将其行星球磨 12 h。随后将烘干处理的浆料置于 1120 °C 马弗炉中预烧 4 h,将预烧的块体粉碎后进行 12 h 二次球磨,烘干过筛后得到了均匀的 BCZTSn 陶瓷微粉。在陶瓷微粉中加入 5%的 PVB 黏合剂进行造粒,并在 20 MPa 下干压成 $\phi 10 \text{ mm}\times 1 \text{ mm}$ 的圆片。将圆片在 600 °C 下排胶 3 h,最后在 1450~1480 °C 下煅烧 4 h 得到陶瓷样品。为了对陶瓷进行压电和介电性能测试,在陶瓷样品的上下表面分别涂覆银浆,并在 800 °C 下热处理 30 min 以制备银电极。随后将样品置于 40 °C 硅油中并在 3 kV/mm 的直流电场下极化 35 min,静置 24 h 后测试电学性能。

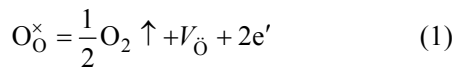
用场发射扫描电镜(Gemini 300, Zeiss, Germany)观察陶瓷样品表面的微观结构。用 X 射线衍射仪(XRD; Rigaku 2500, Japan)对样品进行物相分析,使用 Rietveld 精修和 GSAS 软件分析样品的晶体结构和晶胞参数。使用带有 LCR 表(Agilent 4980A, Agilent, Santa Clara, USA)的定制夹具测试样品在 -40~150 °C 下的介电-温度特性。使用皮安计(Model 4140B, Hewlett-Packard, Santa Clara, USA)测量样品的绝缘电阻 IR。使用准静态 d_{33} 测试仪(ZJ-3A, 中国科学院声学研究所)测定样品的压电常数 d_{33} , 使用

精密阻抗分析仪(4294A, Agilent, Santa Clara, USA)测量样品的介电常数 ϵ_{33}^T , 介电损耗 $\tan\delta$ 以及平面振动模式下的谐振频率 f_r 和反谐振频率 f_a , 计算得到机电耦合系数 k_p 。采用铁电分析仪(TF3000, aixACCT, Aachen, Germany)测量陶瓷的电滞回线和应力应变曲线。

2 结果与讨论

2.1 微观结构分析

图1(a~f)是 $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Ti}_{0.9}\text{Zr}_{0.1-x}\text{Sn}_x)\text{O}_3$ ($x=0.02\sim 0.07$)陶瓷样品表面的SEM照片。如图所示, 所有烧结样品的晶粒均为圆型, 尺寸均一, 晶界清晰且具有致密的微观结构, 没有观察到第二相, 清晰的晶界和均匀的晶粒尺寸能够提高陶瓷的机械强度, 从而改善陶瓷的电学性能^[25]。在图1(e, f)中, 陶瓷样品表面晶粒生长不完整且出现了气孔, 这意味着烧结后陶瓷样品的微观结构不致密, 不均匀会导致压电性能下降。过量掺杂Sn造成陶瓷在烧结过程中缺陷含量增高, 在 BaTiO_3 中添加 SnO_2 和氧元素在高烧结温度下(1450~1480 °C)的挥发都会产生氧空位, 如式(1)所示。



过量掺杂Sn导致缺陷浓度升高, 氧空位增加伴随着载流子浓度提升, 使陶瓷样品导电性增强, 电学性能减弱。随着Sn掺杂量逐渐增加, 陶瓷样品的晶粒尺寸也逐渐增大, 这表明掺杂Sn可以促进陶瓷晶粒生长, 氧空位也会导致通过晶界的质量传输增强, 进而促进晶粒生长^[26-27]。随着晶粒尺寸增大,

不产生压电效应的晶界比例降低, 有助于增强陶瓷的压电性能。小晶粒的晶界比例大, 会给畴壁运动造成阻力, 影响陶瓷的压电性能^[28-29]。因此适量掺杂Sn元素可以使陶瓷的晶粒长大, 增强陶瓷的电学性能。

2.2 物相结构分析

图2是 $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Ti}_{0.9}\text{Zr}_{0.1-x}\text{Sn}_x)\text{O}_3$ ($x=0.02\sim 0.07$)陶瓷样品的XRD图谱, 如图所示, 样品均表现出纯钙钛矿结构, 没有观察到杂质相的存在, 说明 Ca^{2+} 、 Zr^{4+} 、 Sn^{4+} 离子已经完全扩散至 BaTiO_3 晶格中形成固溶体。所有组分的样品与纯 BaTiO_3 的衍射峰匹配度良好, JCPDS 05-0626 和 81-2200 分别对应四方相(T)和正交相(O)结构。将 $2\theta=44.5^\circ\sim 46.0^\circ$ 的衍射峰局部放大后, 可以发现衍射峰逐渐向高角度偏移, 这是 Ti^{4+} 、 Zr^{4+} 、 Sn^{4+} 离子共同占据B位导致的^[30]。而随着Sn的掺杂量逐渐增大, Zr元素的含量减小, Sn^{4+} 离子半径为0.069 nm, 小于 Zr^{4+} (0.072 nm), 故引起晶格收缩, 晶胞的晶面间距逐渐减小, 由布拉格方程 $n\lambda = 2d\sin\theta$ 可知, 衍射角度应向高角度偏移, 符合实验结果。进一步观察得知, $2\theta=45^\circ$ 处的衍射峰并不是由单一的相结构组成, 而是来自于正交相和四方相共存结构。

为了得到样品的晶胞参数, 使用GSAS软件对XRD结果进行了Rietveld精修。精修结果如图3所示, 表1列出了所有BCZTSn陶瓷的晶格参数。图中所示XRD结果与拟合结果相符, 且 R_{wp} 均低于15%, 说明拟合结果可靠。拟合结果表明陶瓷样品由正交相和四方相共同构成, 且不同Sn掺杂量陶瓷的O相与T相的含量也有所不同, 随着Sn掺杂量增大, T相的含量逐渐增大。精修结果证明了

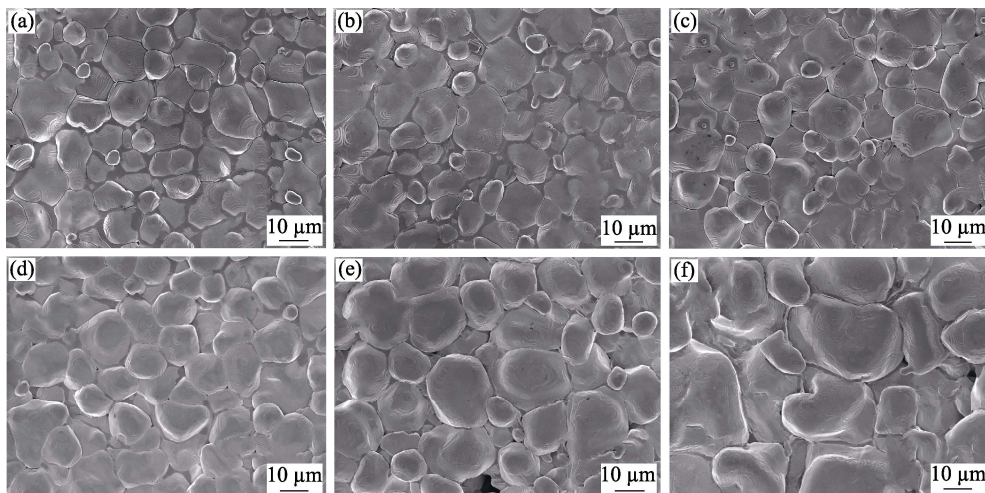


图1 BCZTSn陶瓷样品表面的SEM照片

Fig. 1 SEM images of the surface of BCZTSn ceramic samples
(a) $x=0.02$; (b) $x=0.03$; (c) $x=0.04$; (d) $x=0.05$; (e) $x=0.06$; (f) $x=0.07$

XRD 测试得到的结论: 掺杂 Sn 引起晶格收缩, 进而导致晶胞参数和晶格体积减小。通过晶胞参数得到了四方相结构中 c 与 a 的比值, 在钙钛矿压电陶瓷中, 压电极化主要由 B 位离子形成的氧八面体提供, c/a 表征了压电极化的强弱。随着 Sn 掺杂量的提升, c/a 逐渐增大且在 $x=0.04$ 处达到最大值(1.0024), 而后减小, 这表明 Sn 掺杂量为 0.04 的陶瓷样品具有最大的压电极化效应。

2.3 介电性能分析

为进一步研究和表征相变过程, 在 1 kHz, $-40\sim 160$ °C 条件下测试了 $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Ti}_{0.9}\text{Zr}_{0.1-x}\text{Sn}_x)\text{O}_3$ ($x=0.02\sim 0.07$) 陶瓷样品的介电温谱, 如图 4(a) 所示,

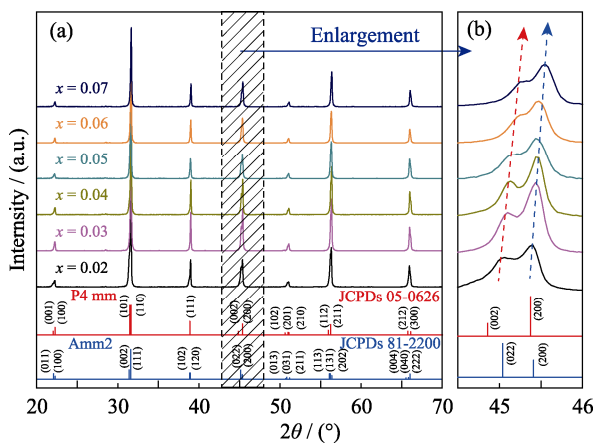


图 2 BCZTSn 陶瓷样品的(a)XRD 图谱和(b)局位放大图
Fig. 2 (a) XRD patterns of BCZTSn ceramic samples and (b) partial magnified views

并将各组分相结构转变点温度总结在图 4(b)中。如图所示, 不同 Sn 掺杂量陶瓷样品的介电曲线都存在三个相结构转变峰: 菱方相转变为正交相的温度在 $-10\sim 5$ °C 之间; 正交相转变为四方相的温度在 $15\sim 30$ °C 之间^[31]; 而居里温度在 $60\sim 90$ °C 之间, 表示体系由铁电相转变为顺电相。此外, 在所有陶瓷的相结构转变点附近同样存在介电损耗的峰值, 且介电损耗都比较低。正交相转变为四方相的温度处于室温附近, 因此室温下陶瓷为正交相与四方相共存, 这与 XRD 得到的结论一致。且随着 Sn 掺杂量增加, 陶瓷的相结构转变点逐渐向低温移动, T 相含量逐渐增大, 体系在室温下处于准同型相界, 在相变温度附近极化的各向异性几乎消失。这使得极化旋转更加容易, 畴壁更加容易运动和翻转, 从而增强陶瓷的极化强度和压电性能^[20,32], 当 $x=0.04$ 时, 相结构转变温度恰好为室温(25 °C), 压电响应显著。当 $x=0.07$ 时, 体系的居里温度移至 60 °C 左右, 温度稳定性差, 极易退极化, 严重影响了陶瓷的压电性能。

2.4 铁电性能分析

图 5(a)是 $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Ti}_{0.9}\text{Zr}_{0.1-x}\text{Sn}_x)\text{O}_3$ ($x=0.02\sim 0.07$) 陶瓷样品在 1 Hz 下测试的电滞回线。最大极化强度、剩余极化强度和矫顽电场见图 5(b)。如图所示, 所有组分的陶瓷样品均具有典型细长的电滞回线, 且随着 Sn 掺杂量逐渐增大, 样品的最大极化强度和剩余极化强度增大, 矫顽电场减小; 在 $x=0.04$ 时达到最优的铁电性能, 最大极化强度为 $19.4 \mu\text{C}\cdot\text{cm}^{-2}$,

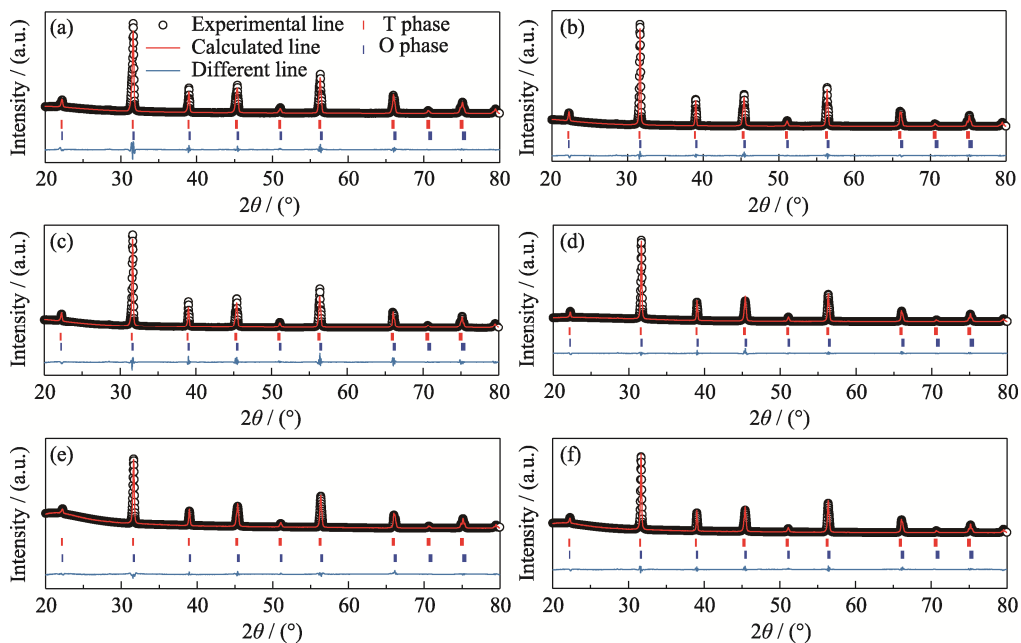


图 3 BCZTSn 陶瓷样品的 XRD 精修结果
Fig. 3 XRD Rietveld refinements of BCZTSn ceramic samples
(a) $x=0.02$; (b) $x=0.03$; (c) $x=0.04$; (d) $x=0.05$; (e) $x=0.06$; (f) $x=0.07$

表 1 BCZT 陶瓷样品的晶格参数

Table 1 Lattice parameters of BCZTSn ceramic samples

Sample	Lattice parameter							Phase ratio/%		$R_{wp}/\%$
	Tetragonal phase				Orthorhombic phase			Tetragonal phase	Orthorhombic phase	
	a/nm	c/nm	V/nm ³	c/a	a/nm	b/nm	c/nm			
x=0.02	0.39986	0.40071	0.06406	1.0021	0.39968	0.56622	0.56836	35	65	7.48
x=0.03	0.39982	0.40070	0.06405	1.0022	0.39949	0.56638	0.56771	37	63	5.91
x=0.04	0.39970	0.40069	0.06401	1.0024	0.39950	0.56597	0.56789	47	53	9.08
x=0.05	0.39909	0.40000	0.06370	1.0022	0.39989	0.56565	0.56669	47	53	6.49
x=0.06	0.39929	0.39960	0.06370	1.0007	0.39935	0.56606	0.56680	54	46	7.61
x=0.07	0.39901	0.39981	0.06365	1.0002	0.39923	0.56707	0.56528	58	42	7.94

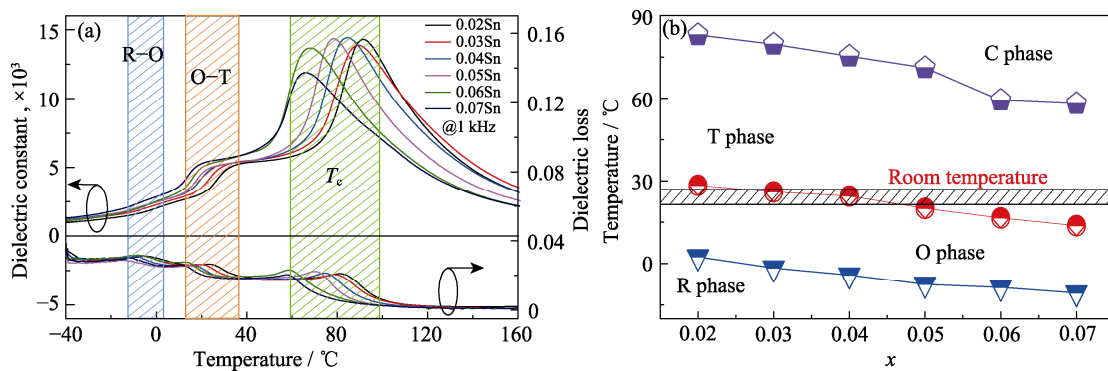


图 4 BCZTSn 陶瓷样品的介电温谱和相转变温度图

Fig. 4 Temperature dielectric spectra and phase transition temperature diagram of BCZTSn ceramic samples

(a) Temperature dielectric spectra; (b) Phase transition temperature diagram

Colorful figures are available on website

剩余极化强度为 $7.5 \mu\text{C}\cdot\text{cm}^{-2}$, 矫顽力电场为 $0.161 \text{ kV}\cdot\text{mm}^{-1}$; Sn 掺杂量继续增加, 最大极化强度和剩余极化强度逐渐减小, 矫顽电场逐渐增大。究其原因: 首先掺杂 Sn 元素会促进晶粒生长, 较大晶粒陶瓷中无铁电相晶界比重低, 因此其铁电性能更优异; 其次室温下的准同型相界使得极化的各向异性几乎消失, 极化旋转变得更加容易, 增强了极化^[20]。当 Sn 的掺杂量大于 0.04 时, 由于烧结样品不致密与相转变温度偏移, 导致其铁电性能减弱。

2.5 压电性能分析

图 6 是 $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Ti}_{0.9}\text{Zr}_{0.1-x}\text{Sn}_x)\text{O}_3$ ($x=0.02\sim 0.07$) 陶瓷样品在 1 Hz, $1 \text{ kV}\cdot\text{mm}^{-1}$ 激励电场中测得的双极应力-应变曲线。如图 6(a)所示, 所有组分样品的双极应力-应变曲线都显示出典型的“蝴蝶”形状和对称结构, 表明陶瓷的缺陷浓度较低。动态压电常数(d_{33}^*)通过最大位移比最大电场强度算出。单极应力-应变曲线表示压电陶瓷在 $1 \text{ kV}\cdot\text{mm}^{-1}$ 电场下获得的应变强度, 直观地表达了陶瓷的压电响应。随着 Sn 掺杂量逐渐增大, 应力-应变曲线都呈现先增大后减小的趋势, 在 $x=0.04$ 处达到了最大值, 位

移达到了 734 nm , 应变达到了 0.09% , 表明陶瓷具有优异的压电响应。

表 2 总结了所有组分陶瓷样品的压电常数(d_{33})、机电耦合系数(k_p)、室温下的介电损耗($\tan\delta$)与介电常数(ϵ_{33}^T)、动态压电常数(d_{33}^*)和绝缘电阻率(IR)。从表中可以看出, 所有样品都具有较低的介电损耗和较高的绝缘电阻率, 这表明陶瓷都具有良好的压电性能。当 Sn 掺杂量较低时($x=0.02\sim 0.03$), 相对细化的晶粒会影响电畴的生长和翻转, 继而直接影响陶瓷的铁电性能和压电性能, 样品具有较低的压电常数和压电响应。当 Sn 掺杂量为 0.04 时, 样品在室温下构建了多相共存区域, 适量掺杂也增大了晶粒尺寸, 样品内部电畴转向的矫顽场减小, 并且在晶粒之中更容易形成铁电畴壁, 电畴转向对应变的贡献增加^[33-36]。两种原因共同促进压电效应显著提升, 此时陶瓷的压电性能最佳: $d_{33}=590 \text{ pC}\cdot\text{N}^{-1}$, $k_p=52.2\%$, $\tan\delta=0.016$, $\epsilon_{33}^T=5372$, $d_{33}^*=734 \text{ pm}\cdot\text{V}^{-1}$, $\text{IR}=57.8 \text{ G}\Omega\cdot\text{cm}$ 。当掺杂量更大时($x=0.05\sim 0.07$), 过多的 Sn 致使缺陷含量增加, 陶瓷烧结并不致密, 介电损耗升高, 直接降低了陶瓷的压电性能, 此外, 突增的介电常数是陶瓷内部空间电荷极化所导致。

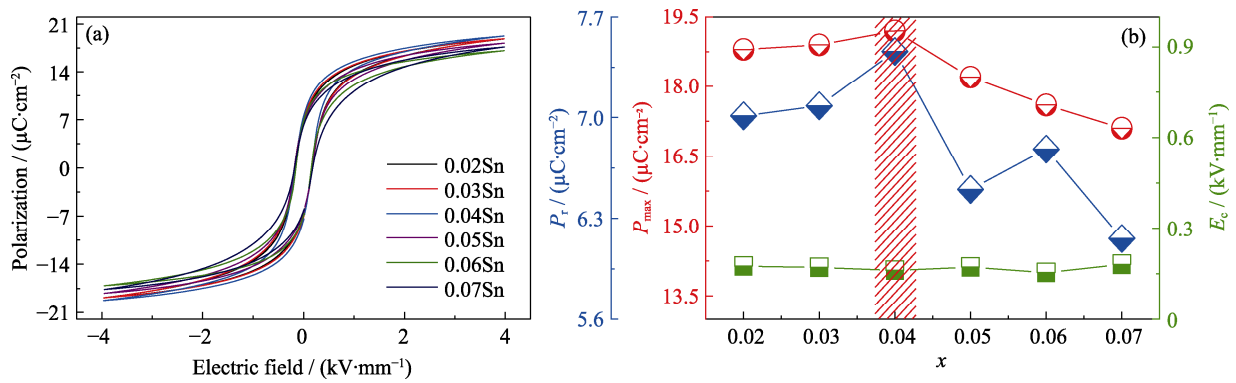


图 5 BCZTSn 陶瓷样品的电滞回线以及数据汇总
 Fig. 5 P - E hysteresis loops of BCZTSn ceramic samples
 (a) P - E hysteresis loops at 1 Hz; (b) Data summary of P_{\max} , P_r and E_c .
 Colorful figures are available on website

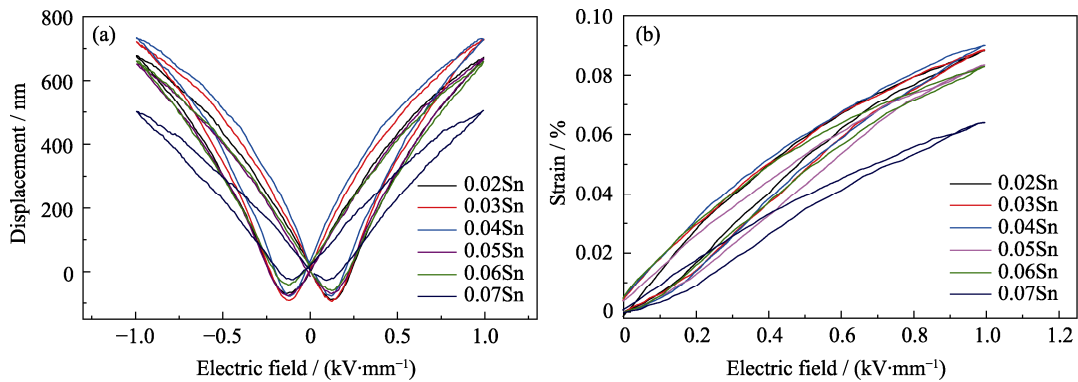


图 6 BCZTSn 陶瓷样品的应力-应变曲线
 Fig. 6 S - E curves of BCZTSn ceramic samples
 (a) Bipolar S - E curves; (b) Unipolar S - E curves
 Colorful figures are available on website

表 2 BCZTSn 陶瓷样品的基本电学性能

Table 2 Basic electric property of BCZTSn ceramic samples

Component	$d_{33}/(\text{pC}\cdot\text{N}^{-1})$	$k_p/\%$	$\tan\delta$	ϵ_{33}^T	$d_{33}^*/(\text{pm}\cdot\text{V}^{-1})$	$\text{IR}/(\text{G}\Omega\cdot\text{cm})$
$x=0.02$	493	45.6	0.019	4773	678	55.5
$x=0.03$	545	47.5	0.017	5083	729	56.3
$x=0.04$	590	52.2	0.016	5372	734	57.8
$x=0.05$	464	42.1	0.018	5152	669	56.8
$x=0.06$	430	41.3	0.019	5446	660	53.9
$x=0.07$	364	32.5	0.02	6237	504	53.4

3 结论

使用固相法制备了组分为 $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Ti}_{0.9}\text{Zr}_{0.1-x}\text{Sn}_x)\text{O}_3$ ($x=0.02\sim 0.07$) 的无铅压电陶瓷。通过调整 Sn 元素的掺杂量, 调控陶瓷的晶粒尺寸和相界区间, 从而优化陶瓷的压电性能。试验结果表明: 陶瓷的微观结构非常致密, 晶粒尺寸随着 Sn 掺杂逐渐增大, 但在高掺杂量下致密度略有下降。样品具有纯钙钛矿结构, 相结构均处于正交相与四方相的共存状态, 当 $x=0.04$ 时, 准同型

相界恰好处于室温, 有利于电畴的生长和翻转。因此随着 Sn 掺杂量增大, 陶瓷的压电性能先增大后减小, 在 $x=0.04$ 处获得最优的压电响应: $d_{33}=590 \text{ pC}\cdot\text{N}^{-1}$, $k_p=52.2\%$, $\tan\delta=0.016$, $\epsilon_{33}^T=5372$, $d_{33}^*=734 \text{ pm}\cdot\text{V}^{-1}$, $\text{IR}=57.8 \text{ G}\Omega\cdot\text{cm}$ 。

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