

铁酸铋基陶瓷的相结构调控及高温压电性能优化

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摘 要: 随着航空航天、汽车、冶金及石油化工行业的快速发展, 压电传感器被要求在高温环境中持续工作。然而多数压电材料存在退极化温度较低的问题, 严重限制其实际应用。铁酸铋基陶瓷因其在高温环境中表现出较强的压电响应而备受关注。基于此, 采用传统陶瓷工艺制备了化学组成为 $0.99(0.7\text{BiFeO}_3-0.3\text{BaTiO}_3)-0.01\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3-x\text{Li}_2\text{CO}_3$ ($x = 0, 0.001, 0.003, 0.005$) 简称为 BFBTBNT- $x\text{Li}$ 的陶瓷。随着 Li_2CO_3 含量的增加, 陶瓷由三方(*R*)相逐渐演变为立方(*PC*)相结构, 其中, 0.3Li 为 *R-PC* 共存相。 Li_2CO_3 掺杂的 BFBTBNT- $x\text{Li}$ 陶瓷, 其居里温度从 483°C 升高至 535°C , 同时样品的介电损耗降低。陶瓷的剩余极化强度随 Li_2CO_3 的增加而增大, 在 0.3Li 到达最高值。随后由于陶瓷矫顽场的升高, 剩余极化强度相应减弱。研究发现, Li_2CO_3 可增大氧空位的迁移势垒从而抑制氧空位的形成, 故陶瓷的绝缘性显著增强。 0.3Li 具有最优的压电常数为 $183\text{pC}\cdot\text{N}^{-1}$ 和高达 380°C 的退极化温度, 在高温压电领域具有潜在应用价值。

关键词: 铁酸铋; 压电陶瓷; 碳酸锂; 温度稳定特性

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压电陶瓷是一类能够在机械能和电能之间实现相互转换的功能材料, 适用于无损检测、电声和调谐、信息处理、精密控制和光电子技术等多个领域。随着原子能、航空航天、汽车、冶金及石油化工行业的快速发展, 人们对压电传感器在高温环境下的工作性能提出了更高要求^[1-3]。许多传统的压电材料, 如 $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ 基陶瓷, 在超过 200°C 时将失去压电特性^[4], 而铅基陶瓷虽然性能良好, 但由于铅的毒性问题而限制了其应用^[5]。因此, 探索能够在高温条件下稳定运行并具备优良压电性能的无铅压电材料和器件, 成为高新技术领域亟待解决的难题。

铁酸铋(BiFeO_3 , BF)作为一种高温压电陶瓷, 其铁电到顺电的相变温度高达 825°C , 同时其理论极化强度约为 $100\mu\text{C}\cdot\text{cm}^{-2}$ ^[6-7]。但铁酸铋基陶瓷制备过程中常会伴随 Bi_2O_3 的挥发和 Fe 元素的价态变化, 这会导致次生相的形成和氧空位的增加, 进而产生漏电流。此外, 氧空位的钉扎效应还会导致矫

顽场升高, 使极化过程变得困难。

近年来, 在国内外研究者的不懈努力下, 从相界构建、A/B 位元素掺杂改性、第三组元引入、烧结工艺优化、极化条件探索等角度出发, 铁酸铋基压电陶瓷的研究迈上了新台阶。Xiang 等在 Sm 掺杂的 $\text{BiFeO}_3-\text{PbTiO}_3$ 中构建了准同型相界, 将 d_{33} 值提高至 $131\text{pC}\cdot\text{N}^{-1}$ ^[8]。Li 等在 Eu 掺杂的 BF-BT 陶瓷中观察到较高的逆压电系数($d_{33}^* = 392\text{pm}\cdot\text{V}^{-1}$)^[9]。Zhu 等在 BF-BT 陶瓷中引入第三组元 $\text{Bi}(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_3$, 将陶瓷的压电系数提高至 $154\text{pC}\cdot\text{N}^{-1}$ ^[10]。Yan 等采用两步烧结法制备了 $0.7\text{BiFe}_{1-x}\text{Al}_x\text{O}_3-0.3\text{BaTiO}_3$ 陶瓷, 获得了高达 $361\text{pm}\cdot\text{V}^{-1}$ 的逆压电系数^[11]。Kim 等对 BF 基压电陶瓷的交流极化条件做了研究。样品在 120°C 的硅油浴中, 采用 $50\text{kV}\cdot\text{cm}^{-1}$ 的直流电场极化之后, 陶瓷的相位角为 -39° , d_{33} 数值为 $69.39\text{pC}\cdot\text{N}^{-1}$; 采用交流和直流极化共同作用后的陶瓷, 相位角为 63° , 极化程度远远高于直流极化的效果, 因此陶瓷的压电常数也得到了显著提高, 大约为直流极化的

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2倍^[12]。基于此,为了在400℃以上操作温度获得较高的压电响应,本工作在0.99(0.7BiFeO₃-0.3BaTiO₃)-0.01Bi_{0.5}Na_{0.5}TiO₃(BFBTBNT)陶瓷中引入Li₂CO₃来优化陶瓷的绝缘性能,通过提高致密度和抑制氧空位,同时提升BF基无铅压电陶瓷的压电响应和退极化温度。研究表明,当 $x=0.003$ 时,陶瓷压电常数和居里温度分别为183 pC·N⁻¹和521℃,并且在高温条件下仍然保持较高的压电响应,退极化温度可达380℃。

1 实验

1.1 样品制备

采用中国医药集团有限公司生产的TiO₂(99%,质量分数)、BaCO₃(99%)、Bi₂O₃(99%)、Fe₂O₃(99%)和Li₂CO₃(99.8%)作为原料,通过高温固相法制备0.99(0.7BiFeO₃-0.3BaTiO₃)-0.01Bi_{0.5}Na_{0.5}TiO₃- x Li₂CO₃+1%(摩尔分数)MnO₂($x=0, 0.001, 0.003, 0.005$;简写为0Li, 0.1Li, 0.3Li, 0.5Li, BFBTBNT- x Li)陶瓷样品。首先,按照化学计量比称取上述原料,置于行星式球磨机球磨12h,球磨介质为无水乙醇,球磨机转速为210 r·min⁻¹。1次球磨后的原料经干燥后置于720℃高温炉中煅烧5h,升温速率为2℃·min⁻¹。煅烧后的样品,按化学计量比添加MnO₂(99.8%)进行2次球磨,球磨时间为12h。干燥处理的2次球磨陶瓷粉,添加浓度为5%(质量分数)的聚乙烯醇(PVA)水溶液进行造粒、压片,制成厚度约为1mm,直径为10mm的圆片。后将上述圆片置于高温炉中以1℃·min⁻¹的

升温速率至600℃并恒温10h,以除去造粒使用的PVA。之后将样品置于高温炉中以3℃·min⁻¹的升温速率至1000℃并恒温3h,得到陶瓷样品。

1.2 样品表征

将陶瓷片研磨成粉状,使用Bruker D2 PHASER型X射线衍射仪(X-ray diffractometer, XRD)进行相结构测试,扫描角度为20°~70°,扫描速率为1(°)/min。使用JSM-5510LV型场发射扫描电子显微镜(SEM)观察样品的表面形貌。将陶瓷的两面打磨抛光至0.4mm厚度,涂覆直径为6mm的银浆,后置于800℃高温炉中煅烧10min,用于测试样品的电学性能。用E4980A和HP 4284A型介电测试系统收集陶瓷的介电损耗、介电常数与温度的变化关系以及复阻抗谱。用Radiant Precision Premier II型铁电测试仪测试陶瓷的电滞回线和漏电流曲线。用PHI-5300型X射线光电子能谱仪分析氧元素的化学态。由Bruker E500型电子顺磁共振波谱仪分析陶瓷的氧空位。由ZJ-3A型准静态压电仪测得陶瓷的压电常数,样品预先在120℃的硅油浴中经过4kV·mm⁻¹的直流电场极化20min。用YE2730A型原位 d_{33} 测试仪收集陶瓷的压电常数随温度的变化关系。

2 结果与讨论

2.1 BFBTBNT- x Li陶瓷样品的相结构

图1a为BFBTBNT- x Li的XRD谱,样品呈现典型的钙钛矿结构。20°~70°范围内未观测到明显杂

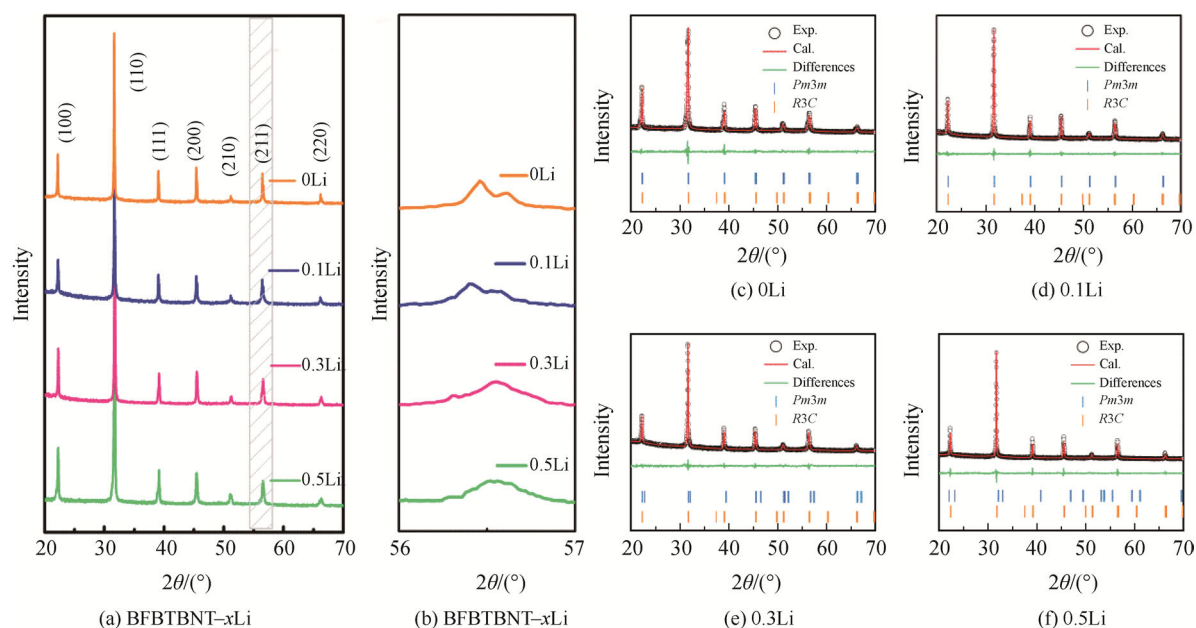


图1 BFBTBNT- x Li陶瓷样品XRD衍射谱和XRD结构精修谱
Fig. 1 XRD patterns and XRD refinement patterns of the BFBTBNT- x Li

质峰,表明制得的陶瓷样品纯度较高。图 1b 为 $56^{\circ}\sim 57^{\circ}$ 范围内的衍射峰,此为陶瓷相结构变化的判据之一。0Li 和 0.1Li 具有明显的分裂峰,此为 R 相的特征;0.3Li 和 0.5Li 则逐渐演变为单峰,此为 PC 相的特征^[13]。随着 Li_2CO_3 含量的逐渐增加,陶瓷由 R 相逐渐演变为 PC 相,0.3Li 表现出 R - PC 共存相特征,此时体系的吉布斯函数趋于扁平化,存在多个自发极化方向,有利于压电性能的提升^[14]。

为了清晰地分析样品的相结构和组成变化,选取了 $R3C$ 和 $Pm3m$ 相的标准 cif 文件作为参照,并将 XRD 数据输入综合结构分析系统(GSAS)软件中

进行结构修正,结果如图 1c~图 1f 和表 1 所示。精修结果的 R 因子均低于 0.10, χ 值也保持在较低水平,这验证了精修结果的可靠性。在未添加 Li_2CO_3 的样品中, R 相的含量高达 78.02%,而 PC 相的含量为 21.88%,表明 0Li 的主相为 R 相结构。随着 Li_2CO_3 的添加,样品中的 R 相含量持续减少,特别是在添加量为 0.003 的 0.3Li 样品中, R 相含量降至 36.78%,表明相结构发生了显著变化,此时为典型的 R - PC 相共存特征。在添加量为 0.005 的 0.5Li 样品中, R 相的含量进一步减少到 18.76%,而 PC 相的含量增加至 81.24%,显示样品中主要是 PC 相结构。

表 1 BFBTBNT- x Li 的 XRD 精修数据
Table 1 XRD refinement data of the BFBTBNT- x Li

Samples	Phase	w/%	Cell volume/ $\text{\AA}^3$	Cell parameters/ $\text{\AA}$	Rietveld factors
0Li	$R3C$	78.02	379.24	$a = b = 5.631\ 2, c = 13.811\ 5$	$R_{\text{wp}} = 0.07, R_p = 0.05$
	$Pm3m$	21.98	60.92	$a = b = 3.743\ 4, c = 3.566\ 5$	$\chi^2 = 3.319$
0.1Li	$R3C$	73.59	381.74	$a = b = 5.643\ 6, c = 13.830\ 1$	$R_{\text{wp}} = 0.08, R_p = 0.05$
	$Pm3m$	26.41	62.97	$a = b = 3.999\ 9, c = 3.928\ 7$	$\chi^2 = 3.246$
0.3Li	$R3C$	36.78	382.80	$a = b = 5.611\ 4, c = 13.925\ 4$	$R_{\text{wp}} = 0.07, R_p = 0.05$
	$Pm3m$	63.22	63.35	$a = b = 3.985\ 4, c = 3.984\ 9$	$\chi^2 = 3.487$
0.5Li	$R3C$	18.76	380.88	$a = b = 5.646\ 0, c = 13.805\ 1$	$R_{\text{wp}} = 0.07, R_p = 0.04$
	$Pm3m$ (81.24%)	81.24	68.59	$a = b = 3.986\ 9, c = 4.010\ 6$	$\chi^2 = 3.356$

w is mass fraction.

2.2 BFBTBNT- x Li 陶瓷样品的显微结构

陶瓷材料的晶粒生长和致密度对其性能有着直接的影响。图 2 为 BFBTBNT- x Li 陶瓷样品的微观形貌。经抛光打磨的陶瓷样品置于 $850\ ^{\circ}\text{C}$ 高温炉中恒温热处理 0.5 h 后用扫描电子显微镜测试。由图 2 可以看出,样品表面光滑,无明显孔洞存在,陶瓷晶粒饱满且晶界清晰,这表明实验所采用的工艺是合适的,并且晶粒生长状况良好。通过粒位分布计算(Nano Measurer)软件分析得到的晶粒尺寸分布呈现出正态分布的特征。逐渐增加的 Li_2CO_3 对晶粒生长起到一定程度的抑制作用。0Li、0.1Li、0.3Li 和 0.5Li 的平均晶粒尺寸分别为 $4.91\ \mu\text{m}$ 、 $4.23\ \mu\text{m}$ 、 $4.04\ \mu\text{m}$ 和 $3.91\ \mu\text{m}$ 。研究表明,晶粒尺寸的减小能够提高陶瓷的致密度,从而增强样品的耐电场击穿能力^[15]。铁酸铋材料的内部缺陷容易聚集在畴壁处,形成钉扎效应而制约电畴的移动,因此铁酸铋基陶瓷普遍存在高矫顽场的特点。压电性能的测试前提是电畴在电场作用下移动并重新取向,所需的极化电场高达 $4\ \text{kV}\cdot\text{mm}^{-1}$ 。该过程中需要陶瓷同时具备高的致密度和强的耐电场击穿能力,添加适量的 Li_2CO_3 无疑有利于极化过程,为陶瓷压电性能的优化提供了先决条件。

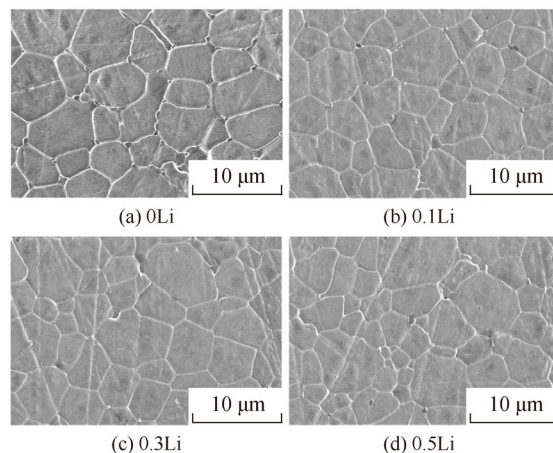


图 2 BFBTBNT- x Li 陶瓷样品的微观形貌图
Fig. 2 Microstructures of the BFBTBNT- x Li

2.3 BFBTBNT- x Li 陶瓷样品的铁电性能

电滞回线作为表征铁电材料特性的关键指标,揭示了材料在外电场影响下的极化响应。在设计传感器和致动器时,必须考虑材料的剩余极化和矫顽场,以确保在特定的电场条件下实现所需的极化状态。图 3a~图 3d 为不同测试场强下 BFBTBNT- x Li 材料的电滞回线,随着电场强度的提高,铁电畴逐渐趋向于与电场一致的方向。低电场强度下样品的

电滞回线并未饱和, 表现为样品的剩余极化强度和矫顽场均随电场强度的增强而显著增加。电滞回线为细长的闭合回线, 说明低电场强度下样品的铁电相特征不明显。当电场强度增加到 $60 \text{ kV} \cdot \text{cm}^{-1}$ 时, 样品的矫顽场随电场强度的进一步增加而变化不再显著, 同时观察到样品的极化强度随外加电场变化有明显的滞后现象, 此时电滞回线接近饱和, 样品具有明显的铁电相特征。图 3e 为 $65 \text{ kV} \cdot \text{cm}^{-1}$ 测试电

场下 BFBTBNT- $x\text{Li}$ 陶瓷的电滞回线。观察显示, Li_2CO_3 显著影响了陶瓷的极化程度。随着 Li_2CO_3 含量的增加, 陶瓷的剩余极化强度也随之增强, 并在 0.3Li 时达到峰值。然而, 受氧空位迁移势垒的影响, Li_2CO_3 含量的持续增加会引起氧空位的钉扎效应, 从而导致矫顽场不断增加(见图 3f)。因此, 添加适量的 Li_2CO_3 有助于提升极化程度并减小矫顽场。

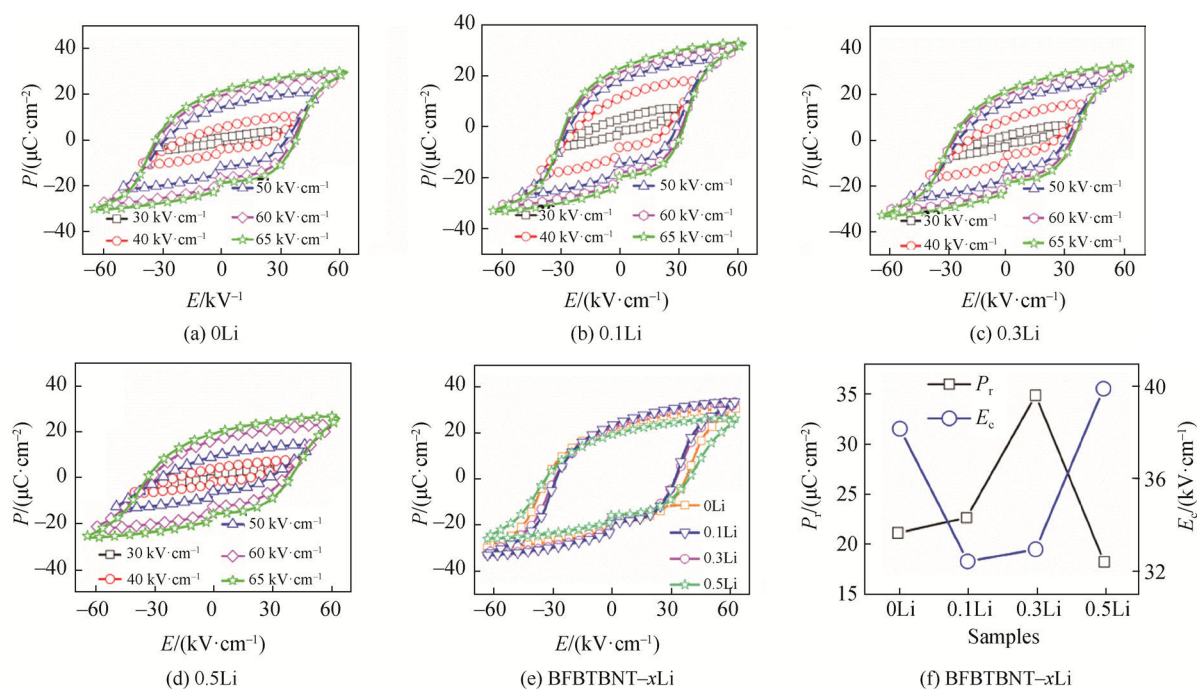


图 3 BFBTBNT- $x\text{Li}$ 陶瓷样品的电滞回线、剩余极化强度与矫顽场随 Li_2CO_3 含量的变化

Fig. 3 Ferroelectric hysteresis loops of BFBTBNT- $x\text{Li}$, residual polarization and coercive field of BFBTBNT- $x\text{Li}$

2.4 BFBTBNT- $x\text{Li}$ 陶瓷样品的绝缘性能

压电陶瓷的绝缘能力是其电气应用中安全性和稳定性的关键因素。良好的绝缘性能表明材料在面临电场时能维持高电阻, 抑制漏电现象, 有效预防电击风险和故障的发生。图 4a~图 4d 为陶瓷样品的复阻抗谱, 使用阻抗分析(Zview)软件对 $320 \sim 400^\circ\text{C}$ 温度区间的测试数据进行了科尔-科尔(Cole-Cole)图拟合。其中, 实线代表实测曲线; 点线代表拟合曲线。样品表现出半圆形复阻抗特征, 归因于晶粒尺寸和电导率的变化对复阻抗的高频响应。由于测试仪器的频率限制, 未能在低频条件下检测到晶界处的复阻抗。此外, 随着温度的升高, 陶瓷样品的电阻呈现下降趋势, 这符合半导体导电机理的特点。根据阿伦尼乌斯(Arrhenius)方程可计算样品的激活能, 由此侧面反映氧空位的变化趋势^[16], 如图 4e 所示。

$$\sigma_b = \frac{h}{s \times R} = \sigma_0 \exp\left(-\frac{E_a}{Tk_B}\right) \quad (1)$$

式中: σ_b 、 h 、 s 、 R 、 k_B 和 T 分别为电导率、样品的厚度、电极面积、电阻、玻尔兹曼常数和绝对温度。根据 Kang 等的研究, 激活能 E_a 在 0.5 eV 到 2.0 eV 之间可以归因为氧空位的影响^[17]。0Li、0.1Li、0.3Li 和 0.5Li 的激活能 E_a 分别为 1.196 、 1.218 、 1.251 eV 和 1.263 eV , 可见氧空位的迁移势垒受 Li_2CO_3 的影响变化较为显著。激活能的逐渐增强表明氧空位的迁移势垒逐渐增强, 材料中氧空位的迁移难度增大。由此可知, Li_2CO_3 增大了氧空位的迁移势垒, 可推测样品的氧空位含量随着 Li_2CO_3 添加量的增多而减少, 陶瓷的绝缘特性有所增强。图 4f 是测试电场为 $65 \text{ kV} \cdot \text{cm}^{-1}$ 时样品的 J - E 曲线。显然 0Li 具有较高的漏电流, 其数值为 $1.9755 \times 10^{-4} \text{ A} \cdot \text{cm}^{-2}$, 经 Li_2CO_3 改性后的 0.1Li、0.3Li 和 0.5Li 样品, 其漏电流得到改善。尤其是 0.5Li 的漏电流, 其数值大幅降低至 $6.1606 \times 10^{-6} \text{ A} \cdot \text{cm}^{-2}$, 相比 0Li 降低了 2 个数量级。

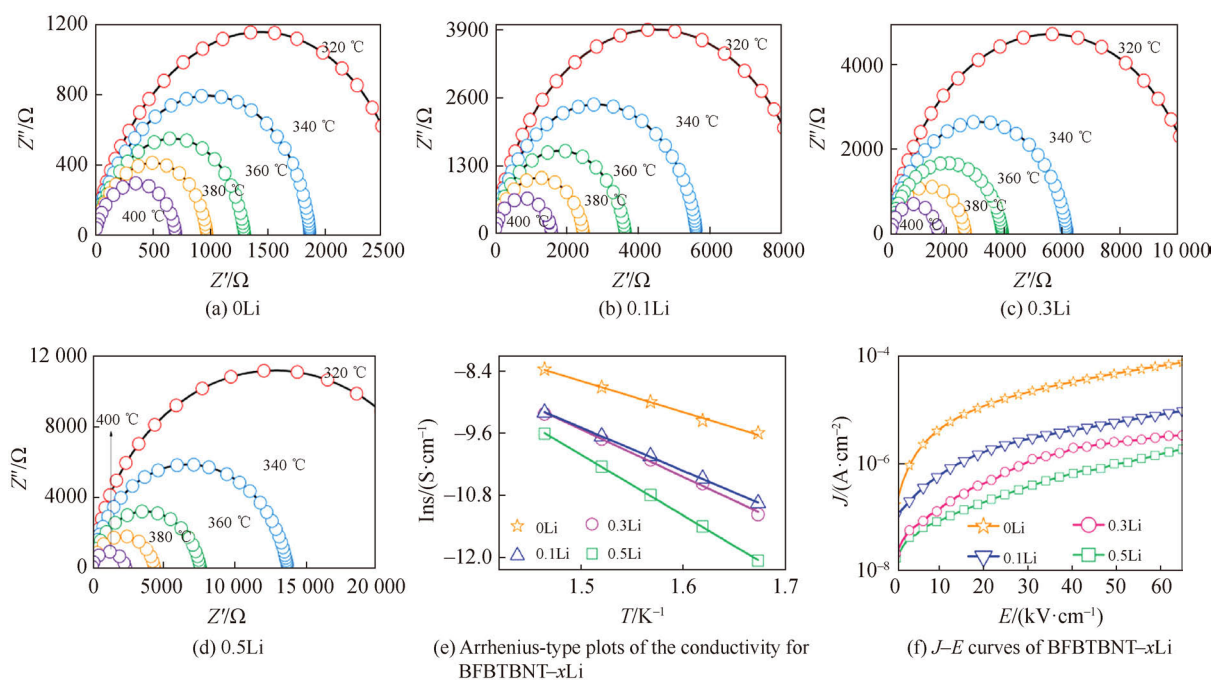


图4 BFBTBNT- x Li 陶瓷样品的复阻抗谱、Arrhenius 拟合导电率和 J - E 曲线
Fig. 4 Complex impedance plots, Arrhenius-type plots of conductivity and J - E curves of BFBTBNT- x Li

为了探明陶瓷样品中氧空位变化, 对其分别进行了 X-射线光电电子能谱和电子顺磁共振谱的分析, 如图 5 所示。O 的 1s 轨道电子通常在 525~535 eV 的范围内出现特征峰。将特征峰经峰值分析(Peakfit)软件拟合得到 3 个峰, 分别归属于晶格氧(529 eV 附近)、氧空位(531 eV 附近)和吸附氧(531 eV 附近)。由图 5a~图 5c 可以看出, 由于受到吸附氧的影响, 氧空位特征峰的积分面积随 Li_2CO_3 的增多变化甚微, 仅在 0.5Li 中观察到有略微的增大, 说明 Li_2CO_3 的添加有可能帮助提高氧空位的迁移势垒而抑制氧空位的形成。以上结果表明, XPS 对氧空位的表征具有一定的局限性, 需要采用更加有效的方法分析氧空位的变化。晶格中的氧原子缺失会留下 1 个未成对电子, 引发磁矩并在 EPR 谱中产生特征性信号, g 因子为 2.303 时, 对应为氧空位的特征信号。图 5d 中 0Li 表现出最高的峰强度, 随着 Li_2CO_3 的增多, 0.1Li 和 0.5Li 的峰强逐渐减弱, 进一步验证了样品中氧空位含量得到了抑制。

2.5 BFBTBNT- x Li 陶瓷样品的介电性能

陶瓷的介电性能是其关键属性, 对陶瓷在电子、电气和通信等领域的应用至关重要。这种性能主要由介电常数和介电损耗等参数决定, 它们体现了陶瓷对电场响应的特性。介电常数衡量陶瓷储存电荷的能力, 介电常数较高的陶瓷能存储更多电荷, 因

此, 常用于制作电容器。介电损耗则表示材料在交流电场中能量损失的程度, 低介电损耗的陶瓷在电子器件中更为理想, 因为它们运行时产生的热量较少, 有助于提高器件的效率和可靠性。Sun 等研究发现, 当 Li_2CO_3 掺杂量为 0.3%(摩尔分数)时, BiFeO_3 - BaTiO_3 - $\text{Bi}(\text{Zn}_{0.5}\text{Ti}_{0.5})\text{O}_3$ - $x\text{Li}_2\text{CO}_3$ 的居里温度(T_c)从 512 °C 升高至 554 °C^[18]。Guan 等探究了 Li_2CO_3 改性的 BiFeO_3 - BaTiO_3 陶瓷, Li_2CO_3 的引入不仅可在较宽的温度范围内呈现出多相特性, 还能一定程度提高样品的居里温度^[19]。图 6a~图 6b 为 BFBTBNT- x Li 陶瓷样品的介电温谱, 在 25~580 °C 范围内介电常数随着温度的升高呈先增大后降低的趋势, 仅呈现出 1 个介电峰, 此为陶瓷的铁电相与顺电相转变温度, 即居里温度。 Li_2CO_3 改性的陶瓷样品铁电相与顺电相转变温度略有升高, 0Li、0.1Li、0.3Li 和 0.5Li 的居里温度分别为 483、502、521 °C 和 535 °C, 与 Sun 和 Guan 的研究结果一致^[18, 19]。BFBTBNT- x Li 的介电损耗随着温度升高整体显著增大, 尤其是当温度超过 150 °C 以后, 缺陷载流子在电场作用下移动, 进一步增大了能量损耗。 Li_2CO_3 改性陶瓷样品的介电损耗明显降低, 尤其在高温环境中更为显著: 一方面致密度的增加降低了材料在交流电场中的能量损失; 另一方面, 缺陷载流子的减少降低了其在电场作用下移动而产生的热量, 陶瓷的介电性能得到优化。

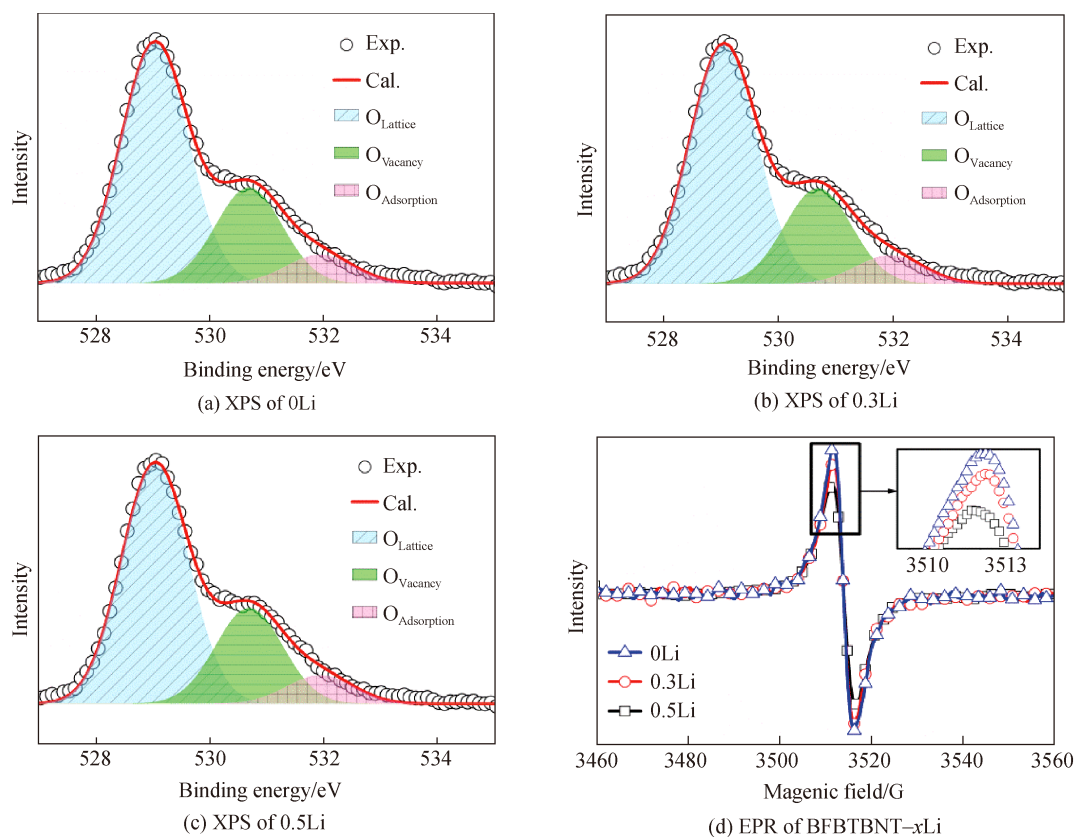


图 5 BFBTBNT-xLi 陶瓷样品的 XPS 谱和 EPR 谱
Fig. 5 XPS patterns and EPR patterns of the BFBTBNT-xLi

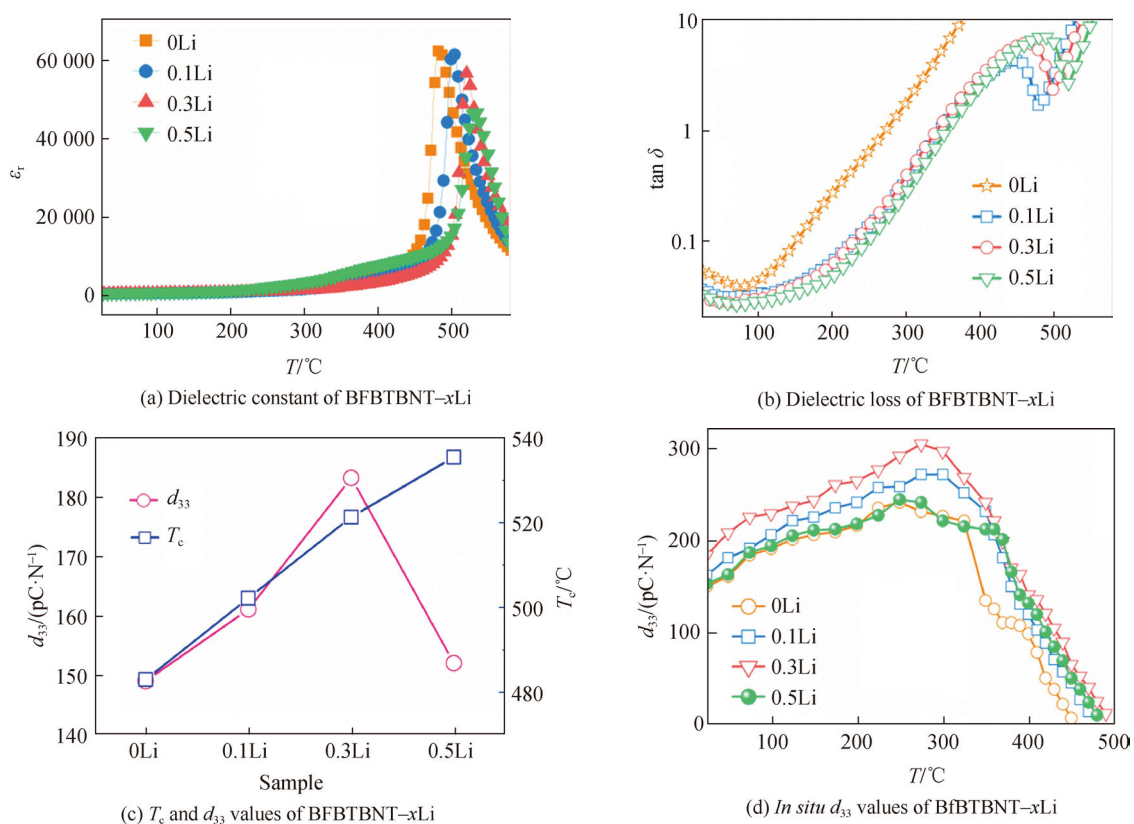


图 6 BFBTBNT-xLi 陶瓷样品的介电温谱、 d_{33} 值和原位 d_{33} 值
Fig. 6 Temperature dependence of ϵ_r and $\tan \delta$ of BFBTBNT-xLi, d_{33} values and *in situ* d_{33} values of BFBTBNT-xLi

2.6 BFBTBNT-*x*Li 陶瓷样品的压电性能及温度稳定特性

完成极化的样品静置 24 h 后, 置于压电测试仪测试其压电常数 d_{33} (见图 6c)。0Li、0.1Li、0.3Li 和 0.5Li 的 d_{33} 值分别为 149、161、183、152 $\text{pC}\cdot\text{N}^{-1}$, 其变化趋势与剩余极化强度一致。0.3Li 样品展现出最高的压电常数, 这是由于该样品的剩余极化强度较高, 且其氧空位迁移势垒较高, 导致氧空位含量和漏电流均较低。除此之外, Li_2CO_3 引起的晶粒细化增强了陶瓷的耐电场击穿能力, 因此, 样品能够更充分地极化, 从而展现出最佳的压电性能。高温压电陶瓷需满足在高温条件下仍有较强的压电响应, 为此, 对极化后的样品进行原位 d_{33} 测试以评估其温度稳定特性, 如图 6d 所示。随着温度的不断升高, 陶瓷的介电常数逐渐增大, 因此压电常数随之升高。当环境温度提高至退极化温度时, 样品的 d_{33} 值呈现大幅度降低趋势。经过 Li_2CO_3 改性的陶瓷展现了较高的温度稳定性, 0Li、0.1Li、0.3Li 和 0.5Li 样品的退极化温度 T_d 分别为 350、370、380 $^{\circ}\text{C}$ 和 390 $^{\circ}\text{C}$, 这表明 BFBTBNT-*x*Li 陶瓷有望应用在高温领域。

3 结论

采用传统陶瓷烧结工艺制备化学组成为 $0.99(0.7\text{BiFeO}_3-0.3\text{BaTiO}_3)-0.01\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3-x\text{Li}_2\text{CO}_3$ 的压电陶瓷。随着 Li_2CO_3 的增加, 陶瓷由 *R* 相逐渐演变为 *PC* 相结构, 0.3Li 表现出明显的 *R-PC* 共存相特征, BFBTBNT-*x*Li 的 *R* 相含量由 78.02% 降低至 18.76%, *PC* 相含量则由 21.98% 增大至 81.24%。 Li_2CO_3 在一定程度上抑制了晶粒生长, 有利于提高致密度而增强陶瓷的耐电场击穿能力。 Li_2CO_3 掺杂的 BFBTBNT-*x*Li 陶瓷中观察到了居里温度的升高现象, 同时样品的介电损耗明显降低, 尤其在高温环境中更为显著。陶瓷的剩余极化强度随 Li_2CO_3 含量的增加而逐渐增大, 在 0.3Li 到达最高值, 随后由于矫顽场持续增大, 故而极化强度开始减弱。陶瓷的氧空位迁移势垒随着 Li_2CO_3 的增多逐渐提高, 从而使氧空位含量得到抑制, 因此, 绝缘性能逐渐增强。0.3Li 的压电常数为 183 $\text{pC}\cdot\text{N}^{-1}$, 退极化温度高达 380 $^{\circ}\text{C}$, 有望应用于高温压电领域。

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范永涛: 数据管理

翟继卫: 审阅与修订

Phase Structures Regulation and High-Temperature Piezoelectric Performances Optimization of BiFeO_3 -Based Ceramics

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Extended Abstract

Introduction In this paper, $0.99(0.7\text{BiFeO}_3-0.3\text{BaTiO}_3)-0.01\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3-x\text{Li}_2\text{CO}_3$ (*i.e.*, $x = 0, 0.001, 0.003, 0.005$; abbreviated as 0Li, 0.1Li, 0.3Li, 0.5Li, BFBTBN $\text{T}-x\text{Li}$) ceramics were prepared by a conventional sintering technique. The ceramics gradually changed from the *R* phase to *PC* phase structures, and the ceramic with 0.3Li showed obvious coexistences of *R* and *PC* phases as the addition of Li_2CO_3 increases. The Curie temperature of Li_2CO_3 -doped BFBTBN $\text{T}-x\text{Li}$ ceramics increases from 483 °C to 535 °C, and the dielectric loss of the samples decreased. The remanent polarization of the ceramics increased with increasing the Li_2CO_3 addition, reaching the maximum value at 0.3Li. Subsequently, the polarization decreased due to the increased coercive field. Li_2CO_3 could enhance the insulation of the ceramics because of the enhanced migration barrier of oxygen vacancies. The ceramic with 0.3Li could be obtained with an optimal piezoelectric constant of $183 \text{ pC}\cdot\text{N}^{-1}$ and a high depolarization temperature of 380 °C. This material displayed a great potential in high-temperature piezoelectric application.

Methods The $0.99(0.7\text{BiFeO}_3-0.3\text{BaTiO}_3)-0.01\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3-x\text{Li}_2\text{CO}_3 + 1\% \text{MnO}_2$ ($x = 0, 0.001, 0.003, 0.005$; abbreviated as 0Li, 0.1Li, 0.3Li, 0.5Li, BFBTBN $\text{T}-x\text{Li}$) ceramics were prepared by a conventional sintering process. The raw materials were weighed according to the stoichiometric ratio and ground for 12 h. After grinding, the ground raw materials were firstly sintered at 720 °C for 5 h, and then the mixtures with MnO_2 were further ground for 12 h. After granulating and pressing, the samples were heated at 600 °C for 10 h. Afterwards, the samples were heated at 1000 °C for 3 h.

The phase structure of the ceramics was analyzed by X-ray diffraction (XRD, Bruker Co., Germany). The microstructures of the ceramics were determined by scanning electron microscopy (SEM, JSM Co., Japan). In order to test the electrical properties of the BFBTBN $\text{T}-x\text{Li}$ ceramics, the silver paste was coated on the surface of the samples and fired at 800 °C for 10 min to form silver electrodes. Afterwards, the dielectric constant and loss as a function of temperature and impedance spectroscopy was determined by impedance analysis (Agilent E4980A). The ferroelectric performance and *J-E* curves was measured by ferroelectric analysis (Precision Premier II, Radiant Co., USA). The chemical binding state of O was tested by X-ray photoelectron spectroscopy (XPS, PHI Co., USA). The electron paramagnetic resonance measurements were performed by the EPR spectroscopy (EPR, Bruker Co., Germany). The d_{33} values at room temperature were measured by a quasi-static piezoelectric constant apparatus (ZJ-3A, China). The *in-situ* d_{33} values were collected by a quasi-static d_{33} apparatus (YE2730A, Sinocera Co., China).

Results and discussion The content of the *R* phase continuously decreased with increasing Li_2CO_3 addition, especially in the sample with 0.3Li. The content of the *R* phase reduced to 36.28%, which was the MPB. The content of the *R* phase in the sample with 0.5Li further decreased to 18.76%, while the content of the *PC* phase increased to 81.24%, indicating that the sample is mainly composed of the *PC* phase. The microstructure showed that the surface of the sample was smooth without obvious holes, and the ceramic grains were full and the grain boundaries were clear. The addition of Li_2CO_3 could refine the grains, which was beneficial to improving the toughness against breakdown. The Curie temperatures (T_C) of the samples with 0Li, 0.1Li, 0.3Li and 0.5Li were 483, 502, 521 °C and 535 °C, respectively. The dielectric loss of the BFBTBN $\text{T}-x\text{Li}$ showed a significant increase with increasing temperature, especially when the temperature exceeded 150 °C. The dielectric loss of the ceramic samples modified by Li_2CO_3 was significantly reduced, especially more significantly in the high-temperature environment. The residual polarization of the ceramics with the addition of Li_2CO_3 increased, reaching a peak value for the ceramic with 0.3Li. The samples exhibited semi-circular complex impedance characteristics, and the resistance of the ceramics decreased with increasing temperature, which was in line with the characteristics of the semiconductor conduction mechanism. The activation energies (E_a) of the ceramics with 0Li, 0.1Li, 0.3Li and 0.5Li were 1.196, 1.218, 1.251 eV and 1.263 eV, respectively. The oxygen vacancies were inhibited with the gradual addition of

Li_2CO_3 , thereby enhancing the insulating properties of the ceramics. The leakage current of the samples with 0.1Li, 0.3Li and 0.5Li modified by Li_2CO_3 was improved; especially the leakage current of the sample with 0.5Li reduces to $10^{-6} \text{ A}\cdot\text{cm}^{-2}$, which was reduced by two orders of magnitude. The d_{33} values of the ceramics with 0Li, 0.1Li, 0.3Li and 0.5Li were 149, 161, 183 $\text{pC}\cdot\text{N}^{-1}$ and 152 $\text{pC}\cdot\text{N}^{-1}$, respectively, showing a consistent with the residual polarization. The ceramic with 0.3Li exhibited the maximum piezoelectric constant because of the higher residual polarization, fewer oxygen vacancies and leakage current, thus enabling a more complete polarization and demonstrating the optimum piezoelectric performance. The ceramics modified by Li_2CO_3 showed a high-temperature stability, and the de-polarization temperatures (T_d) of the ceramics with 0Li, 0.1Li, 0.3Li and 0.5Li were 350, 370, 380 $^{\circ}\text{C}$ and 390 $^{\circ}\text{C}$, respectively.

Conclusions The 0.99(0.7BiFeO₃–0.3BaTiO₃)–0.01Bi_{0.5}Na_{0.5}TiO₃– $x\text{Li}_2\text{CO}_3$ ($x = 0, 0.001, 0.003, 0.005$; abbreviated as 0Li, 0.1Li, 0.3Li, 0.5Li) ceramics were prepared by a conventional sintering process. The ceramics gradually changed from the *R* to *PC* phase structure as the addition of Li_2CO_3 increased. The ceramic with 0.3Li showed obvious coexistences of the *R* and *PC* phases. The content of *R* phase in the ceramics BFBTBNT– $x\text{Li}$ decreased from 78.02% to 18.76%, while the content of *PC* phase increased from 21.98% to 81.24%. The addition of Li_2CO_3 could refine the grains, which was beneficial to improving the toughness against breakdown. The Curie temperature increased in the ceramics BFBTBNT– $x\text{Li}$ doped with Li_2CO_3 , and the dielectric loss of the ceramics was significantly reduced, especially at high temperatures. The remanent polarization of the ceramics increased gradually with increasing the Li_2CO_3 addition, reaching the maximum value for the ceramic with 0.3Li. The oxygen vacancies in the ceramics were suppressed as the Li_2CO_3 addition increased, thus enhancing the insulation performances. The piezoelectric constant of the ceramic with 0.3Li was 183 $\text{pC}\cdot\text{N}^{-1}$, and the depolarization temperature was as high as 380 $^{\circ}\text{C}$, which could be promising for high-temperature piezoelectric applications.

Keywords bismuth ferrite; piezoelectric ceramics; lithium carbonate; temperature stability