

用于多层陶瓷电容器的抗还原 BaTiO_3 基介质陶瓷王 震^{1,2}, 郝 华^{1,2}, 蒋松松^{1,2}, 张 洁², 曹明贺², 尧中华^{1,2}, 甘小燕^{1,2}, 刘韩星^{1,2}

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摘 要: 电子工业发展使多层陶瓷电容器的需求大增, 为降低成本, 适用于贱金属电极的介质陶瓷成为研究热点。选择 MnO_2 掺杂 $0.95\text{BaTiO}_3-0.05\text{BiCoO}_3$ 陶瓷, 经调整掺杂比例, 其抗还原与介电性能大幅提升。结果表明: 还原气氛下 Mn 离子变价使晶胞体积膨胀, 形成不均匀结构使 Curie 峰分裂并展宽, 介温稳定性提高, $x=0.5$ 时性能最佳, $\epsilon(25^\circ\text{C})=2354$, $\tan\delta=0.0075$, 稳定性符合 X8R。同时, 元素变价的过程有助于降低电子浓度, 电阻率提高至 $1.84\times 10^{13}\ \Omega\cdot\text{cm}$, 最大耐压达到 210 kV/cm。热激励退化漏电流测试表明 Co、Mn 结合氧空位形成缺陷偶极, 进一步增强抗还原性能。

关键词: 多层陶瓷电容器; 钛酸钡; 电阻率; 缺陷偶极子; 介电性能

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多层陶瓷电容器 (MLCC) 是由陶瓷介质和内电极交替堆叠并在高温下烧结而成的层状结构, 因其容量大、介电温度稳定性好和击穿强度高而成为最有前景的介质电容器^[1-4]。为适应 MLCC 高容量和小型化的发展趋势, 应减小介质层的厚度, 同时增加电极的比例。传统的 MLCC 采用昂贵的银钯金属作为内电极材料, 近几年出于节约成本的考虑, 人们开始采用镍或铜等贱金属作为新的内电极, 但需要在还原气氛中与介质层共烧^[5-7]。

BaTiO_3 陶瓷因其介电常数高、介电损耗低、绝缘性能优异而成为 MLCC 主要的介质材料^[8-10]。 BaTiO_3 陶瓷在还原气氛下进行烧结时, 将生成众多氧空位及自由电子, 促使 Ti^{4+} 向 Ti^{3+} 发生转变, 陶瓷出现半导化^[11-12]。同时, BaTiO_3 陶瓷的尖锐介电峰值出现在高温端 (125°C), 导致其温度稳定性较差。随着贱金属电极多层陶瓷电容器行业的不断发展, 对兼具出色抗还原特性与良好介电温度稳定性的介电材料的需求与日俱增。

近年来, 人们对 $\text{BaTiO}_3-\text{Bi}(\text{Me})\text{O}_3$ ($\text{Me}=\text{Fe}^{3+}$ 、

Co^{3+} 、 Y^{3+} 等) 固溶体的弛豫特性和介电性能进行了广泛的研究, 通过引入不同半径和价态的阳离子来共同取代 A 和 B 位, 会破坏长程铁电有序性, 引起扩散相变, 并使介电温度曲线变宽^[13-17]。另一方面, 为了提高 BaTiO_3 基陶瓷的抗还原性能, 通常采用等价掺杂、受主掺杂、施主掺杂和施主-受主共掺杂等方法来捕获自由电子、减少电荷载流子的浓度并增加氧离子溢出的能垒。例如, 较大半径的等价离子 (如 Zr^{4+}) 取代 Ti^{4+} 位, 会增加氧从晶格中逸出的能垒, 从而改善陶瓷的抗还原性能。少量的稀土离子 (如 Sm^{3+}) 掺杂会导致 BaTiO_3 基陶瓷的半导化, 但通过增加掺杂量可以改善其绝缘性能^[18-21]。此外, Zn^{2+} 、 Mg^{2+} 、 Mn^{4+} 、 Co^{3+} 作为受主掺杂剂被掺入到 BaTiO_3 基陶瓷中, 与氧空位形成缺陷偶极子, 束缚自由电荷的移动。其中, 多价态离子可以结合电子来改变价态调整陶瓷内的电子浓度, 降低 Ti^{4+} 转化为 Ti^{3+} 的可能性^[22-25]。

以 $0.95\text{BaTiO}_3-0.05\text{BiCoO}_3$ 介电陶瓷为基体, 选

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择 0.1%、0.2%、0.3% 和 0.4% (质量分数) 的 MnO₂ 对其进行掺杂改性, 缩写为 0.95BT-0.05BC-*x*%Mn (*x*=0.1、0.2、0.3、0.4、0.5), 并在还原气氛中烧结。对其物相结构、显微形貌、介电性能和抗还原性能进行了表征, 并研究了其抗还原的内在机制。

1 实验

1.1 样品制备

通过固相法制备 0.95BaTiO₃-0.05BiCoO₃ 基体, 在其基础上掺杂 *x*% (质量分数) MnO₂ (*x*=0.1, 0.2, 0.3, 0.4 和 0.5) 陶瓷。以钛酸钡(BaTiO₃, 国药集团, 99.99%, 质量分数, 下同), 三氧化二钴(Co₂O₃, 国药集团, 99%), 三氧化二铋(Bi₂O₃, 国药集团, 99.8%) 为原料, 根据化学配比进行称量配料, 由于 Bi₂O₃ 在高温烧结时会部分挥发, 为补偿其挥发需添加过量 5%。以无水乙醇作为溶剂进行球磨, 球磨时间为 6 h。将球磨后的浆料放入 100 °C 的鼓风干燥箱中烘干 24 h, 随后在空气中 900 °C 预烧 2 h 以得到陶瓷的主相。在预烧后的粉末中按计算的质量比加入二氧化锰(MnO₂, 国药集团, 98.8%) 配料, 进行二次球磨后烘干, 采用质量分数 5% PVA 作为粘结剂按 2 滴/g 加到粉体中, 研磨并过 150 μm 筛网。将造粒后的粉末在 150~200 MPa 压力下压制成直径为 12 mm 的陶瓷圆片, 在空气中 600 °C 保温 2 h 以排出 PVA, 然后在还原气氛 (99.5% N₂+0.5% H₂, 体积分数) 条件下, 1275 °C 保温 2 h, 得到致密的陶瓷样品。最后把陶瓷样品在砂纸上减薄抛光, 在陶瓷片两面涂覆上银浆电极, 在马弗炉中 580 °C 保温 10~15 min, 用于电性能测量。

1.2 样品表征

利用荷兰 PANalytical X'Pert Pro 型 X 射线衍射仪(XRD)分析样品的物相结构。利用美国 FEI Quanta 450 FEG 型场发射扫描电镜(SEM)拍摄样品断面的微观形貌。利用美国 PolyK PK-CPT1705 型低温介电测试仪测试样品的介电性能。利用德国 Novocontrol Concept 80 的频模块测试陶瓷的绝缘电阻率。利用美国 PolyK PK-CPE1801 型铁电极化回线和介电击穿测试系统测试样品的铁电性能。利用美国 ESCALAB 250Xi 型 X 射线光电子能谱仪(XPS)对元素价态进行分析。利用德国 Novocontrol Concept 80 的热激励退极化漏电流模块(TSDC)对陶瓷进行热激励退极化漏电流测试。

2 结果与讨论

2.1 物相结构分析

所有组分的陶瓷样品在 10°~80° 的范围内的 XRD 谱如图 1 所示。在 *x*=0.1~0.5 的的掺杂范围内, 所有陶瓷样品为赝立方钙钛矿结构, 没有明显的第二相, 说明 MnO₂ 掺杂进入了晶格。此外, 从 44°~46° 的 XRD 放大谱可以看出, 随着 MnO₂ 掺杂量的增加, (200)峰向低角度偏移。根据 Bragg 方程 $2d\sin\theta=n\lambda$, 衍射峰向低角度偏移表明陶瓷的晶面间距增大。这是由于 Mn⁴⁺(0.053 0 nm, 配位数为 6)、Mn³⁺(0.064 5 nm, 配位数为 6)和 Mn²⁺(0.083 0 nm, 配位数为 6)的离子半径与 Ti⁴⁺(0.060 5 nm, 配位数为 6)相近, 更容易取代 Ti⁴⁺ 而不是 Ba²⁺(0.161 0 nm, 配位数为 12), Mn⁴⁺在还原气氛下烧结时被还原为 Mn³⁺或 Mn²⁺, Mn³⁺和 Mn²⁺的离子半径都大于 Ti⁴⁺的离子半径, 导致陶瓷发生晶格畸变, 晶胞体积增大^[23, 26]。

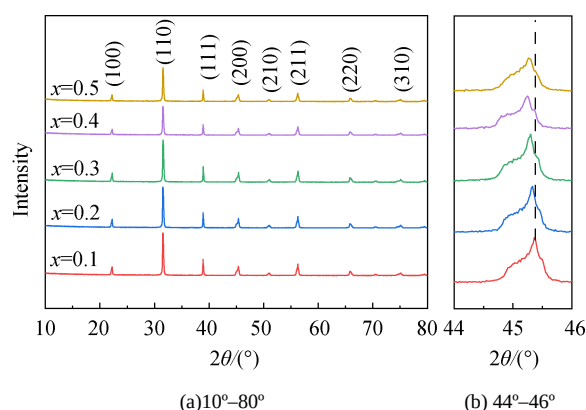


图 1 0.95BT-0.05BC-*x*%Mn 陶瓷的 XRD 谱
Fig. 1 XRD patterns of 0.95BT-0.05BC-*x*%Mn ceramics

2.2 显微形貌分析

图 2 为 0.95BT-0.05BC-*x*%Mn 陶瓷断面的 SEM 照片。由图 2 可见, 所有样品均显示出高结晶度, 没有第二相。所有样品断面的晶粒排列紧密, 随 Mn 掺杂量不断增多, 大晶粒逐渐消失, 小晶粒增多, 晶粒尺寸分布更加均匀。当 Mn 进入晶格时会引起晶格畸变或形成不均匀结构, 阻碍晶界的迁移, 使陶瓷具有较细的晶粒尺寸^[4]。晶界的占比增加可以限制氧空位在晶界之间的传输, 有助于提升陶瓷的抗还原性能^[27]。

2.3 介电性能分析

还原气氛下烧结的所有陶瓷样品的室温介电性能如表 1 所示。多种价态的 Mn 占据 Ti 的位置导致

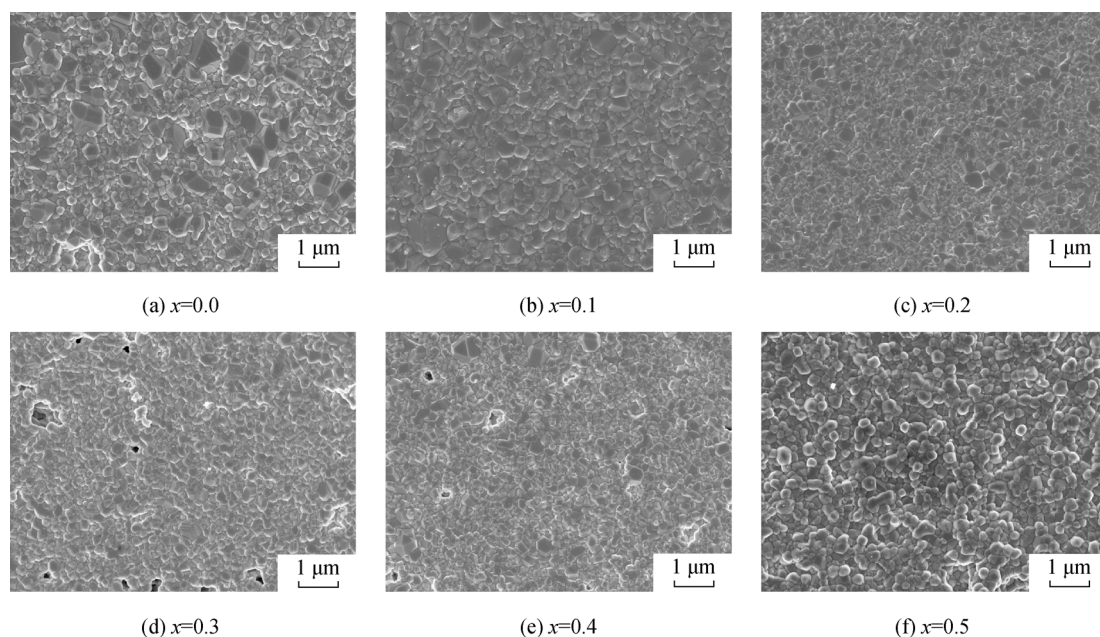


图2 0.95BT-0.05BC- x %Mn 陶瓷的显微形貌
Fig. 2 SEM images of 0.95BT-0.05BC- x %Mn ceramics

表1 0.95BT-0.05BC- x %Mn 陶瓷 1 kHz 的介电性能
Table 1 Dielectric properties of 0.95BT-0.05BC- x %Mn ceramics at 1 kHz

x value	$\varepsilon(25\text{ }^{\circ}\text{C})$	$\tan\delta(25\text{ }^{\circ}\text{C})$	$\Delta C/C(25\text{ }^{\circ}\text{C}) \leq \pm 15\%$
$x=0.1$	2688	0.022 0	$-1\text{ }^{\circ}\text{C}$ to $87\text{ }^{\circ}\text{C}$
$x=0.2$	2510	0.007 4	$-23\text{ }^{\circ}\text{C}$ to $73\text{ }^{\circ}\text{C}$
$x=0.3$	2565	0.007 5	$-32\text{ }^{\circ}\text{C}$ to $70\text{ }^{\circ}\text{C}$
$x=0.4$	2526	0.008 3	$-36\text{ }^{\circ}\text{C}$ to $73\text{ }^{\circ}\text{C}$
$x=0.5$	2354	0.007 5	$-55\text{ }^{\circ}\text{C}$ to $154\text{ }^{\circ}\text{C}$

晶格畸变,同时被捕获的电子被限制在 Mn 离子周围,难以自由移动参与极化过程,从而导致材料的极化程度减弱,介电常数从 2688 降低至 2354,介电损耗由 0.022 0 降低为 0.007 5。陶瓷的介电常数和介电损耗随温度的变化曲线如图 3 所示。当掺杂含量较低时,125 $^{\circ}\text{C}$ 左右的居里峰强度高且尖锐,随 Mn 掺杂量的增加,明显观察到居里峰向低温移动,强度也出现了明显地下降,这与 Mn 取代 Ti 位有关。当 $x \geq 0.3$ 时居里峰分裂成 2 个峰,峰 1 为 BaTiO₃ 的居里峰,峰 2 是由于 Mn 掺杂后陶瓷内部形成非均匀的结构导致^[18]。在 $x=0.2 \sim 0.4$ 过程中介电常数值保持在 2500 左右,差距不明显,这是因为峰 2 此时并没有影响到室温的介电性能。当 $x=0.5$ 时,居里峰进一步被压低展宽,峰 2 向低温方向扩展,导致室温介电常数的下降,陶瓷的介电温度稳定性提升,在 $-55 \sim 154\text{ }^{\circ}\text{C}$ 温度范围内 $\Delta C/C(25\text{ }^{\circ}\text{C}) \leq$

$\pm 15\%$,符合 X8R 标准。

2.4 抗还原性能分析

还原气氛下烧结的所有陶瓷样品的室温电阻率如图 4 所示。在还原气氛下烧结时, BaTiO₃ 陶瓷中会产生氧空位并电离出自由电子导致陶瓷电阻率下降。当 Mn 掺杂量较低时($x=0.1$),陶瓷的室温电阻率为 $3.32 \times 10^{11} \Omega \cdot \text{cm}$,随 Mn 掺杂量增多电阻率不断增大,当 $x=0.5$ 时,绝缘电阻率增加到 $1.84 \times 10^{13} \Omega \cdot \text{cm}$ 。陶瓷内的 Co 和 Mn 都是变价元素,在还原气氛下烧结时能够俘获自由电子发生变价,有效地抑制自由电子浓度,抗还原性能提高。

为进一步验证 Mn 掺杂后陶瓷的抗还原性能提升,将 0.95BT-0.05BC- x %Mn 陶瓷在 1 kHz 的流电场下测试其电滞回线,持续提高测试电压直至样品被击穿,最高电压下的电滞回线如图 5 所示。由图 5 可见,随着 Mn 含量的增加,0.95BT-0.05BC- x %Mn 陶瓷的 $P-E$ 曲线逐渐细化。当 $x=0.1$ 时,最大耐压强度 E 为 70 kV/cm。随着 Mn 掺杂量的增加,耐压强度 E 整体呈上升趋势,当 $x=0.5$ 时,最大耐压强度 $E=210\text{ kV/cm}$,0.95BT-0.05BC-0.5%Mn 陶瓷具有良好的抗还原性能。

2.5 抗还原机理分析

变价离子通常可以俘获陶瓷内的自由电子并发生变价,如 $\text{Mn}^{4+} \rightarrow \text{Mn}^{3+} \rightarrow \text{Mn}^{2+}$ 或 $\text{Co}^{3+} \rightarrow \text{Co}^{2+}$,降低自由电子浓度,从而提高陶瓷的绝缘性。

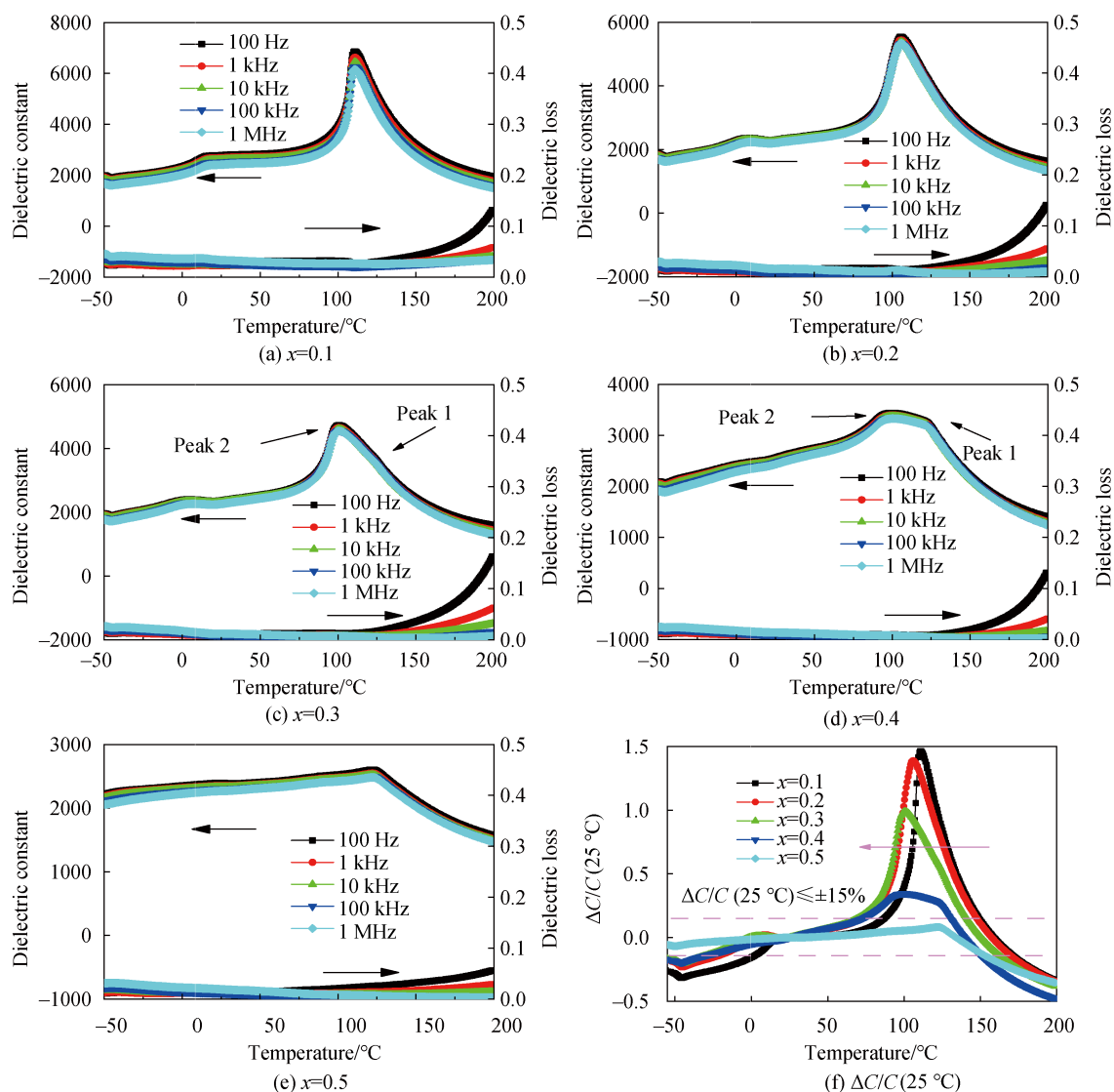


图 3 0.95BT-0.05BC- x %Mn 陶瓷在不同温度下的介电性能
Fig. 3 Dielectric properties of 0.95BT-0.05BC- x %Mn ceramics at different temperatures

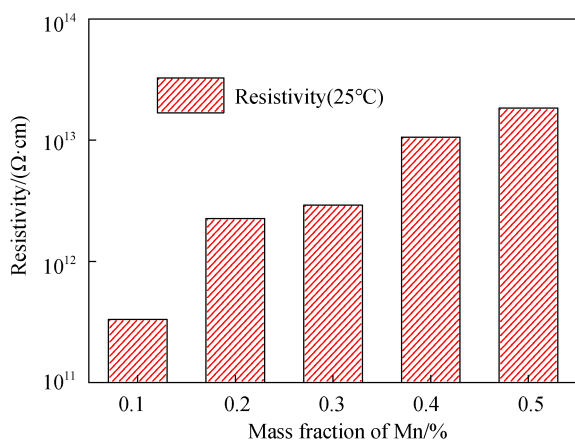


图 4 0.95BT-0.05BC- x %Mn 陶瓷的电阻率
Fig. 4 Resistivity of 0.95BT-0.05BC- x %Mn ceramics

对还原气氛烧结的 0.95BT-0.05BC-0.5%Mn 陶瓷进行 XPS 测试, 由于本工作中 Mn 掺杂量较低, XPS 无法探测到明显信号, 故仅对 Co 离子在还原气氛下烧结价态变化情况进行分析, Co 2p 的 XPS 谱如图 6 所示。从图 6 可以观察到 2 个峰劈裂明显, 表明样品中存在多种价态的 Co 离子。对 Co 2p 的 XPS 谱拟合分峰, 可以分为 4 个峰, Co 2p_{1/2} 和 Co 2p_{3/2} 分别位于 779.6 eV 和 794.9 eV 的峰代表着处于低价态的 Co²⁺, 位于 782.3 eV 和 797.5 eV 处的较高结合能则代表高价态的 Co³⁺[28-29]。XPS 结果表明, 还原气氛下烧结的陶瓷样品中的 Co 有 2 种价态存在, 这表明有部分 Co³⁺被还原成 +2 价, 有效抑制了电子浓度的增加, 提高了抗还原性能。

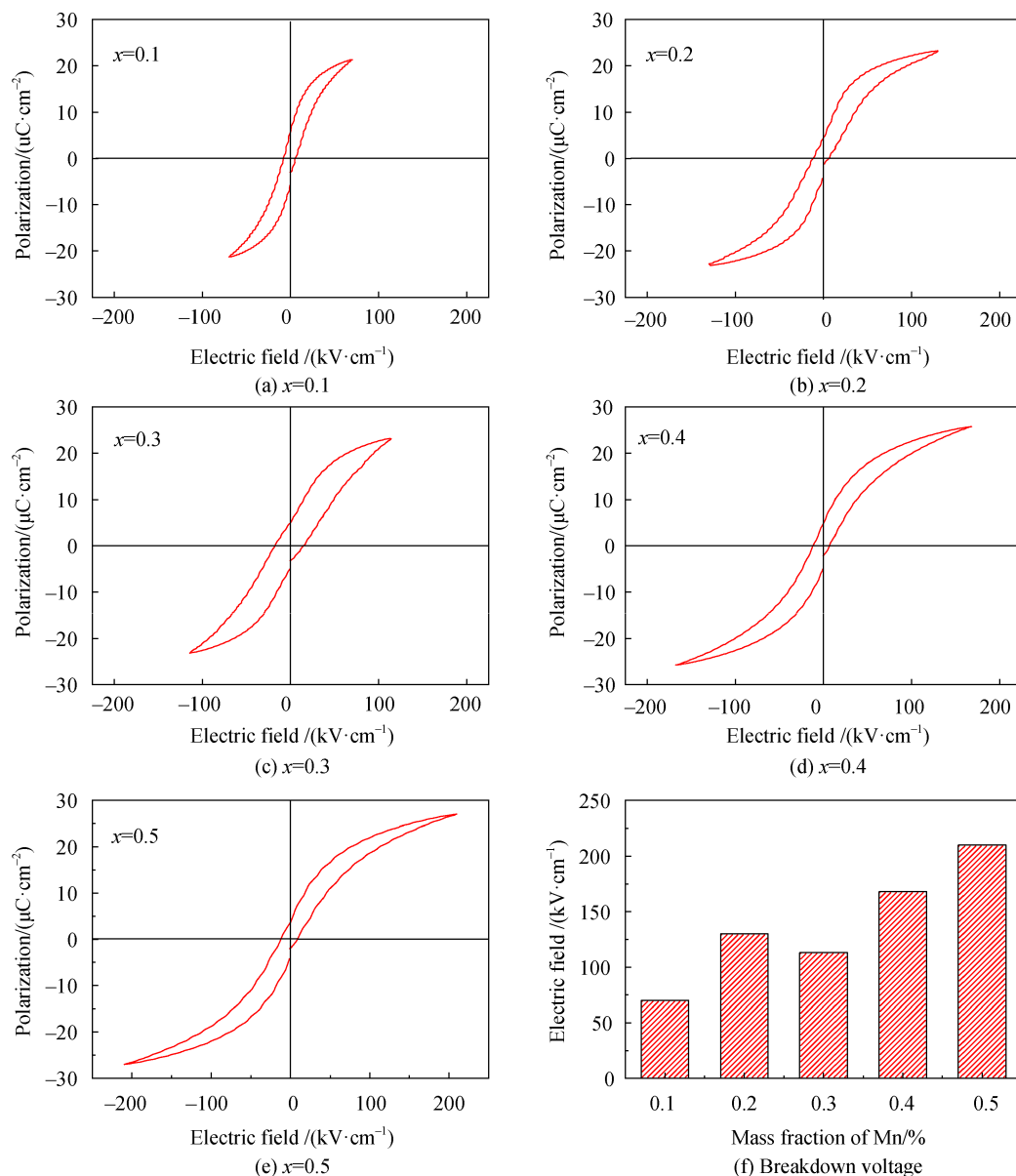


图5 0.95BT-0.05BC- x %Mn 陶瓷在 1 kHz 下的电滞回线和击穿电压
Fig. 5 P - E loops and breakdown voltage of 0.95BT-0.05BC- x %Mn ceramics at 1 kHz

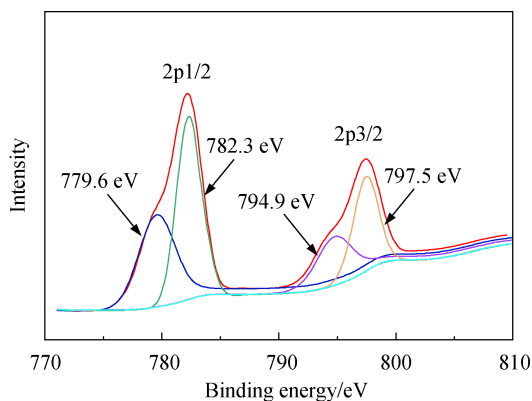


图6 0.95BT-0.05BC-0.5%Mn 陶瓷 Co 2p 的 XPS 谱
Fig. 6 XPS spectra of Co 2p for 0.95BT-0.05BC-0.5%Mn ceramic

热激励去极化漏电流测试可以确定陶瓷内部的缺陷结构^[30-32]。将 0.95BT-0.05BC-0.5%Mn 陶瓷分别在 0.4、0.6、0.8 kV/mm 和 1.0 kV/mm 电压下对样品进行极化，急速冷却后测试其升温过程的电流。测试结果如图 7 所示，在整个测试的温度范围中，可以观察到 3 个电流峰。其中，峰 1 随着极化电场的增大向低温方向移动，结果表明在 0.95BT-0.05BC-0.5%Mn 陶瓷内部存在被俘获电荷，这与变价受主离子 Co 和 Mn 的价态变化相关。峰 2 和峰 3 的峰位不随电场的增强而发生偏移，表明在陶瓷内部存在 2 种缺陷偶极子，Co 和 Mn 在作为受主取代的同时产生氧空位，这 2 个电流峰的出现可能是因

为 Co 和 Mn 与氧空位形成的缺陷偶极子 $[\text{Mn}_{\text{Ti}}^{\bullet} - \text{V}_{\text{O}}^{\bullet}]$ 和 $[2\text{Co}_{\text{Ti}}^{\bullet} - \text{V}_{\text{O}}^{\bullet}]$ 。缺陷偶极子的存在, 有效降低了陶

瓷的载流子浓度, 阻碍了氧空位和自由电子的迁移, 进一步提高了陶瓷的抗还原性能。

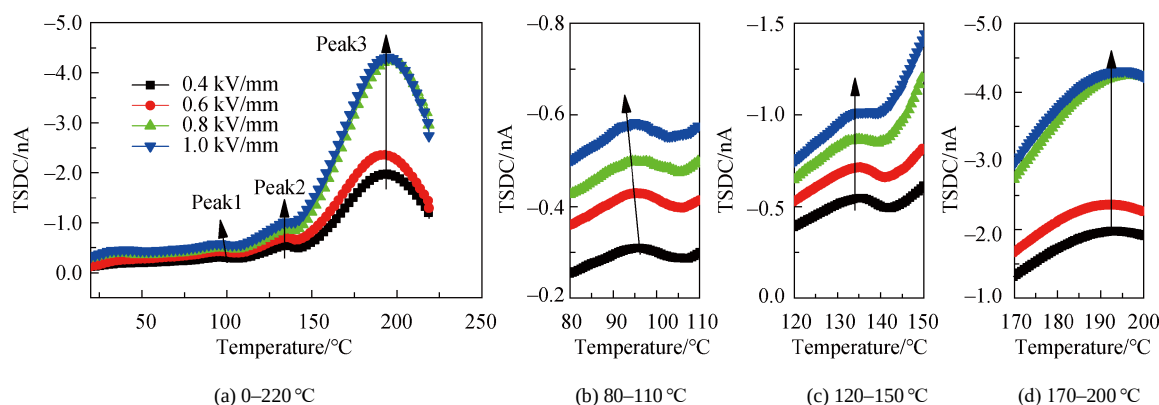


图 7 0.95BT-0.05BC-0.5%Mn 陶瓷的 TSDC 图谱

Fig. 7 Thermally stimulated depolarization current (TSDC) spectra for 0.95BT-0.05BC-0.5%Mn ceramic

3 结论

通过固相法合成的 0.95BT-0.05BC- $x\%$ Mn ($x=0.1, 0.2, 0.3, 0.4$ 和 0.5) 陶瓷, 探究了 MnO₂ 掺杂对 0.95BT-0.05BC 陶瓷的物相结构, 显微形貌, 介电性能和抗还原性能的影响。XRD 表明, 还原气氛下烧结的 Mn⁴⁺变为离子半径更大的 Mn³⁺或 Mn²⁺引起晶胞体积膨胀。Mn 掺杂可以有效压低展宽居里峰, 改善了 0.95BT-0.05BC 陶瓷的介电温度稳定性。当 $x=0.5$ 时, 得到 $\varepsilon(25\text{ }^{\circ}\text{C})=2354$, $\tan\delta=0.0075$, 在 $-55\sim 154\text{ }^{\circ}\text{C}$ 范围内 $\Delta C/C(25\text{ }^{\circ}\text{C})\leq\pm 15\%$, 符合 X8R 标准。陶瓷的抗还原性能提高, 室温电阻率增大至 $1.84\times 10^{13}\text{ }\Omega\cdot\text{cm}$, 最大耐压强度提高至 210 kV/cm 。XPS 测试表明陶瓷中存在 2 价和 3 价的 Co 离子, Co 离子可以俘获自由电子使价态降低。TSDC 测试发现存在 2 种缺陷偶极子, 与 Co 和 Mn 的受主取代有关。在 2 种效应的共同作用下, 降低了陶瓷的载流子浓度, 阻碍了氧空位和自由电子的迁移, 提高了陶瓷的抗还原性能。

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Anti-Reduction BaTiO_3 -Based Dielectric Ceramics for Multi-Layer Ceramic Capacitors

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Extended Abstract

Introduction Multi-layer ceramic capacitor (MLCC) is a highly promising dielectric capacitor due to its high capacitance, favorable dielectric temperature stability, and high breakdown strength. The conventional MLCC uses expensive silver and palladium metals as inner electrode materials. In recent years, base metals such as nickel or copper are employed as inner electrodes to reduce the related costs. However, these metals must be co-fired with the dielectric layer in a reducing atmosphere. BaTiO_3 ceramics are the principal dielectric materials used in the manufacture of MLCC. The sintering of BaTiO_3 ceramics in a reducing atmosphere generates a significant number of oxygen vacancies and free electrons, which significantly impair the insulation performance and reduce the insulating properties. Also, the pronounced dielectric peak of BaTiO_3 ceramics occurs at the elevated temperature end (*i.e.*, 125°C), leading to an inadequate temperature stability.

Recent research focus on the relaxation properties and dielectric properties of $\text{BaTiO}_3\text{-Bi}(\text{Me})\text{O}_3$ ($\text{Me} = \text{Fe}^{3+}$, Co^{3+} , Y^{3+} , etc.) solid solutions. The co-substitution of the A and B sites *via* introducing cations with different ion radius and valence states is shown to disrupt the long-range ferroelectric ordering, induce diffusive phase transitions, and broaden the dielectric temperature profile.

Furthermore, Zn²⁺, Mg²⁺, Mn⁴⁺, Co³⁺, and other rare-earth element ions are introduced into BaTiO₃-based ceramics as host-accepted dopants with the objective of forming defective dipoles with oxygen vacancies, which can bind the free charge movement. Among these, multivalent ions can bind electrons, thereby modifying the valence and regulating the electron concentration within the ceramics. This reduces the likelihood of conversion of Ti⁴⁺ to Ti³⁺.

In this paper, 0.95BaTiO₃-0.05BiCoO₃ dielectric ceramics were used as a matrix. A small amount of MnO₂ was selected for doping and modification, and subsequently sintered in a reducing atmosphere. The structure, micro-morphology, dielectric, and insulating properties were characterized, and the mechanism of anti-reduction was investigated.

Methods In the preparation of the ceramics with a composition of 0.95BaTiO₃-0.05BiCoO₃- $x\%$ (in mass) MnO₂ ($x=0.1, 0.2, 0.3, 0.4$, and 0.5), the materials were sintered at 1275 °C for 2 h under a reducing atmosphere (99.5%N₂+0.5%H₂, in volume fraction), forming dense ceramic samples. Subsequently, the ceramic samples were thinned and polished, and silver paste electrodes were applied to the both sides to measure their electrical properties.

The physical structure of the samples was analyzed using a model X'Pert Pro X-ray diffractometer (XRD, PANalytical Co., the Netherlands). The microscopic morphology of the sample section was determined by a model 450 FEG field emission scanning electron microscope (FE-SEM, FEI Quanta Co., USA). The dielectric properties of the samples were measured by a model PolyK PK-CPT1705 low temperature dielectric tester. The resistivity of the ceramic samples was tested by a model Concept 80 low frequency module (Novocontrol Co., Germany). The ferroelectric properties of the samples were analyzed by a model PK-CPE1801 ferroelectric polarisation return and dielectric breakdown test system (PolyK Co., USA). The elemental valence analysis was conducted by a model 250Xi X-ray photoelectron spectrometer (XPS, Escalab Co., USA). The thermally stimulated depolarization currents (TSDC) of the samples were carried out by a model Concept 80 TSDC (Novocontrol Co., Germany).

Results and discussion All the ceramic samples exhibit a pseudo-cubic perovskite structure. The crystal surface spacing of the ceramics increases as the amount of MnO₂ doping increases. This indicates that Mn⁴⁺ is reduced to Mn³⁺ or Mn²⁺ during sintering in a reducing atmosphere. The radius of Mn³⁺ or Mn²⁺ is larger than that of Ti⁴⁺ (i.e., 0.060 5 nm, CN=6) ionic radius, leading to the crystal lattice distortion and increased cell volume. The cross section of the ceramics reveals fine grains (i.e., 0.24–0.32 μm), clear grain boundaries, and a close arrangement between grains. The change in valence of Mn effectively inhibits the concentration of free electrons. When $x = 0.5$, the insulation resistivity increases to $1.84 \times 10^{13} \Omega \cdot \text{cm}$, the breakdown voltage reaches 210 kV/cm, thus improving the anti-reduction performance of ceramics. The introduction of Mn reduces the dielectric loss of the ceramics and improves their dielectric temperature stability. The optimum dielectric properties are achieved when $x = 0.5$ (i.e., a dielectric constant of 2354, a dielectric loss of 0.0075, and $\Delta C/C(25^\circ\text{C}) \leq \pm 15\%$ at -55 to 154°C). The XPS spectra reveal the presence of both divalent and trivalent Co ions in the ceramics. The result of TSDC test shows a TSDC peak associated with trapped charge, which is related to the change in valence states of the variable valency acceptor ions Co and Mn. Two TSDC peaks are also related to defect dipoles, which are formed by Co and Mn with oxygen vacancies in the ceramic sample.

Conclusions The effect of MnO₂ doping on the phase structure, microstructure, and electrical properties of 0.95BT–0.05BC ceramics was investigated. The results demonstrated that Mn⁴⁺ ions underwent a conversion to Mn³⁺ or Mn²⁺ ions during sintering process in a reducing atmosphere, having the larger ionic radius. This transformation led to an expansion of the cell volume. Mn doping significantly impacted the broadening of the Curie peak and enhanced the dielectric temperature stability of 0.95BT–0.05BC ceramics. Specifically, as $x = 0.5$, the dielectric constant at 25 °C was 2354, and the dielectric loss was 0.007 5. Furthermore, at -55 to 154°C , $\Delta C/C(25^\circ\text{C}) \leq \pm 15\%$. The resistivity at room temperature increased to $1.84 \times 10^{13} \Omega \cdot \text{cm}$, and the breakdown voltage increased to 210 kV/cm. The XPS spectra revealed the presence of both divalent and trivalent Co ions in the ceramic, indicating that Co ions could capture free electrons and reduce their valence state. The result of TSDC test further demonstrated the existence of two types of defective dipoles, which were associated with the acceptor substitution of Co and Mn. The combination of these two factors reduced the carrier concentration in the ceramics, thereby hindering the migration of oxygen vacancies and free electrons and improving the anti-reduction performance.

Keywords multi-layer ceramic capacitor; barium titanate; resistivity; defect dipole; dielectric property