

Er³⁺掺杂无铅铁电陶瓷的电学和光致发光性能

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摘 要: 无铅多功能铁电陶瓷在各类信息的检测、转换、存储及处理中具有广泛的应用, 且稀土元素由于其特殊的电子结构和稳定的发光特性, 有望赋予铁电陶瓷新的发光性能并改善其电学性能, 为设计新型光电器件提供了可能。采用传统的高温固相反应法制备稀土 Er³⁺掺杂 Ba_{0.85}Ca_{0.15}Ti_{0.90}Zr_{0.10}O₃(BCTZ)无铅多功能铁电陶瓷, 系统研究 Er³⁺掺杂浓度对 BCTZ 铁电陶瓷微观结构、电学性能及光致发光的影响及内在联系。研究表明, 陶瓷平均晶粒尺寸随 Er³⁺掺杂浓度的增加单调减小, 由 7.59 μm 减小至 3.82 μm, 减小约 49.67%; 陶瓷可释放的能量密度(W_{rec})和储能效率(η)可分别提高约 29.81%和 122.79%。Er³⁺掺杂 BCTZ 陶瓷表现出强烈的绿光发射(548 nm)且发光强度相对可调性可达 173.09%。Er³⁺掺杂 BCTZ 陶瓷优异、特殊的光电性能, 在电介质储能电容器和光学器件等领域具有潜在应用前景。

关键词: 稀土掺杂; 锆钛酸钡钙; 铁电; 储能; 光致发光

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铁电材料在各类信息的检测、转换、处理及存储中具有广泛的应用^[1-12], 目前工业上广泛使用的铁电陶瓷多数仍为锆钛酸铅 PbZr_xTi_{1-x}O₃(PZT)^[13]和铌镁酸铅 (1-x)Pb(Mg_{1/3}Nb_{2/3})O₃-xPbTiO₃(PMN-PT)^[14]等铅基材料, 但这类材料在生产使用过程中对人体大脑和生态环境都有较大的危害。因此, 开发和研究非铅基绿色环保的铁电陶瓷十分紧迫且意义重大^[15-17]。

BaTiO₃(BT)基铁电陶瓷是最早发现、最早实用化的无铅铁电陶瓷, 因其具有较大的压电常数($d_{33} \approx 180$ pC/N)、较小的介电损耗和良好的铁电性受到研究者的普遍青睐^[18]。但由于 BaTiO₃ 陶瓷工作的温度区间较窄, 各性能参数的温度稳定性较差, 因此对于 BaTiO₃ 陶瓷, 研究者们尝试通过掺杂改性, 来获得更高的温度稳定性以及更好的铁电性^[19-22]。2009年, Liu等^[23]报道了 Ba_{0.85}Ca_{0.15}Ti_{0.90}Zr_{0.10}O₃(BCTZ)锆钛酸钡钙体系的无铅压电陶瓷。通过引入 Ca²⁺和 Zr⁴⁺分别对 BT 基进行 A (Ba²⁺)、B (Ti⁴⁺)位取代, 提高 BT 基陶瓷的铁电性能, 发现其 d_{33} 值高达 620 pC/N, 具有介电损耗小, 铁电性能优异等特点, 能够与 PZT

基等相媲美, 因而有望取代铅基陶瓷材料。此外, 除了对 BT 基陶瓷进行 A、B 位原位取代, 在此基础上, 由于稀土元素具有稳定优异的发光性能且不太可能影响基体的相结构, 因此将稀土元素引入到无铅铁电陶瓷中, 既赋予铁电材料新的光学性能, 又有望通过改变掺杂稀土元素的含量来调整或改变铁电陶瓷的电学性能, 实现电学和光学领域的相互耦合^[24-25]。Chen 等^[26]研究了相结构对 Er³⁺掺杂 x(Bi_{0.5}Na_{0.5})TiO₃-(1-x)BaTiO₃(xNBT-BT:Er³⁺, 0.00 ≤ x ≤ 0.90)无铅陶瓷上转换(UC)光致发光(PL)和介电性能的影响, 发现 UC 强度随着四方性的增加而显著增强, 通过 UC 绿色发光强度比揭示了 xNBT-BT:Er³⁺陶瓷的温感性能。Ma 等^[27]设计并制备了稀土 Tb³⁺掺杂(K_{0.465}Na_{0.465}Li_{0.07})(Nb_{0.93}Bi_{0.07})O₃(KNNLB-x%Tb)无铅透明铁电陶瓷, 发现通过光照和热处理交替刺激可以实现可逆的光致变色且在原位电场刺激下可以提高发光对比度。虽然稀土掺杂铁电陶瓷在光学和电学领域已经有了一些研究成果, 但无铅铁电陶瓷作为一种储能电容器, 其低的储能密度和储能效率, 严重阻碍了它们的实际应用, 因此开发

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具有高储能密度和高储能效率的陶瓷电容器意义重大^[28], 稀土元素对陶瓷储能密度和储能效率的影响及其内在机理的研究至关重要。在稀土元素中, Er^{3+} 因其同时具有下转换和上转换发光的性能及优异的绿色发光强度, 被广泛应用于激光、照明等^[29]。因此, 本工作采用高温固相反应法制备了稀土 Er^{3+} 掺杂的 BCTZ 无铅铁电陶瓷, 系统研究 Er^{3+} 掺杂量对 BCTZ 陶瓷微观结构、铁电、储能以及光致发光性能的调控及其内在联系, 以拓宽其在光电材料中的应用领域。

1 实验

采用高温固相反应法制备 Er^{3+} 掺杂的 $\text{Ba}_{0.85}\text{Ca}_{0.15}\text{Ti}_{0.90}\text{Zr}_{0.10}\text{O}_3(\text{BCTZ}:x\%\text{Er}^{3+}, x=0.0, 0.2, 0.4, 0.6, 0.8, 1.0, \text{摩尔分数})$ 陶瓷。实验原料为 CaCO_3 (99.9%)、 ZrO_2 (99.9%)、 TiO_2 (99.9%)、 BaCO_3 (99.9%)、 Er_2O_3 (99.9%)。实验步骤如下: 配料后球磨 12 h, 烘干进行预烧, 预烧温度为 1 100 $^{\circ}\text{C}$, 保温 6 h; 随后进行造粒压片, 在 1 300 $^{\circ}\text{C}$ 保温 6 h, 进行烧结, 最后自然冷却至室温。采用 X 射线衍射仪(XRD, D8 ADVANCE, 德国)分析陶瓷样品的晶体结构。采用扫描电子显微镜(SEM, JEOL JEM-7800F, 日本)对样品表面形态进行表征。采用 TF 分析仪(TF Analyzer 3000E, 德国)测试陶瓷的电学性能。采用荧光光谱仪(FS5, 爱丁堡, 英国)来测

试陶瓷的发光性能。

2 结果与讨论

图 1 为 $\text{BCTZ}:x\%\text{Er}^{3+}$ 陶瓷在 20 $^{\circ}$ ~80 $^{\circ}$ 范围内的 XRD 谱。由图 1 可见, 所有样品均具有良好的结晶性, 得到单一的钙钛矿结构, 无杂相产生。 Er^{3+} 的离子半径(1.22 Å)与 Ba^{2+} (1.61 Å)和 Ca^{2+} (1.35 Å)相近, 又远大于 Ti^{4+} (0.64 Å)和 Zr^{4+} (0.59 Å), 故从离子半径相近角度, 根据相似相溶原理, Er^{3+} 更容易进入钙钛矿结构的 A 位与 Ca^{2+} 、 Ba^{2+} 发生取代反应。为了观察 Er^{3+} 的掺杂浓度大小对 BCTZ 晶体结构的影响, 对(220)衍射峰进行了局部慢扫描, (220)为次强峰, 其侧重于对晶格对称性的描述。由图 1b 可见, 当 Er^{3+} 掺杂量较低时, 由于 Er^{3+} 优先取代 A 位离子, 离子半径相差不大, 故该峰位未发生偏移, 当掺杂量较高时, 如 0.8% 和 1.0%, 峰位向低角度一侧偏移。晶面间距与晶粒尺寸成反比, 根据 Bragg 方程可知, 晶面间距增大。通过 Scherrer 公式计算其他角度衍射峰发现, 掺杂量较多时, 晶粒尺寸 d 减小, 这是由于 Er^{3+} 已经取代 A 位 Ba^{2+} 、 Ca^{2+} 的位置, 将会逐渐占据间隙位置或取代 B 位离子, 晶格畸变较多, 从而导致晶面间距增大, 晶格对称性降低, 峰位偏移。晶格对称性越差, 光致发光性能越好, 这与图 5 光致发光的光谱结果相对应, 光致发光强度在掺杂量为 0.8% 时达到最大, 在 1.0% 时为次大光强。

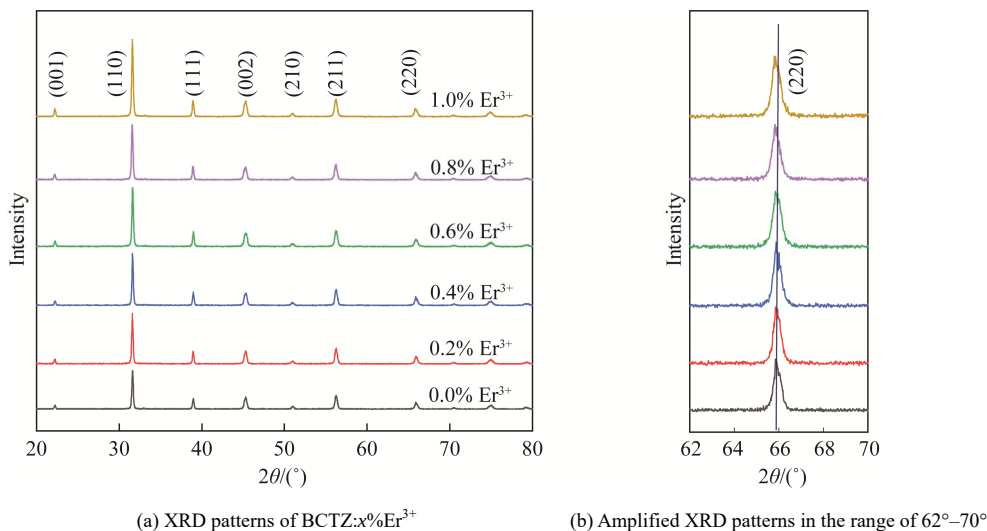


图 1 样品的 XRD 谱

Fig. 1 XRD patterns of samples

Yan 等^[30]发现晶粒尺寸大小对 BCTZ 陶瓷的铁电和储能性能有着极大的影响, 因此对 $\text{BCTZ}:x\%\text{Er}^{3+}$ 的微观表面形貌进行了扫描, 图 2 为其扫描电子显

微镜照片(SEM)。由图 2 可见, 所有样品晶粒紧密排列, 其晶界清晰可见。从表征结果可以明显看出, $\text{BCTZ}:x\%\text{Er}^{3+}$ 陶瓷平均晶粒尺寸随 Er^{3+} 浓度的增

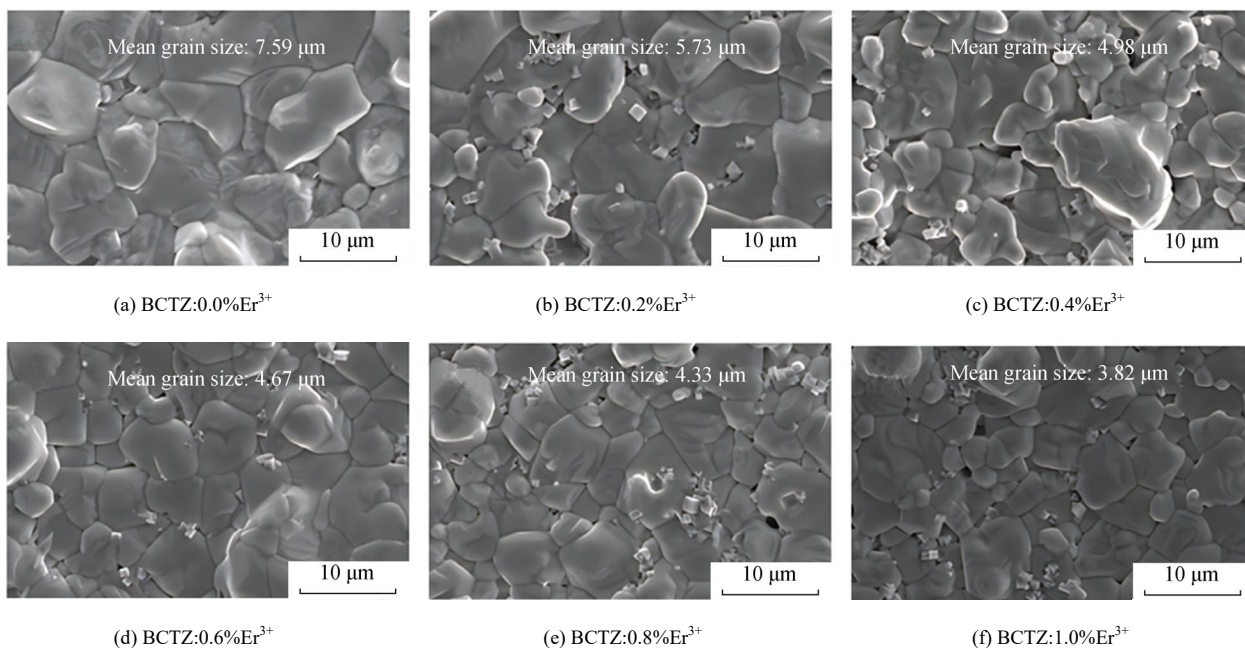
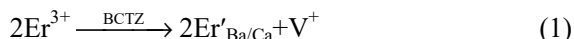


图2 样品的 SEM 照片
Fig. 2 SEM images of samples

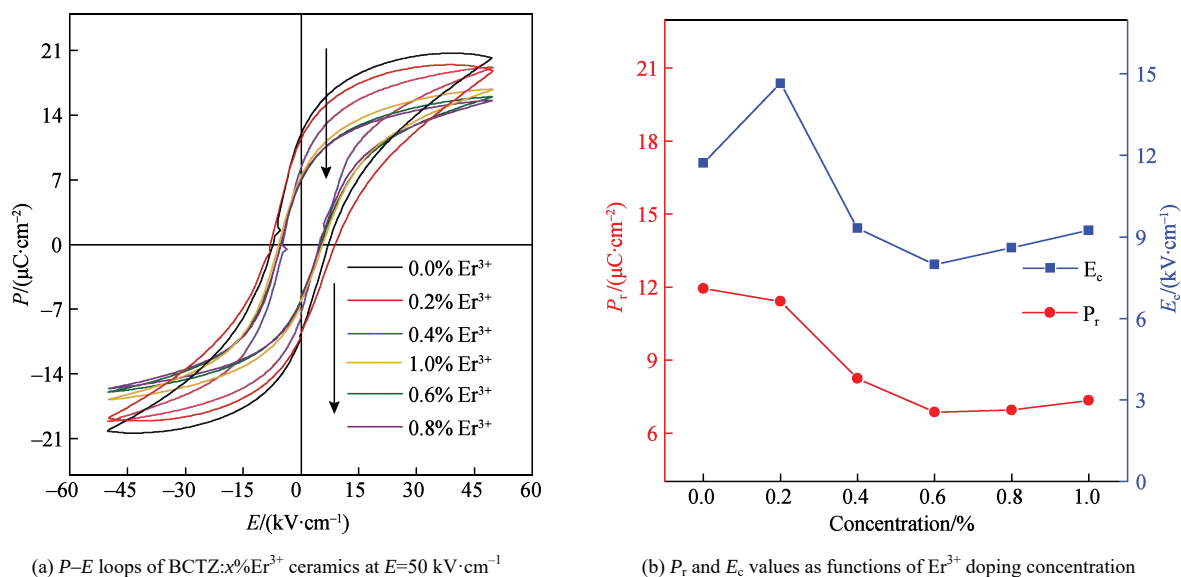
大单调减小,当 $x=1.0$ 时,平均晶粒尺寸为 $3.82\ \mu\text{m}$,与未掺杂 Er^{3+} 的纯 BCTZ ($7.59\ \mu\text{m}$) 相比,减小了 49.67% 。这是由于 Er^{3+} 的离子半径比 Ba^{2+} 和 Ca^{2+} 小,又比 Ti^{4+} 和 Zr^{4+} 大,优化了陶瓷的内部结构,使得晶粒大小分布更加均匀^[31]。此外, Er^{3+} 优先取代 A 位(Ba^{2+} 和 Ca^{2+}),即采用高价态离子取代低价态离子的方式,为维持电中性,将会有部分阳离子空位(V^+)产生,且由于受主与施主离子半径不同,将会造成点阵畸变,缺陷增多,因此晶粒的迁移受到抑制,晶粒尺寸减小。其产生阳离子空位的缺陷方程式为:



为了研究 Er^{3+} 掺杂浓度对 BCTZ 陶瓷铁电性能的影响,在频率为 $10\ \text{Hz}$ 和 $50\ \text{kV}\cdot\text{cm}^{-1}$ 的电场下测量了 BCTZ: $x\%\text{Er}^{3+}$ 陶瓷样品电滞回线,如图 3a 所示。所有陶瓷均表现出优异的铁电性,且电滞回线的形状可以通过改变 Er^{3+} 掺杂浓度进行调控。这是由于掺入不同含量的 Er^{3+} 所引起的晶格畸变和晶粒尺寸变化不同,从而导致铁电畴的翻转和密度有所差异。为了更直观地观察不同 Er^{3+} 浓度掺入对 BCTZ 陶瓷铁电性能之间的影响,对剩余极化强度(P_r)和矫顽场(E_c)随 Er^{3+} 浓度的变化进行了汇总,如图 3b 所示。随着 Er^{3+} 浓度的增加, P_r 逐渐减小,由 $11.930\ \mu\text{C}\cdot\text{cm}^{-2}$ (BCTZ:0.0% Er^{3+}) 减小到 $6.851\ \mu\text{C}\cdot\text{cm}^{-2}$ (BCTZ:0.6% Er^{3+}),减小了约 42.57% 。这是由于 Er^{3+} 掺杂可以破

坏 BCTZ 结构中的长程有序和电畴之间的作用,诱导产生了极性纳米区域,使得 P_r 减小^[24]。由于材料的铁电性与晶格类型、晶粒尺寸、晶体缺陷和畴结构等密切相关,当适量 Er^{3+} 掺入时,能够优化陶瓷内部的微观结构,使晶体的对称性增加,铁电性减弱。但随着掺杂浓度的进一步增加, P_r 略有增大,由 $6.851\ \mu\text{C}\cdot\text{cm}^{-2}$ (BCTZ:0.6% Er^{3+}) 增大到 $7.340\ \mu\text{C}\cdot\text{cm}^{-2}$ (BCTZ:1.0% Er^{3+}),这是由于 Er 离子半径与 Ca^{2+} 、 Ba^{2+} 相近,根据相似相溶原理, Er^{3+} 更容易取代 BCTZ 的 A 位与 Ca^{2+} 、 Ba^{2+} ,产生阳离子空位,形成 P 型半导体,抑制铁电畴的翻转。当撤去外加电场后,有较多铁电畴保持极化时的状态,使 P_r 增大,铁电性增强。 E_c 随 Er^{3+} 掺杂浓度的增加先升高后降低,在掺杂浓度为 0.2% 时达到最大值。这是由于少量的 Er^{3+} 占据 BCTZ 晶体的间隙位置,将会限制铁电畴的翻转切换,使 E_c 增大。 $x>0.2$,随着 Er^{3+} 含量的增加,不等价离子的掺杂使得陶瓷缺陷增多,原子间距增大,使铁电畴的翻转切换更加容易,故 E_c 降低。

BCTZ 陶瓷作为重要的储能电容器,其充电、放电时的能量损耗不可避免。为探究 Er^{3+} 掺杂对 BCTZ 陶瓷储能性能的影响,通过对极化轴与电滞回线的充电、放电曲线的有效面积进行了积分计算分别得到了陶瓷充电储能密度,即总储能密度(W)和可释放的能量密度(W_{rec}),并绘制了 BCTZ: $x\%\text{Er}^{3+}$

图 3 BCTZ: $x\%\text{Er}^{3+}$ 陶瓷的铁电性能变化Fig. 3 Changes of ferroelectric properties of BCTZ: $x\%\text{Er}^{3+}$ ceramics

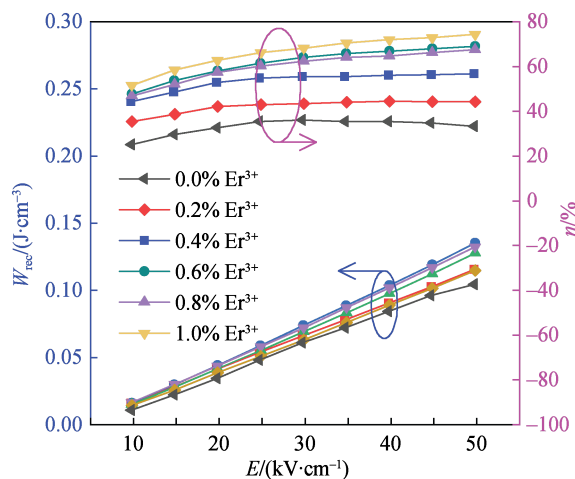
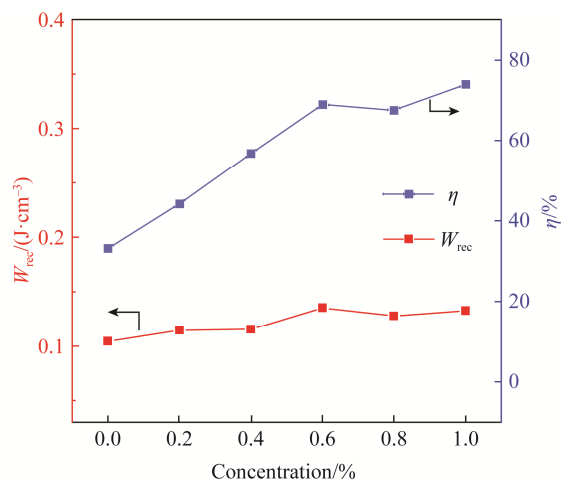
在不同电场下可释放的能量密度和储能效率变化曲线,如图 4a 所示。所有 BCTZ: $x\%\text{Er}^{3+}$ 陶瓷 W_{rec} 和 η 随着电场的增大而增大。进一步研究储能性能对 Er^{3+} 浓度的依赖性,对 BCTZ: $x\%\text{Er}^{3+}$ 陶瓷的 W_{rec} 和 η 值随掺杂浓度的变化进行了总结,如图 4b 所示。其中铁电材料总储能密度(W)、可释放的能量密度(W_{rec})和储能效率(η)的计算公式如下^[24]:

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

$$W_{\text{rec}} = \int_{P_r}^{P_{\text{max}}} E dP \quad (3)$$

$$\eta = (W_{\text{rec}} / W) \times 100\% \quad (4)$$

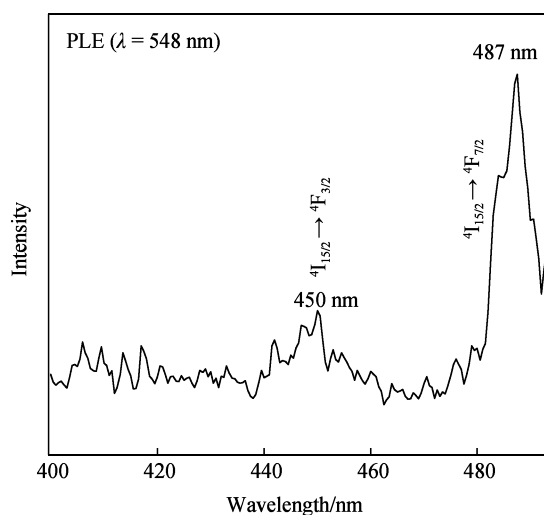
式中: P_{max} 为最大极化强度; P_r 为剩余极化强度, E 为能量。BCTZ: $x\%\text{Er}^{3+}$ 陶瓷的储能效率 η 值随掺杂浓度的增加而增大,由 33.21% (BCTZ:0.0% Er^{3+})提高到 73.99% (BCTZ:1.0% Er^{3+}),提高约 122.79%。可释放的能量密度 W_{rec} 值随掺杂浓度的增加先增大后减小,在掺杂浓度为 0.6% 时达到最大值, W_{rec} 值由 $0.104 \text{ J}\cdot\text{cm}^{-3}$ (BCTZ:0.0% Er^{3+})增大到 $0.135 \text{ J}\cdot\text{cm}^{-3}$ (BCTZ:0.6% Er^{3+}),提高约 29.81%。随着掺杂浓度继续增加至 0.8% 和 1.0%,与 BCTZ:0.6% Er^{3+} 相比, W_{rec} 值分别减小至 $0.128 \text{ J}\cdot\text{cm}^{-3}$ 和 $0.133 \text{ J}\cdot\text{cm}^{-3}$,但与纯 BCTZ 陶瓷相比, W_{rec} 值分别提高约 23.1% 和 27.9%。这一结果与 Yao 等^[32]报道的 $0.475\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3-0.525\text{Ba}_{0.85}\text{Ca}_{0.15}\text{Ti}_{0.9}\text{Zr}_{0.1}\text{O}_3$ 在 $50 \text{ kV}\cdot\text{cm}^{-1}$ 电压下的储能密度相当。结合 W_{rec} 计算公式,可以发现这种变化趋势取决于 P_{max} 和 P_r 之间的差值 ΔP ,由于 Er^{3+} 的掺入使 BCTZ 陶瓷微观结构更加均匀致密,平均

(a) W_{rec} and η values as functions of electric field for ceramics(b) W_{rec} and η values as functions of Er^{3+} doping concentration at $50 \text{ kV}\cdot\text{cm}^{-1}$ 图 4 BCTZ: $x\%\text{Er}^{3+}$ 陶瓷的储能性能变化Fig. 4 Changes of energy storage properties of BCTZ: $x\%\text{Er}^{3+}$ ceramics

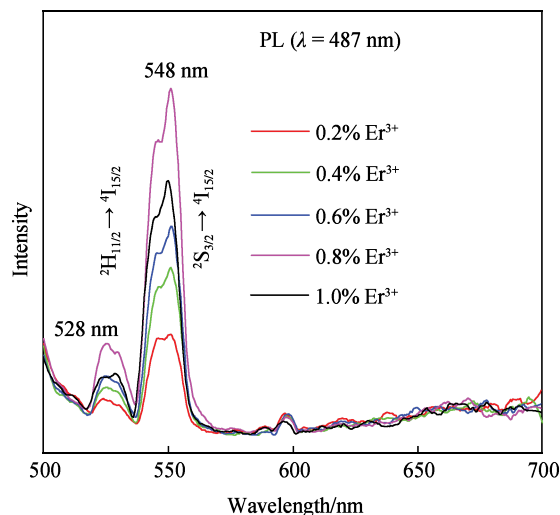
晶粒尺寸发生明显改变, 由此导致了不稳定的极化状态, 从而使 Er^{3+} 掺杂的 BCTZ 陶瓷较纯 BCTZ 陶瓷表现出较大 ΔP , 使得陶瓷的可释放的能量密度和储能效率得到提高。这一结果说明可以通过掺杂 Er^{3+} 来改变 BCTZ 陶瓷的微观结构从而获得更加优异的储能性能。

图 5a 为 BCTZ:0.2% Er^{3+} 陶瓷的激发(PLE)光谱, 其中发射波长为 548 nm。由图 5a 可见, PLE 光谱中有 450 nm 和 487 nm 2 个较强的激发峰, 分别对应 4f-4f 电子层中的 $^4\text{I}_{15/2} \rightarrow ^4\text{F}_{3/2}$ 和 $^4\text{I}_{15/2} \rightarrow ^4\text{F}_{7/2}$ 的跃迁^[31]。图 5b 为以 487 nm 作为激发波长测试 BCTZ: $x\%\text{Er}^{3+}$ 陶瓷的光致发光(PL)光谱。由图 5b 可见, 其主要发射峰在 528 nm 和 548 nm, 分别对

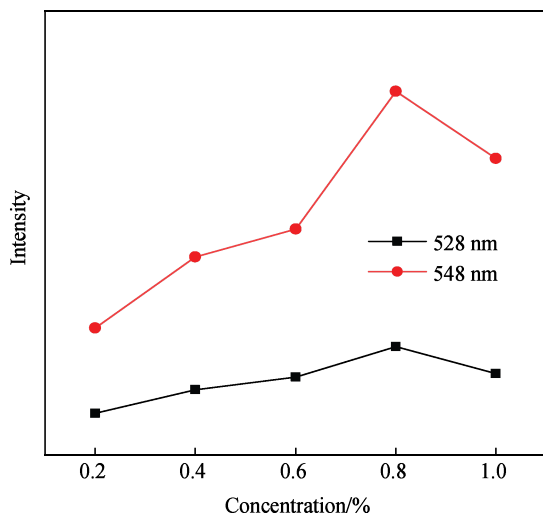
应 $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ 和 $^2\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ 跃迁。不同掺杂浓度下 PL 的发射峰位置没有偏移, 但 Er^{3+} 掺杂浓度不同, PL 强度有明显的差异。图 5c~图 5d 为分别对 528 nm 和 548 nm 的 PL 强度和 PL 强度的相对变化的汇总图。PL 强度和 PL 强度的相对变化均先增大后减小: 当 $x < 0.8$ 时, 掺杂浓度较低, 随着掺杂浓度的增加, 发光中心的数量随之增加, 故发光强度逐渐增大; 在 $x = 0.8$ 时, PL 强度达到最大值; 当 $x > 0.8$ 时, 由于发光离子增多, 发光离子间距减小, 将会发生交叉弛豫现象, 从而造成荧光猝灭, 故发光强度迅速下降^[24]。BCTZ:0.8% Er^{3+} 陶瓷 PL 强度的相对变化与 BCTZ:0.2% Er^{3+} 陶瓷相比, 增强约 173.09%。



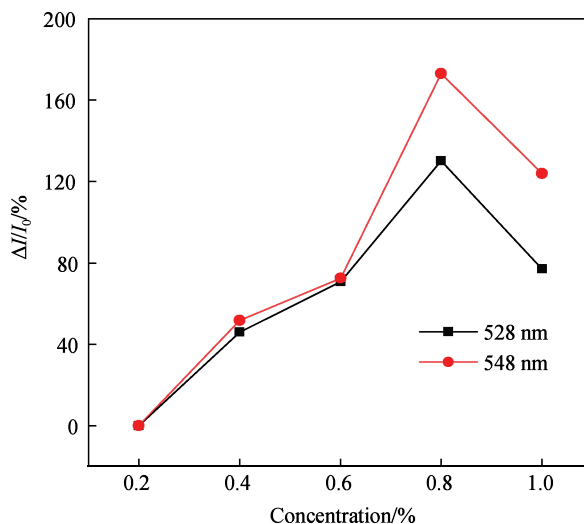
(a) Photoluminescence excitation (PLE) spectrum of BCTZ:0.2% Er^{3+} ceramic



(b) PL spectra of BCTZ: $x\%\text{Er}^{3+}$ ceramics under excitation of 487 nm light



(c) PL emission intensity (528 nm, 548 nm) of BCTZ: $x\%\text{Er}^{3+}$ ceramics under excitation of 487 nm light



(d) PL (528 nm, 548 nm) relative change intensity of BCTZ: $x\%\text{Er}^{3+}$ ceramics

图 5 BCTZ: $x\%\text{Er}^{3+}$ 陶瓷的光致发光性能变化

Fig. 5 Changes of photoluminescence(PL) properties of BCTZ: $x\%\text{Er}^{3+}$ ceramics

3 结论

通过高温固相反应法制备了不同 Er^{3+} 掺杂浓度的 BCTZ 陶瓷($\text{BCTZ}:x\%\text{Er}^{3+}$, $x=0.0$ 、 0.2 、 0.4 、 0.6 、 0.8 、 1.0 , 摩尔分数), 并对其微观结构、铁电性能、储能性能和光致发光性能进行了系统的研究。随着 Er^{3+} 掺杂浓度的增大, 陶瓷平均晶粒尺寸单调减小, 且组织更为致密均匀。 Er^{3+} 掺杂可以破坏 BCTZ 结构中的长程有序和电畴之间的作用, 诱导产生了极性纳米区域, 使得 P_r 减小, 铁电性降低。但陶瓷可释放的能量密度和储能效率随掺杂浓度的增加逐渐提高, 可释放的能量密度 W_{rec} 在掺杂浓度为 0.6% 时达到最大值 $0.135 \text{ J}\cdot\text{cm}^{-3}$, 与纯 BCTZ 陶瓷 W_{rec} ($0.104 \text{ J}\cdot\text{cm}^{-3}$) 相比, 提高约 29.81% 。储能效率 η 值由 33.21% ($\text{BCTZ}:0.0\%\text{Er}^{3+}$) 提高到 73.99% ($\text{BCTZ}:1.0\%\text{Er}^{3+}$), 提高约 122.79% 。此外, 在 487 nm 近紫外光的激发下, $\text{BCTZ}:x\%\text{Er}^{3+}$ 陶瓷在 548 nm 左右表现出强烈的绿光发射。 $\text{BCTZ}:x\%\text{Er}^{3+}$ 陶瓷丰富的物理现象和光电性能, 为开发节能环保、低能耗的新型多功能材料奠定了基础。

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Electrical and Photoluminescent Properties of Er³⁺-Doped Lead-Free Ferroelectric Ceramics

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Extended Abstract

Introduction Ferroelectric materials are widely used in detection, conversion, storage and information processing. The development of energy-saving, environmental protection, multi-functional, miniaturized lead-free multi-functional ceramics becomes inevitable. However, lead-free ferroelectric ceramics as dielectric ceramic capacitors with a low energy storage density and a poor energy storage efficiency seriously hinder their practical application. The development of ceramic capacitors with a high energy storage density and a high energy storage efficiency thus greatly expands the applications of ferroelectric ceramics in the field of energy storage. Doping rare-earth elements is a simple, direct and effective modification method. Rare-earth elements with special electronic structure and stable luminescence properties are expected to give new luminescent properties and improve the electrical properties of ferroelectric ceramics. Ba_{0.85}Ca_{0.15}Ti_{0.90}Zr_{0.10}O₃ (BCTZ) lead-free piezoelectric ceramics have a small dielectric loss and superior electrical characteristics. Rare-earth element Er³⁺ is widely used in laser and lighting due to its excellent green luminous intensity. In this paper, the effect of Er³⁺ doping amount on the microstructure, ferroelectric, energy storage and photoluminescence properties of BCTZ ceramics and their internal relations was investigated to broaden the applications in photoelectric materials.

Methods Er³⁺ doped Ba_{0.85}Ca_{0.15}Ti_{0.90}Zr_{0.10}O₃ (BCTZ: x%Er³⁺, x=0.0, 0.2, 0.4, 0.6, 0.8 and 1.0, in mole fraction) ceramics were prepared by a high-temperature solid-state reaction method. CaCO₃ (99.9%), ZrO₂ (99.9%), TiO₂ (99.9%), BaCO₃ (99.9%), Er₂O₃ (99.9%) were used as raw materials. The raw materials were firstly mixed and ground in a ball mill for 12 h, and then pre-burned at 1 100 °C for 6 h after drying. The pre-burned materials were naturally cooled to room temperature, granulated and pressed. The pressed samples were sintered at 1 300 °C for 6 h. The crystal structure of ceramic samples was analyzed by a model D8 ADVANCE X-ray diffractometer (XRD, Germany). The surface morphology of the samples was characterized by a model JEM-7800F scanning electron microscope (SEM, JEOL Co., Japan). The electrical properties of ceramics were tested by a model TF Analyzer 3000E (Germany), and the both sides of the ceramics were plated with silver electrodes before testing. The luminescent properties of ceramics were determined by a model FS5 fluorescent spectrometer (Edinburgh Co., UK).

Results and discussion Rare-earth Er³⁺ doped BCTZ ceramics all have a well-crystallization with a single perovskite structure and little impurities. The results show that the mean grain size of the ceramics decreases monotonically with the increase of Er³⁺ doping concentration, from 7.59 μm to 3.82 μm, which is decreased by 49.67%.

All the ceramics exhibit superior ferroelectric properties. The ferroelectric domains are overturned and the density are different because of the lattice distortion and grain size change caused by the addition of different contents of Er³⁺, resulting in unstable polarization states. Therefore, the Er³⁺-doped BCTZ ceramics have a larger $\Delta P(P_{\max}-P_r)$ rather than pure BCTZ ceramic. The released energy density (W_{rec}) and energy storage efficiency (η) of the ceramics are increased by 29.81% and 122.79%, respectively.

The worse the lattice symmetry, the better the photoluminescent (PL) performance. At a great doping amount of Er³⁺, Er³⁺ replace the A-position Ba²⁺ and Ca²⁺ positions, gradually occupying the gap position or replacing the B-position ions, resulting in more lattice distortion, reducing the lattice symmetry, and significantly enhancing the photoluminescent intensity. When the doping amount is 0.8% (in mole), PL strength reaches the maximum value. As the doping amount is greater than 0.8%, a cross relaxation

phenomenon occurs due to the increase of luminescent ions and the decrease of luminescent ion spacing, resulting in fluorescence quenching and a decreased luminous intensity. The relative change in PL strength of $\text{BCTZ}:0.8\%\text{Er}^{3+}$ ceramic is enhanced by 173%, compared with $\text{BCTZ}:0.2\%\text{Er}^{3+}$ ceramic.

Conclusions The mean grain size of the lead-free multifunctional ferroelectric ceramics decreased monotonously, and the microstructure became more compact and uniform with the increase of Er^{3+} doping concentration. All the ceramics had the superior ferroelectric properties. Er^{3+} doping could destroy the long-range order in BCTZ structure and the interaction between electric domains, so that the released energy density (W_{rec}) and energy storage efficiency (η) of the ceramics were increased by 29.81% and 122.79%, respectively, as Er^{3+} doping concentration increased. In addition, $\text{BCTZ}:x\%\text{Er}^{3+}$ ceramics exhibited an intense green emission at 548 nm under excitation of 487 nm near-ultraviolet light, and the luminous intensity was relatively adjustable up to 173.09%. The rich physical and photoelectric properties of $\text{BCTZ}:x\%\text{Er}^{3+}$ ceramics could lay a foundation for the development of new multi-functional materials with energy saving, environmental protection and low energy consumption.

Keywords rare-earth doping; barium calcium zirconate titanate; ferroelectric; energy storage; photoluminescence