

掺铈锆钛酸铅镧反铁电薄膜的反常电控光致发光效应

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摘 要: 光致发光效应的电场调控可以用于光信息存储与通信等领域。如何在薄膜材料中实现光致发光强度的巨幅调控至关重要。以铈离子(Er^{3+})掺杂的锆钛酸铅镧($\text{Pb}_{0.98}\text{La}_{0.02}\text{Zr}_{0.95}\text{Ti}_{0.05}\text{O}_3$, PLZT-Er)反铁电薄膜为对象, 深入分析其电控光致发光效应。在外加电场为 $830\text{ kV}\cdot\text{cm}^{-1}$ 时, 可逆光致发光强度调控幅度达 $\sim 85\%$, 远超 PLZT-Er 陶瓷材料($+30\%$)。完全相反的电控光致发光变化趋势表明了 PLZT-Er 薄膜与陶瓷材料在电场作用下存在结构演化差异。PLZT-Er 薄膜在电场作用下反常的光致发光强度减弱现象揭示了薄膜中 Er^{3+} 周围局部晶体场对称性在电场调制下增强, 其原因可归结于基底钳位效应导致的反铁电正交相向铁电正交相的相变过程, 以及电场强度不足时亚铁电相向反铁电相的不完全相变。

关键词: 稀土掺杂; 光致发光; 电场调控; 相变; 薄膜

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稀土离子掺杂材料的光致发光性能主要由稀土离子周围局部晶体对称性决定^[1-3]。目前, 研究人员已经实现了基于外加刺激(如电场、磁场、机械应力等)的光致发光性能的实时调控策略^[4-8]。其中, 采用外加电场对光致发光性能进行调控与现代电子科技具有良好的兼容性, 在光信息存储和光通信等前沿领域具有广阔的应用前景^[9-11]。

在稀土离子掺杂的铁电体中, 外加电场诱导的铁电体结构变化(包括极化翻转、晶格畸变以及相变等)可以有效调控稀土离子周围的晶体场环境^[12], 进而对光致发光强度实现动态调控(即电控光致发光效应)^[3, 13, 14], 然而, 铁电体存在的滞后效应会导致铁电体在撤去外加电场后无法完全恢复到初始状态, 限制了光致发光强度的调控范围^[15, 16]。

在外加电场的作用下发生可逆翻转, 变为平行排列(即反铁电相向铁电相的相变); 当撤去外加电场后, 电偶极矩可无滞后地自发恢复至反平行状态^[17]。这一特性使反铁电材料在巨幅可逆光致发光电场调

控方面极具潜力。张宇等报道: 铈离子(Er^{3+})掺杂的 $\text{Pb}_{0.96}\text{La}_{0.04}\text{Zr}_{0.90}\text{Ti}_{0.10}\text{O}_3$ (PLEZT) 反铁电陶瓷的光致发光强度在施加外电场后可提升 30% ^[5]; Er^{3+} 掺杂的 AgNbO_3 (AEN) 反铁电陶瓷的光致发光强度在施加电场后则降低了 25% ^[6]。PLEZT 与 AEN 陶瓷的光致发光调控均发生在各自的反铁电-铁电相变过程中, 该相变过程会改变 Er^{3+} 周围的局部晶体对称性, 进而调控其光致发光性能。但是, 二者截然相反的调控趋势表明, 这类电控光致发光效应的真实影响因素是反铁电-铁电相变过程中的晶体结构演化过程。在 PLEZT 陶瓷中, 发生的是正交反铁电相 (AFE_o , 空间群 $Pbam$) 到菱方铁电相 (FER , 空间群 $R3c$) 的相变^[5]; 而 AEN 中则是正交反铁电相到正交铁电体 (FE_o , 空间群 $Pmc2_1$) 的相变^[6]。

然而, 在反铁电薄膜中, 衬底产生的基底钳位效应可能会对电场诱导的相变过程中晶体结构的演变产生显著影响^[18, 19]。研究表明, 锆酸铅 (PZO) 薄膜在未外加电场的初始状态下为亚铁电相, 其电偶极

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子呈三调制周期($\downarrow\uparrow\downarrow$); 在较小电场作用下, 其转变为具有四调制周期的反铁电相($\downarrow\uparrow\uparrow$), 而在较大电场作用下进一步转变为电偶极子平行排列的铁电相^[20, 21]。因此, 与陶瓷材料相比, 在稀土离子掺杂的锆酸铅基反铁电薄膜中有望观察到独特的电控光致发光现象。

在本工作中, 采用溶胶-凝胶法制备了 1%(摩尔分数)Er³⁺掺杂的 Pb_{0.98}La_{0.02}Zr_{0.95}Ti_{0.05}O₃(PLZT-Er)反铁电薄膜, 并研究了其中的电控光致发光效应。与 PLEZT 陶瓷相比, PLZT-Er 薄膜的电控光致发光趋势完全相反。通过对 Er³⁺周围晶体对称性的详细分析, 对这一现象的内在机制展开讨论。

1 实验

1.1 样品制备

制备 PLZT-Er 薄膜使用的原材料包括三水合乙酸铅[PbC₄H₆O₄·3H₂O, 纯度 99.99%, 阿拉丁]、六水合硝酸镧[LaN₃O₉·6H₂O, 纯度 99%(433.03), 阿拉丁]、1%(摩尔分数)五水合硝酸铒[Er(NO₃)₃·5H₂O, 纯度 99.9%(443.37), 阿拉丁]、丙醇锆[C₁₂H₂₈O₄Zr, 纯度 70%(327.56), 阿拉丁]和丁醇钛[C₁₆H₃₆O₄Ti, 纯度 ≥99.0%(340.32), 阿拉丁]。为弥补铅的损失并防止形成烧绿石相, 在溶液配制过程中额外添加 10%的铅源。

1.2 样品制备

采用多层旋涂法制备 PLZT-Er 薄膜, 每层薄膜在真空旋涂仪(VTC-100, 沈阳科晶自动化设备有限公司)中 4000 r/min 转速下匀胶 30 s, 使胶体均匀地分布在衬底表面, 形成湿膜, 将其放到加热台(JF966-2020, Jftoois, 金峰电子有限公司)上, 在

100 °C 干燥 2 min, 后在管式炉(OTF-1200X, 合肥科晶材料技术有限公司)中 450 °C 热解 5 min, 将重复以上程序 6 次得到的薄膜放入快速退火炉(TF-1200X, 合肥科晶材料技术有限公司)中, 700 °C 退火 30 min 得到厚度为约 360 nm 的 PLZT-Er 薄膜。

1.3 样品表征

采用 X 射线衍射仪(XRD, Ultima III, Rigaku)对样品晶体结构进行表征。采用原子力显微镜(AFM, ICON, Bruker)观察其形貌。采用铁电分析仪(AIX ACT, TF2000)在 1 kHz 频率下对其电滞回线($P-E$)和电流曲线($I-E$)进行测试。在 405 nm 和 532 nm 激光激发下, 通过荧光光谱仪(ULS2048x64TEC, Avantes)测量下转换光致发光(down-conversion photoluminescence, DCPL)发射光谱, 激光的功率为 0.7 mW(功率范围为 260 μW~13 mW), 光斑直径约为 3 μm, 于室温 25 °C, 避免阳光直射环境下进行测试。在电场调控光致发光测试中, 使用电压源表(Keithley 2450, 吉利时仪器)施加电场, 电场类型为直流, 测试温度为室温。PLZT-Er 薄膜的光致发光强度变化量(ΔI)通过以下公式计算:

$$\Delta I = \frac{I_E - I_0}{I_0} \times 100\% \quad (1)$$

式中: I_0 和 I_E 分别为未施加电场时与施加电场时的光致发光强度。

2 结果与讨论

图 1 为 PLZT-Er 和 PLZT 薄膜的 XRD 谱。由图 1a 可见, 薄膜衍射峰与标准 PLZT(PDF 46-0336)吻合良好, 证明已形成纯钙钛矿结构。XRD 局部放大谱显示, PLZT-Er 薄膜的(110)和(200)晶面衍射峰

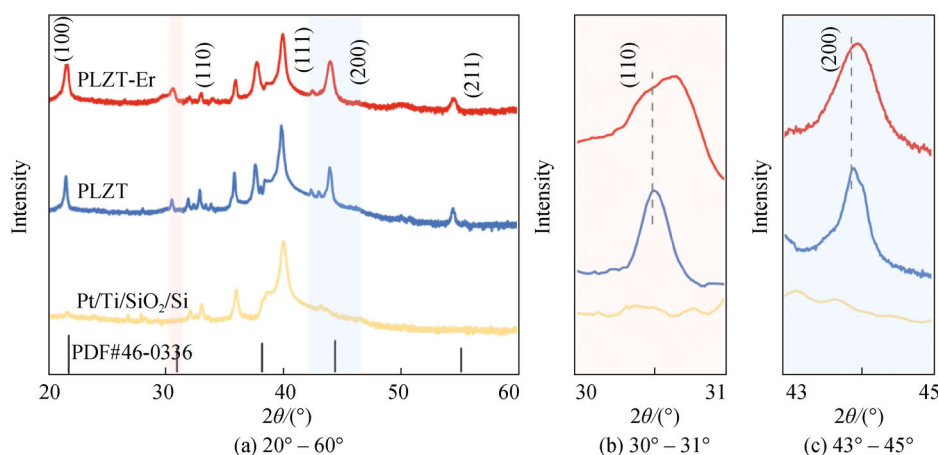


图 1 PLZT-Er 和 PLZT 薄膜的 XRD 谱

Fig. 1 XRD patterns of the PLZT-Er and PLZT thin films

向高角度方向偏移, 表明 Er^{3+} 的掺杂引发了 PLZT 晶格的收缩。在反铁电 PLZT 中, Er^{3+} 取代 B 位的形成能显著高于取代 A 位的形成能。因此, Er^{3+} 优先占据 Pb^{2+} 的位置(即 A 位)^[22, 23]。因为 Er^{3+} 的离子半径(0.124 nm, 配位数 CN=12)小于 Pb^{2+} (0.149 nm, 配位数 CN=12), 所以这种 A 位取代会导致晶格收缩^[24]。此外, Er 掺杂导致了(110)衍射峰发生劈裂, 说明 Er^{3+} 的掺杂仅使部分 PLZT 晶格发生收缩(部分未收缩区域呈现同纯 PLZT 相同的衍射峰位)。

图 2 为 PLZT-Er 薄膜的 AFM 图像和电滞回

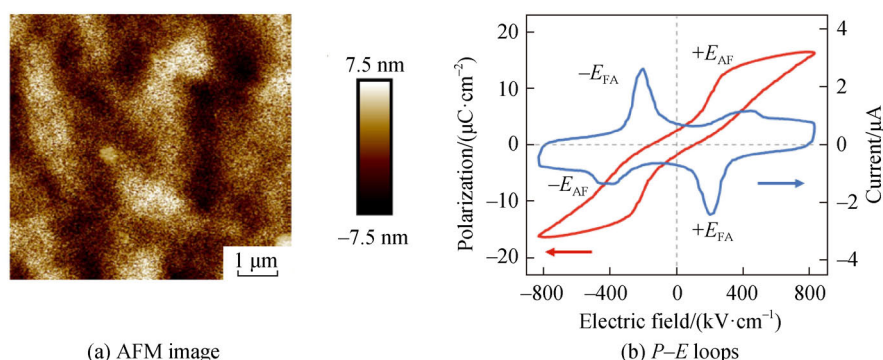


图 2 PLZT-Er 薄膜的 AFM 图像和电滞回线
Fig. 2 AFM image and P - E loops of PLZT-Er thin film

图 3 为 PLZT 薄膜与 PLZT-Er 薄膜在 405 nm 和 532 nm 激发下的光致发光强度对比及相应的发光机制。图 3a 对比了在 405 nm 激发下, PLZT-Er 薄膜与 PLZT 薄膜的下转换发光光谱。PLZT-Er 薄膜出现 2 个特征发射带: 487 nm 处的蓝绿光和 610 nm 处的橙红光, 分别对应于 Er^{3+} 的 $^4\text{F}_{7/2} \rightarrow ^4\text{I}_{15/2}$ 跃迁以及 $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ 跃迁^[27, 28]。每个发射带均呈现多组斯塔克分裂峰, 这是由晶体场诱导的 Er^{3+} 能级分裂所致。对应的能量传递机制如图 3b 所示: 在 405 nm 激光激发下, PLZT 晶格中 Pb^{2+} 或者氧空位缺陷吸收光子能量, 通过非辐射跃迁将能量传递至 Er^{3+} 的 $^4\text{F}_{7/2}$ 激发态。处于激发态的电子随后通过 2 条互相竞争的弛豫路径释放能量: 一是直接辐射复合至 $^4\text{I}_{15/2}$ 基态, 产生 487 nm 处的蓝绿光; 二是通过多声子弛豫(MPR)非辐射弛豫至 $^4\text{F}_{9/2}$ 激发态, 再经过辐射衰减至 $^4\text{I}_{15/2}$ 基态, 产生 610 nm 处的橙红光^[29]。这种双发射过程证实, PLZT-Er 薄膜中存在高效的能量传递与转换。

图 3c 为在 532 nm 激发下, PLZT-Er 薄膜与 PLZT 薄膜的下转换发光光谱。由图 3c 可见, PLZT-Er 薄膜出现 3 个特征发射带: 位于 560 nm 处的绿光、位于 660 nm 处的红光以及位于 850 nm 处的近红外光,

线。由图 2a 可见, PLZT-Er 薄膜的表面形貌光滑, 粗糙度(R_q)为 3.20 nm。良好的表面质量可以提升薄膜与 ITO 电极的接触效果^[25], 进而提升抗击穿场强(E_b)并减小在电场作用下的漏电流^[26]。由图 2b 可见, 典型的双电滞回线形状证实了样品的反铁电性能。在对应的 I - E 回线中, 出现了 4 个与电场诱导反铁电-铁电相变相关的电流峰, 其中: 2 个 E_{AF} 峰位于 $\pm 452 \text{ kV} \cdot \text{cm}^{-1}$, 对应反铁电 $\rightarrow$ 铁电相变; 2 个 E_{FA} 峰位于 $\pm 199 \text{ kV} \cdot \text{cm}^{-1}$, 对应铁电 $\rightarrow$ 反铁电相变。

分别对应于 Er^{3+} 的 $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ 跃迁^[30]、 $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ 跃迁以及 $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{13/2}$ 跃迁^[31]。图 3d 为 532 nm 激光激发下 Er^{3+} 能级图以及其下转换发光机制: 在 532 nm 激光激发下, 处于 $^4\text{I}_{15/2}$ 基态的电子通过基态吸收(GSA)跃迁至 $^4\text{F}_{7/2}$ 能级激发态吸收(ESA)跃迁至 $^4\text{F}_{5/2}$ 能级; 室温下, 这些激发态电子通过热弛豫过程快速非辐射跃迁至 $^4\text{S}_{3/2}$ 能级, 随后通过辐射跃迁至 $^4\text{I}_{15/2}$ 基态, 产生位于 560 nm 处的绿光。与此同时, 部分位于 $^4\text{S}_{3/2}$ 能级的电子通过 MPD 非辐射衰减至 $^4\text{I}_{15/2}$ 基态, 产生位于 660 nm 处的红光。此外, 有部分处于 $^4\text{S}_{3/2}$ 能级的电子会跃迁至较低的 $^4\text{I}_{13/2}$ 激发态, 由于 $^4\text{S}_{3/2}$ 能级与 $^4\text{I}_{13/2}$ 能级能级差较小, 电子在此跃迁过程中释放的能量较低, 对应产生位于 850 nm 处的近红外光^[32]。

图 4a 为 405 nm 激光激发下, PLZT-Er 薄膜的电场调控光致发光光谱。由图 4a 可见, 随着电场的增大, 487 nm 处和 610 nm 处的 2 个发射光的发光强度均显著下降。由图 4b 可见, 在电场的作用下, PLZT-Er 薄膜呈现可逆且负向的发光调控特性, 光致发光强度可明确划分为 2 个状态: 状态 0(低场区域, 对应较高的发光强度)和状态 1(高场区域, 对应较低的发光强度)。这 2 种状态均与 PLZT 基体的反

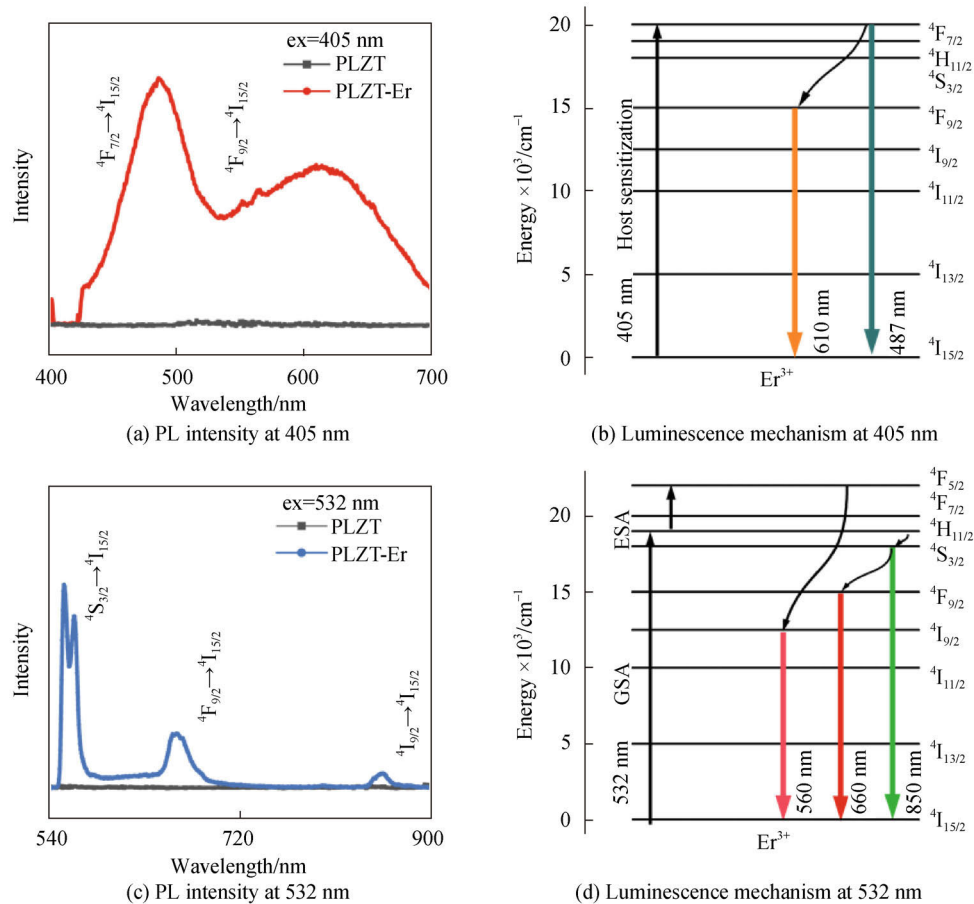


图3 PLZT薄膜与PLZT-Er薄膜在405 nm和532 nm激发下的光致发光强度对比及相应的发光机制

Fig. 3 Comparative PL intensity and luminescence mechanism of PLZT and PLZT-Er thin films under 405 nm and 532 nm excitation

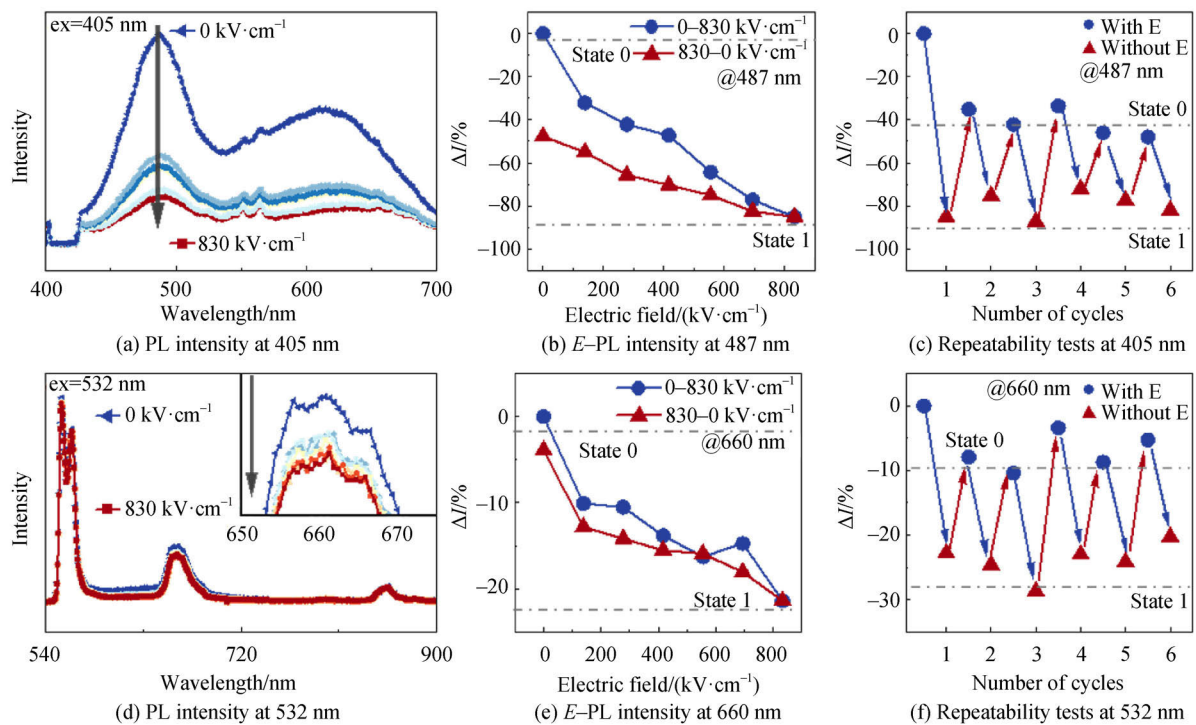


图4 不同电场下PLZT-Er薄膜的光致发光光谱、相应的电控光致发光变化曲线及6次循环性能

Fig. 4 PL spectra, E-PL loops, and the six cycles repeatability tests of PLZT-Er thin films under different E

铁电相和铁电相相关^[33]。当电场达到 $830 \text{ kV} \cdot \text{cm}^{-1}$ 时, 发光强度实现了 -85.14% 的最大调控幅度; 随着电场逐渐降低至 $0 \text{ kV} \cdot \text{cm}^{-1}$, 发光强度有所恢复, 但相较于初始状态, 恢复后仍降低 47.76% 。电滞回线显示薄膜样品存在一定的剩余极化强度, 这说明铁电相没有完全回到反铁电情况, 这是发光强度无法恢复到初始状态的原因。同时, ITO 电极与 PLZT-Er 薄膜的功函数差异会导致界面电荷的积累, 从而影响材料内部电场分布的均匀性。因此, 通过改善电极制作工艺, 有望增加发光强度的可调控幅度。图 4c 中 6 次连续的电场调控发光的测试进一步证实了该电控光致发光效应的可逆性, 表明材料具有稳定的

开关特性, 在光数据存储和光通信领域具有应用潜力^[34]。同样地, 在 532 nm 激光激发下, PLZT-Er 薄膜呈现可逆的电控光致发光现象(见图 4d~图 4f)。

表 1 对比了 PLZT-Er 反铁电薄膜与其他反铁电陶瓷及铁电薄膜的电场调控光致发光性能。由表 1 可知, PLZT-Er 薄膜实现了可逆的电场调控光致发光, 调控幅度约为 -85% , 远高于 PLZT-Er 陶瓷, 这一优异性能源于薄膜材料相较于块体陶瓷具有更高的耐击穿场强。需要指出, PLZT-Er 薄膜所需的实际电压约为 30 V , 远小于陶瓷所需的电压(800 V)。由此可知, PLZT-Er 薄膜是光存储和光通信器件的优良候选材料。

表 1 AFE 和 FE 陶瓷及薄膜的 E -PL 性能比较

Table 1 Comparison of E -PL performances among AFE- and FE-type ceramics and thin films

$\Delta I/\%$	$E_{\text{max}}/(\text{kV} \cdot \text{cm}^{-1})$	Reversibility	Materials	Type	Reference
-85.14	830	Yes	PLZT-Er	AFE thin film	This work
30	80	Yes	PLZT-Er	AFE ceramics	[5]
-25	150	Yes	ANO-Er	AFE ceramics	[6]
88.7	160	No	$(\text{C}_4\text{H}_9\text{NH}_3)_2\text{CsPb}_2\text{Br}_7\text{-Mn}$	FE thin film	[40]
6.6	10	Yes	$\text{Ba}_{0.85}\text{Ca}_{0.15}\text{Ti}_{0.9}\text{Zr}_{0.1}\text{O}_3\text{-Pr}$	FE thin film	[41]
7	10	Yes	0.94BNT-0.06BT-Eu	FE thin film	[42]
-55	10	Yes	$\text{CsPbBr}_3\text{/PMN-PT}$	FE thin film	[43]
170	125	Yes	$\text{BaTiO}_3\text{-Yb/Er}$	FE thin film	[9]
15	50	Yes	$\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-BT-Yb/Er}$	FE thin film	[44]
-25	10	Yes	$\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-BT-Yb/Er}$	FE thin film	[45]

然而, 表 1 说明 PLZT-Er 薄膜与 PLEZT 陶瓷之间存在相反的电场调控光致发光趋势。根据 Judd-Ofelt (J-O) 理论, 具有 $4f^N$ 电子组态的 Er^{3+} 会与晶体场中邻近电子态发生耦合, 进而实现电子在不同能级间的跃迁^[9, 35]。基态(Ψ_J)与激发态(Ψ_J^*)之间跃迁的自发辐射概率(A_{ED})可以通过以下公式计算:

$$A_{\text{ED}} = \frac{64\pi^4 e^2}{3h(2J+1)\lambda^3} \left[\frac{n(n^2+2)^2}{9} \right] S_{\text{ED}} \quad (2)$$

$$S_{\text{ED}} = \sum_{t=2,4,6} Q_t |\Psi_J U^{(t)} \Psi_J^*|^2 \quad (3)$$

式中: e 为电子电荷; λ 为跃迁的平均波长; n 为折射率; h 为普朗克常数; J 为总角动量量子数; S_{ED} 为电偶极子谱线强度; $U^{(t)}$ 为基于单电子张量算符计算所得的约化矩阵元; Q_t ($t=2,4,6$) 为强度参数。 Q_2 与发光中心(即 Er^{3+})周围的晶体结构畸变密切相关, 尤其关联于基体的极化程度和局部对称性^[36]; 而 Q_4 与 Q_6 则主要与氧化物配体的电子云密度相关, 与晶体对称性的变化无显著关联^[37]。因此, 降低 Er^{3+} 周围晶体的局部对称性会提高能级间的跃迁概率,

进而增强光致发光强度; 反之, 提高 Er^{3+} 周围晶体的局部对称性则会减弱光致发光强度^[38, 39]。

从这一角度分析, 相反的电场调控光致发光趋势表明, 在反铁电-铁电相变过程中, PLZT-Er 薄膜与 PLEZT 陶瓷遵循截然不同的结构变化路径。对于 PLEZT 陶瓷, 其晶体结构由反铁电正交(AFE_o)的 $Pbam$ 相转变为铁电菱方(FE_R)的 $R3c$ 相(图 5a)^[46]。在此过程中, 铁电相 PLEZT 的晶体结构不对称性降低了 Er^{3+} 周围的晶体对称性, 进而提升其光致发光强度。通常, PLZT-Er 薄膜的晶体对称性变化应当遵循相同的规律。因此, PLZT-Er 薄膜中出现的反常电场调控光致发光现象, 预示着其存在非典型的结构变化路径。以下将针对 Er^{3+} 周围的晶体对称性反常升高的 2 种机制展开讨论。

第 1 种机制为基底钳位效应, 该效应迫使 PLZT-Er 薄膜在电场的作用下维持正交/四方晶相, 已有多项研究表明, 在基底诱发的钳位效应的作用下, PLZT 可在电场的作用下由反铁电正交相转变为铁电正交相/铁电四方相(FE_o/FE_T), 在此情况下,

Pb^{2+} 沿同一方向发生位移,相较于反铁电正交相中 Pb^{2+} 的反平行排列方式,该体系的局部晶体对称性更高^[18, 19, 47, 48];第2种机制为PLZT-Er薄膜发生了电场诱导的亚铁电相到反铁电相的不完全相变。有报道称,模拟计算与原位透射电子显微镜(TEM)结果表明,在电场为 $0\text{ kV}\cdot\text{cm}^{-1}$ 时,PLZT薄膜中存在本征的亚铁电相而非反铁电相^[20, 21];施加电场后,亚铁电相会先转变为反铁电相,再进一步转变为铁电相。由图5c和图5d可见,在亚铁电相中, Er^{3+} 可占据3种不同的 Pb^{2+} 位置,对应电偶极子的“ $\downarrow\uparrow\downarrow$ ”

排列方式;而在反铁电相中, Er^{3+} 可占据4种不同的 Pb^{2+} 位置,对应电偶极子的“ $\downarrow\downarrow\uparrow\uparrow$ ”排列方式。对比2种相中晶体结构的对称性可见,在电场诱导的亚铁电-反铁电相变过程中, Er^{3+} 周围晶体的对称性发生了显著变化。据此推断,PLZT-Er薄膜中出现的负向电场调控光致发光效应,应是薄膜内部存在亚铁电相,且该相在外加电场不足的条件仅发生向反铁电相的不完全相变所致。若此推论成立,进一步提高电场的强度或可使薄膜的光致发光强度产生更显著的变化。

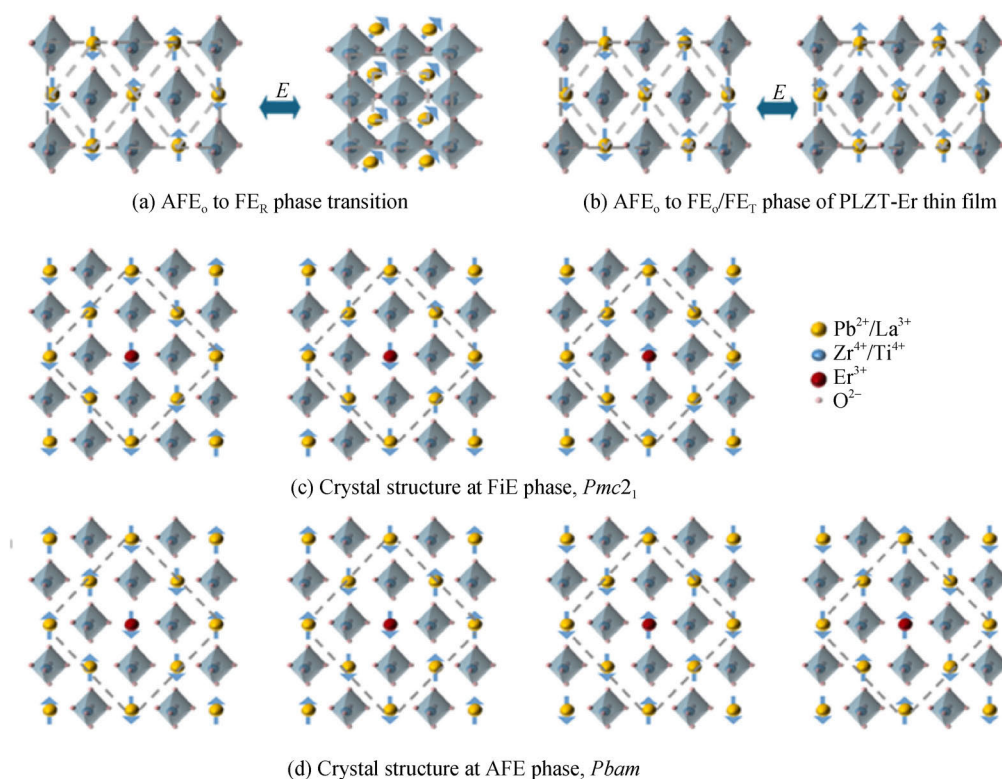


图5 不同情况下PLZT-Er薄膜中 Er^{3+} 周围晶体结构示意图

Fig. 5 Schematic of crystal structure around Er^{3+} in PLZT-Er thin films under different conditions

3 结论

Er^{3+} 掺杂 $\text{Pb}_{0.98}\text{La}_{0.02}\text{Zr}_{0.95}\text{Ti}_{0.05}\text{O}_3$ (PLZT-Er)薄膜具有可逆的电控光致发光效应。在 405 nm 激光激发下,当外加电场达到 $830\text{ kV}\cdot\text{cm}^{-1}$ 时,薄膜的光致发光强度调幅可达 $\sim 85\%$ 。这种负向的电场调控光致发光趋势与块体PLZT-Er陶瓷的调控趋势恰好相反。针对这一反常现象,本工作提出了2种潜在的机理解释:一是PLZT-Er薄膜中发生反铁电正交相转变为铁电正交相/铁电四方相的相变;二是PLZT-Er薄膜中发生电场诱导的亚铁电相到反铁电相的不完全相变。这2种情况均会使 Er^{3+} 周围的局布晶体结构

对称性升高。对于本工作中出现的发光强度恢复不完全的问题,可能需要通过优化薄膜制备工艺、改善电极接触质量等措施解决;未来可探索更高电场下的相变行为及薄膜的长期循环稳定性。

参考文献:

- [1] 陈猛, 殷俊, 郑伊娜. 稀土 Er/Nb 共掺 $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ 高温铁电陶瓷的上转换发光及电性能[J]. 硅酸盐学报, 2018, 46(4): 499–504.
CHEN Meng, YIN JUN, DENG Yina. J Chin Ceram Soc, 2018, 46(4): 499–504.
- [2] MA Y M, YANG S X, ZHAO C L, et al. Photochromic and electric field-regulating luminescence in high-transparent (K, Na) NbO_3 -based ferroelectric ceramics with two-phase coexistence[J]. ACS Appl Mater Interfaces, 2022, 14(31): 35940–35948.

- [3] LIN J F, LU Q L, WU X, et al. In situ boost and reversible modulation of dual-mode photoluminescence under an electric field in a tape-casting-based Er-doped $K_{0.5}Na_{0.5}NbO_3$ laminar ceramic[J]. *J Mater Chem C*, 2019, 7(26): 7885–7892.
- [4] HUANG L J, XIONG R, XIE J X, et al. Curvature-dependent strain-induced photoluminescence modulations in flexible Er-doped $Pb_{0.98}La_{0.02}Zr_{0.95}Ti_{0.05}O_3$ antiferroelectric thin films prepared by the sol-gel method[J]. *J Eur Ceram Soc*, 2023, 43(16): 7455–7462.
- [5] ZHANG Y, HUANG L J, LEUNG C M, et al. Phase stability and dual-mode photoluminescence modulation in Er-doped lead zirconate titanate antiferroelectrics[J]. *ACS Appl Mater Interfaces*, 2023, 15(11): 14596–14604.
- [6] ZHANG Y, HUANG Y, HUANG L J, et al. Direct photoluminescence manipulation in Er-doped $AgNbO_3$ lead-free antiferroelectrics via reversible electric-field-induced symmetry modulations[J]. *Ceram Int*, 2023, 49(18): 30409–30416.
- [7] 张怡笑, 王小丽, 杨健, 等. Er^{3+} 掺杂无铅铁电陶瓷的电学和光致发光性能[J]. *硅酸盐学报*, 2024, 52(5): 1656–1663.
ZAHNG Yixiao, WANG Xiaoli, ZHANG Jian, et al. *J Chin Ceram Soc*, 2024, 52(5): 1656–1663.
- [8] ZHOU Y, XIONG R, WANG P, et al. Strain and illumination triggered regulations of up-conversion luminescence in Er-doped $Bi_{0.5}Na_{0.5}TiO_3BaTiO_3$ /Mica flexible multifunctional thin films[J]. *J Materiomics*, 2022, 8(3): 586–595.
- [9] HAO J H, ZHANG Y, WEI X H. Electric-induced enhancement and modulation of upconversion photoluminescence in epitaxial $BaTiO_3$: Yb/Er thin films[J]. *Angew Chem Int Ed*, 2011, 50(30): 6876–6880.
- [10] ZHANG Y Y, LUO L H, LI K X, et al. Large and reversible *in-situ* up-conversion photoluminescence modulation based on photochromism via electric-field and thermal stimulus in ferroelectrics[J]. *J Eur Ceram Soc*, 2018, 38(9): 3154–3161.
- [11] 刘芳, 江向平, 陈超, 等. Sm^{3+} 掺杂 $SrBi_4Ti_4O_{15}-Bi_4Ti_3O_{12}$ 压电陶瓷的结构、电学和光致发光性能[J]. *硅酸盐学报*, 2023, 48(3): 325–331.
LIU Fang, JIANG Xiangping, CHEN Chao, et al. *J Chin Ceram Soc*, 2023, 48(3): 325–331.
- [12] WU X, LAU C M, KWOK K W. Photoluminescence properties of Er/Pr-doped $K_{0.5}Na_{0.5}NbO_3$ ferroelectric ceramics[J]. *J Am Ceram Soc*, 2015, 98(7): 2139–2145.
- [13] ZHANG Q W, SUN H Q, ZHANG Y. Polarization-induced photoluminescence quenching in $(Ba_{0.7}Ca_{0.3}TiO_3)-(BaZr_{0.2}Ti_{0.8}O_3)$: Pr ceramics[J]. *J Am Ceram Soc*, 2014, 97(3): 868–873.
- [14] YAO Q R, WANG F F, XU F, et al. Electric field-induced giant strain and photoluminescence-enhancement effect in rare-earth modified lead-free piezoelectric ceramics[J]. *ACS Appl Mater Interfaces*, 2015, 7(9): 5066–5075.
- [15] CAO W Q, LIU P Z, CHEN Y, et al. Effect of hysteresis of dipole on remnant polarization in ferroelectrics[J]. *Acta Phys Sin*, 2016, 65(13): 137701.
- [16] LIU G, ZHANG S J, JIANG W H, et al. Losses in ferroelectric materials[J]. *Mater Sci Eng R Rep*, 2015, 89: 1–48.
- [17] HAO X H, ZHAI J W, KONG L B, et al. A comprehensive review on the progress of lead zirconate-based antiferroelectric materials[J]. *Prog Mater Sci*, 2014, 63: 1–57.
- [18] PAN H, ZHU M L, BANYAS E, et al. Clamping enables enhanced electromechanical responses in antiferroelectric thin films[J]. *Nat Mater*, 2024, 23(7): 944–950.
- [19] ZHU M, XU M, PAN H, et al. In situ atomic-scale imaging unveils clamping-enhanced strain and phase transition pathways in antiferroelectric thin films[J]. *Microsc Microanalysis*, 2025, 31(Supplement_1): 1070–1072.
- [20] JIANG R J, CAO Y, GENG W R, et al. Atomic insight into the successive antiferroelectric-ferroelectric phase transition in antiferroelectric oxides[J]. *Nano Lett*, 2023, 23(4): 1522–1529.
- [21] QIAO H M, ZHUO F P, LIU Z, et al. Local probing of the non-uniform distribution of ferroelectric and antiferroelectric phases[J]. *Nano Res*, 2023, 16(2): 3021–3027.
- [22] SHANNON R D. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides[J]. *Acta Crystallogr Sect A*, 1976, 32(5): 751–767.
- [23] ZHAO L, GAO J, LIU Q, et al. Silver niobate lead-free antiferroelectric ceramics: Enhancing energy storage density by B-site doping[J]. *ACS Appl Mater Interfaces*, 2018, 10(1): 819–826.
- [24] IBRAHIM F A, EL-DESOKY M M. Erbium-doped $(Pb_{0.9}-Er_{0.01}-Zr_{0.09})$ and $(Pb_{0.9}-Er_{0.01}-Zr_{0.045}-Ti_{0.045})$ nano-crystalline films and nano-rods ceramic synthesis by sol-gel technique for energy-storage application[J]. *Sci Rep*, 2023, 13(1): 4192.
- [25] KATAYAMA R, SAKATA T. Effect of surface modification on the fundamental electrical characteristics of solution-gated indium tin oxide-based thin-film transistor fabricated by one-step sputtering[J]. *Langmuir*, 2023, 39(12): 4282–4290.
- [26] LEE K B, CHO J, KIM D, et al. $RbNO_3$ wet chemical treatment for contact engineering and enhanced performance of a-IGTO TFTs with improved stability[J]. *ACS Appl Mater Interfaces*, 2025, 17(32): 45874–45887.
- [27] PUSHPENDRA, KUNCHALA R K, KALIA R, et al. Excitation dependent visible and NIR photoluminescence properties of Er^{3+} , Yb^{3+} co-doped $NaBi(MoO_4)_2$ nanomaterials[J]. *RSC Adv*, 2020, 10(25): 14525–14530.
- [28] LAVANYA D R, RADHA KRUSHNA B R, MANJUNATHA K, et al. Enhanced down-conversion emission, high-level security, and advanced latent fingerprint visualization in $La_2Zr_2O_7$: Er^{3+} nanophosphor through surface modification and deep learning analysis[J]. *ACS Appl Opt Mater*, 2024, 2(6): 1094–1116.
- [29] RUAN D, HUANG Z Y, TANG Z, et al. Bi^{3+} -sensitized $La_2Zr_2O_7$: Er^{3+} transparent ceramics with efficient up/down-conversion luminescence properties for photonic applications[J]. *J Phys Chem C*, 2020, 124(1): 913–920.
- [30] LU Y, ZHAO T, YE L, et al. Polymer-derived Er^{3+} -doped $La_2Zr_2O_7$ nanocrystals: Synthesis, microstructure and photoluminescence[J]. *Mater Sci Technol*, 2020, 36(18): 1930–1935.
- [31] KLINKOV V A, SEMENCHA A V. Time-resolved spectroscopy of 4 $S_3/2$ energy state in Er^{3+} -doped fluoroaluminate glass in a wide temperature range[J]. *Phys Status Solidi B*, 2021, 258(11): 2100285.
- [32] SINGH V, RAI V K, LEDOUX-RAK I, et al. NIR to visible up-conversion, infrared luminescence, thermoluminescence and defect centres in Y_2O_3 :Er phosphor[J]. *J Phys D Appl Phys*, 2009, 42(6): 065104.
- [33] KUMADA A, TODA G, OTOMO Y. An electrooptic image storage device using field induced reversible transitions between AFE and FE phases of PLZT ceramics[J]. *Ferroelectrics*, 1974, 7(1): 367–369.
- [34] HU Z, HUANG X J, YANG Z W, et al. Reversible 3D optical data storage and information encryption in photo-modulated transparent glass medium[J]. *Light-Sci Appl*, 2021, 10(1): 140.
- [35] TANABE S, OHYAGI T, SOGA N, et al. Compositional dependence

- of Judd-Ofelt parameters of Er^{3+} ions in alkali-metal borate glasses[J]. Phys rev B, Condens matter, 1992, 46(6): 3305–3310.
- [36] OFELT G S. Intensities of crystal spectra of rare-earth ions[J]. Chem Phys, 1962, 37(3): 511–520.
- [37] LU H Y, GAO Y C, HAO H Y, et al. Judd-Ofelt analysis and temperature dependent upconversion luminescence of $\text{Er}^{3+}/\text{Yb}^{3+}$ codoped $\text{Gd}_2(\text{MoO}_4)_3$ phosphor[J]. J Lumines, 2017, 186: 34–39.
- [38] WANG Y M, WANG X L, MAO Y B, et al. Impact of Sc^{3+} -modified local site symmetries on Er^{3+} ion upconversion luminescence in Y_2O_3 nanoparticles[J]. J Phys Chem C, 2022, 126(28): 11715–11722.
- [39] JIA H, JIANG H M, CHEN Z, et al. Near-infrared light-induced photoresponse in $\text{Er}^{3+}/\text{Li}^{+}$ -codoped $\text{Y}_2\text{O}_3/\text{poly}(\text{methyl methacrylate})$ composite film[J]. J Phys Chem Lett, 2022, 13(15): 3470–3478.
- [40] SUN L W, LI X Q, SONG L, et al. Temperature-dependent surface plasmon enhanced photoluminescence in CsPbBr_3 thin film[J]. Phys Lett A, 2022, 422(6): 127795.
- [41] ZHENG M, SUN H L, CHAN M K, et al. Reversible and nonvolatile tuning of photoluminescence response by electric field for reconfigurable luminescent memory devices[J]. Nano Energy, 2019, 55: 22–28.
- [42] ZHENG M, YANG J, ZHANG Y X, et al. Controllable and reversible electric field tuning of photoluminescence response in lanthanide ions doped ferroelectric films[J]. Appl Mater. Today, 2024, 38(7): 102209.
- [43] LIU N N, ZHAO Z E, GAO W X, et al. Giant modulation of photoluminescence in CsPbBr_3 films through polarization switching of PMN–PT[J]. Appl Phys Lett, 2021, 119(25): 6.
- [44] WANG F, LIU D, CHEN Z, et al. *In situ* reversible tuning of photoluminescence of an epitaxial thin film via piezoelectric strain induced by a $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ – PbTiO_3 single crystal[J]. J Mater Chem. C, 2017, 5(35): 9115–9120.
- [45] WU Z, ZHANG Y, BAI G, et al. Effect of biaxial strain induced by piezoelectric PMN–PT on the upconversion photoluminescence of $\text{BaTiO}_3:\text{Yb}/\text{Er}$ thin films[J]. Opt Express, 2014, 22(23): 29014–29019.
- [46] CRACIUN F, CORDERO F, CIUCHI I V, et al. Refining the phase diagram of $\text{Pb}_{1-x}\text{La}_x(\text{Zr}_{0.9}\text{Ti}_{0.1})_{1-x/4}\text{O}_3$ ceramics by structural, dielectric, and anelastic spectroscopy investigations[J]. J Appl Phys, 2015, 117(18): 184103.
- [47] 梁岑, 李伟, 楚丙凯, 等. Sm/Sb 共掺 $(\text{Bi}_{0.5}\text{Na}_{0.5})_{0.935}\text{Ba}_{0.065}\text{TiO}_3$ 陶瓷的电致应变与光致发光特性[J]. 硅酸盐学报, 2020, 48(3): 351–355.
- LIANG Cen, LI Wei, CHU Bingkai, et al. J Chin Ceram Soc, 2020, 48(3): 351–355.
- [48] BREWER A, LINDEMANN S, WANG B, et al. Microscopic piezoelectric behavior of clamped and membrane (001)PMN–30PT thin films[J]. Appl Phys Lett, 2021, 119(20): 202903.

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高 畅: 设计研究方法/实验方案/模型算法、绘制图表、撰写初稿
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 吴世喆: 软件使用、项目管理
 裴家杰: 提供资源、获取资助
 徐泽东: 监督指导、获取资助
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 林 枫: 提供资源、获取资助、项目管理、监督指导
 高 旻: 论文构思、设计研究方法/实验方案/模型算法、监督指导、

审阅与修订

Anomalous Electric-Field-Modulation of Photoluminescence in Er^{3+} -Doped Antiferroelectric $\text{Pb}_{0.98}\text{La}_{0.02}\text{Zr}_{0.95}\text{Ti}_{0.05}\text{O}_3$ Thin Films

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Extended Abstract

Introduction The photoluminescence (PL) of rare-earth-doped materials is predominantly controlled by the local crystal field symmetry around rare-earth ions. Using electric fields (E) to modify the PL properties is particularly intriguing as it is compatible with modern electronics and is promising for advanced applications in optical information storage and communication. It is reported that the E -induced structural evolution in host ferroelectrics (FEs) can effectively manipulate the crystal field environment surrounding rare-earth ions, consequently enabling a dynamic modulation of PL intensity (*i.e.*, the E –PL effect). However, the hysteresis behavior in FEs limits the PL modulation range. Antiferroelectrics (AFEs) show a reversible AFE–FE phase transform with zero remanent polarization, particularly promising for realizing reversible E –PL modulation with large tunability. In AFE thin films, the clamping effect from the substrate may exert a significant influence on the structural evolution during the E –induce phase transition. Therefore, compared with the ceramic forms, it is possible to analyze distinct E –PL behavior in rare-earth doped AFE thin films.

Methods 1% Er^{3+} -doped $\text{Pb}_{0.98}\text{La}_{0.02}\text{Zr}_{0.95}\text{Ti}_{0.05}\text{O}_3$ (PLZT–Er) thin films were prepared on Pt/Ti/SiO₂/Si substrates by a sol–gel/spin-coating method with lead acetate trihydrate ($\text{PbC}_4\text{H}_6\text{O}_4 \cdot 3\text{H}_2\text{O}$, 99.99%(379.33), Aladdin Co., China), lanthanum nitrate hexahydrate ($\text{LaN}_3\text{O}_9 \cdot 6\text{H}_2\text{O}$, 99%(433.03), Aladdin Co., China), erbium trinitrate pentahydrate ($\text{Er}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, 99.9%(443.37), Aladdin Co., China), zirconium propoxide ($\text{C}_{12}\text{H}_{28}\text{O}_4\text{Zr}$, 70%(327.56), Aladdin Co., China), and titanium butoxide ($\text{C}_{16}\text{H}_{36}\text{O}_4\text{Ti}$, $\geq 99.0\%$ (340.32), Aladdin Co., China) as the raw materials. The crystal structure was characterized by X-ray diffraction (XRD, Ultima

III, Rigaku Co., Japan). The surface morphology was observed using atomic force microscopy (AFM, ICON, Bruker Co., Germany). The polarization (P - E) and current (I - E) loops were measured by a ferroelectric analyzer (AIX ACT, TF2000) at 1 kHz. The down-conversion photoluminescence (DCPL) emission spectra were measured by fluorescence spectroscopy (ULS2048x64TEC, Avantes Co., the Netherlands) under 405 nm and 532 nm laser excitation. For the E -PL tests, 20 nm-thick transparent indium tin oxide (ITO) top electrodes were deposited on the surfaces of PLZT-Er thin film by magnetron sputtering in argon atmosphere (2.0 Pa) at 320 W.

Results and discussion The structural, PL, and E -PL properties of PLZT-Er AFE thin films are systematically investigated. The XRD patterns confirm a pure perovskite structure with a lattice shrinkage due to the substitution of Er^{3+} at A-sites, whereas the AFM analysis reveals a smooth surface with a roughness of approximately 3 nm. The double P - E loop and characteristic I - E peaks verify the AFE nature of PLZT-Er thin films, with reversible AFE $\rightarrow$ FE transitions at $\pm 452 \text{ kV}\cdot\text{cm}^{-1}$ and FE $\rightarrow$ AFE transitions at $\pm 199 \text{ kV}\cdot\text{cm}^{-1}$. Under 405 nm excitation, the PLZT-Er exhibits 487 nm ($^4\text{F}_{7/2}\rightarrow^4\text{I}_{15/2}$) and 610 nm ($^4\text{F}_{9/2}\rightarrow^4\text{I}_{15/2}$) emissions, whereas an excitation at 532 nm induces 560 nm ($^4\text{S}_{3/2}\rightarrow^4\text{I}_{15/2}$), 660 nm ($^4\text{F}_{9/2}\rightarrow^4\text{I}_{15/2}$), and 850 nm ($^4\text{S}_{3/2}\rightarrow^4\text{I}_{13/2}$) emissions, all originating from efficient energy transfer and relaxation of Er^{3+} ions. The results of E -PL tests demonstrate a remarkable reversible modulation. In $830 \text{ kV}\cdot\text{cm}^{-1}$, the emission at 487 nm shows an 85.14% reduction, with stable switching over six cycles. This performance outperforms PLZT-Er ceramics (+30% modulation) and most reported FE/AFE materials, which is attributed to their higher breakdown strength. The opposite E -PL tuning compared to PLZT-Er ceramics is explained by increased local crystal field symmetry around Er^{3+} ions, arising from either substrate clamping-induced antiferroelectric orthorhombic $\rightarrow$ ferroelectric orthorhombic phase transition or incomplete ferroelectric $\rightarrow$ antiferroelectric transition in an insufficient electric field. These findings highlight the PLZT-Er thin films as promising candidates for optical information storage and communication devices.

Conclusions Er^{3+} -doped $\text{Pb}_{0.98}\text{La}_{0.02}\text{Zr}_{0.95}\text{Ti}_{0.05}\text{O}_3$ (PLZT-Er) thin films exhibited a reversible electric-field-modulated photoluminescence (E -PL) effect. Under 405 nm laser excitation, a PL reduction of $\sim 85\%$ could be achieved in an applied electric field of $830 \text{ kV}\cdot\text{cm}^{-1}$. This negative E -PL tuning trend was anomalously opposite to that in bulk PLZT-Er ceramics. Two potential mechanisms could be proposed to explain this anomalous phenomenon, *i.e.*, either the antiferroelectric orthorhombic (AFE_o) to ferroelectric orthorhombic (FE_o) phase transition or the incomplete ferroelectric (FiE) to antiferroelectric (AFE) phase transition in PLZT-Er thin films could increase the local crystal field symmetry around Er^{3+} ions.

Keywords rare-earth doping; photoluminescence; electric-field-modulation; phase transition; thin films