

稀土 Dy/Eu 掺杂对铌酸钾钠基压电陶瓷结构与性能的影响

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摘 要: 采用传统固相合成法制备了稀土(Dy/Eu)掺杂的 $0.96(\text{K}_{0.48}\text{Na}_{0.52})(\text{Nb}_{0.95}\text{Sb}_{0.05})\text{O}_3-0.04\text{Bi}_{0.5}(\text{Na}_{0.82}\text{K}_{0.18})_{0.5}\text{ZrO}_3$ 无铅压电陶瓷, 系统研究了 Dy/Eu 对其结构和电学性能的影响。结果表明, Dy/Eu 的引入促使陶瓷的相结构由菱方-四方共存相逐步向立方相结构转变。适量的掺杂有效提升材料的铁电性能与电致应变性能, 其中: 0.10%(摩尔分数)Dy 和 0.05%Eu 掺杂的样品在 70 kV/cm 电场下的单向应变 S_{uni} 分别达 0.257% 和 0.241%, 对应的压电应变系数 d_{33}^* 分别为 367 pm/V 和 344 pm/V。同时, 0.05%Dy 和 0.05%Eu 掺杂样品在 25~100 °C 温度区间的电致应变波动幅度小于 10%, 表现出优异的温度稳定性, 在压电驱动器方面展现出良好应用前景。此外, 稀土 Dy/Eu 掺杂还使陶瓷具备优异的光致发光特性: 在蓝光激发下, Dy^{3+} 掺杂样品呈现强黄光发射, 而 Eu^{3+} 掺杂样品则发出明亮的橙红色光。该材料兼具电学性能与发光特性, 在光电耦合器件中具有潜在的应用价值。

关键词: 无铅压电陶瓷; 铌酸钾钠; 电致应变性能; 温度稳定性

中图分类号: TM282 文献标志码: A 文章编号: 0454-5648(2026)06-1937-08

网络出版时间: 2026-05-13



压电陶瓷材料在传感和能量转换器件中扮演着关键角色, 广泛应用于驱动、能量转换/存储和微机电系统等领域。然而, 目前商用的压电陶瓷体系仍以 $\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PZT) 为代表的含铅陶瓷为主^[1], 该类材料在制备、加工与废弃过程中, 其所含超过 60% 的有毒铅元素易向环境释放, 造成严重污染, 与全球可持续发展的战略目标相悖。为此, 研究者们高度重视无铅压电材料的开发, 致力于寻找环境友好的替代材料体系^[2-4]。

在众多无铅压电陶瓷体系中, $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ (KNN) 基压电材料不仅具备与 PZT 相媲美的高驱动电压和大电致应变, 同时, 还表现出低的滞后与能量损耗, 在精密驱动器领域展现出重要应用价值。长久以来, 多晶型相界构建与微结构调控成为提升 KNN 基电致应变性能的主要途径^[5,6]。研究报道显示, 多种掺杂策略能有效调控 KNN 基陶瓷的结构与性能。无论是离子掺杂^[7-9]与氧化物掺杂^[10-12], 还是钙钛矿组元复合^[13-18], 均能将其相变温度调整至

室温附近, 从而在体系中构建出正交-四方(O-T)、菱方-四方(R-T)和菱方-正交-四方(R-O-T)多晶型相界, 进而显著增强材料的压电与电致应变性能。近期研究表明, 构筑缺陷偶极子是提升电场诱导应变的有效途径^[19,20]。A/B 位掺杂形成的缺陷偶极子, 其方向与铁电畴自发极化一致时, 可直接增强电致应变; 同时, 它会在畴内形成内电场, “硬化”铁电畴。比如, 通过 B 位掺杂(Cu^+ , Fe^{2+}), 辅以 Ar 气氛烧结, 在 KNN 中诱导形成 $(\text{FeNb}^{\text{III}}-\text{V}_{\text{O}}^{\bullet})'$ 与 $(\text{CuNb}^{\text{III}}-\text{V}_{\text{O}}^{\bullet})''$ 缺陷偶极子, 实现了优异电致应变性能^[21]; A 位 Sr^{2+} 掺杂则在 $[\text{K}_{0.5(1-x)}\text{Na}_{0.5(1-x)}\text{Sr}_x]\text{NbO}_3$ 中构建了 $\text{V}_{\text{K/Na}}'-\text{V}_{\text{O}}^{\bullet}$ 缺陷偶极子, 获得巨大电致应变^[22]。尽管掺杂大幅度提升了 KNN 基陶瓷的压电性能, 但也导致了其温度稳定性的恶化。因此, 仍需通过进一步改性来赋予 KNN 基陶瓷实际应用所需的温度稳定性。

稀土离子是调控 KNN 基压电材料电致应变性能的有效改性剂^[23-26], 稀土离子可有效提高 KNN

收稿日期: 2025-12-06。 修订日期: 2026-01-04。

基金项目: 山东省自然科学基金(ZR2025MS781, ZR2024ME2013)。

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Received date: 2025-12-06. Revised date: 2026-01-04.

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基陶瓷的弛豫性,同时,将陶瓷低温区的 O-T 转变区域移至室温以下,从而对陶瓷的温度稳定性进行优化。同时,由于稀土离子属于典型的发光活性离子,其凭借自身丰富的能级结构与长寿命激发态,在掺杂后能赋予材料丰富的吸收和荧光发射光谱。近年来,利用稀土掺杂策略,在 KNN 基铁电材料中同步实现电致应变性能增强与发光行为,对于开发新一代光电集成和耦合器件具有重要研究价值。

本工作选择具有多晶型相变特征的 $0.96(\text{K}_{0.48}\text{Na}_{0.52})(\text{Nb}_{0.95}\text{Sb}_{0.05})\text{O}_3-0.04\text{Bi}_{0.5}(\text{Na}_{0.82}\text{K}_{0.18})_{0.5}\text{ZrO}_3(0.96\text{KNNS}-0.04\text{BNKZ})$ 陶瓷为基体^[27],选择稀土氧化物 Dy_2O_3 和 Eu_2O_3 为改性剂,系统研究了稀土氧化物掺杂对 $0.96\text{KNNS}-0.04\text{BNKZ}$ 陶瓷的结构、铁电/电致应变性能以及光致发光性能的影响。一方面, Dy/Eu 掺杂可通过诱导晶格畸变,调控多晶型相变行为,从而优化材料的电致应变性能与温度稳定性;另一方面, Dy 与 Eu 作为高效发光中心,赋予陶瓷显著的光致发光特性。该工作旨在通过稀土一掺杂策略,在无铅压电陶瓷中实现电-光多功能特征。

1 实验

1.1 样品制备

以 K_2CO_3 (99%)、 Na_2CO_3 (99.8%)、 Nb_2O_5 (99.96%)、 Sb_2O_3 (99%)、 Bi_2O_3 (99.5%)、 ZrO_2 (99%)、 Eu_2O_3 (99.9%)、 Dy_2O_3 (99.9%) 等为原料,采用传统固相反应法制备了 $0.96\text{KNNS}-0.04\text{BNKZ}-x$ (摩尔分数)%Dy/Eu (简写为 $x\%\text{Dy}/\text{Eu}$, $x=0, 0.05, 0.10, 0.20, 0.40$) 无铅铁电陶瓷。根据化学计量比计算各原料所需要的用量,将原料经精准称量后放入球磨罐中,以氧化锆球作为球磨介质、无水乙醇作为分散剂在行星式球磨机中球磨 24 h。将浆料烘干后得到的粉料压制成药片并在 $850\text{ }^\circ\text{C}$ 煅烧 4 h 合成前驱体粉末,随后将粉末进行 2 次球磨 24 h。待粉料干燥后,添加质量分数为 10% 的聚乙烯醇黏结剂,经造粒后压制直径 10 mm、厚度 0.5 mm 的生坯片。经 $550\text{ }^\circ\text{C}$ 排除黏结剂后,在 $1130\sim 1200\text{ }^\circ\text{C}$ 保温 2 h 得到陶瓷样品。稀土 Dy/Eu 掺杂促使陶瓷的最佳烧结温度逐渐升高:未掺杂(0%)时为 $1130\text{ }^\circ\text{C}$,掺杂量为 0.05%、0.10%、0.20% 和 0.40% 时,分别升高至 1160 、 1170 、 $1180\text{ }^\circ\text{C}$ 和 $1200\text{ }^\circ\text{C}$ 。陶瓷样品经抛光后涂覆银浆在 $650\text{ }^\circ\text{C}$ 烧制形成电极,用于后续性能测试。

1.2 样品表征

采用 X 射线衍射仪(D8 advance)分析陶瓷样品

的物相结构。采用场发射扫描电子显微镜(Merlin compact, 德国 Carl Zeiss)观察陶瓷表面形貌。采用拉曼光谱仪(LabRAM HR800)对样品进行结构分析。采用宽频介电阻抗谱仪(Novocontrol Concept 40)测试样品的介电常数随温度的变化。采用铁电分析仪(TF 2000)联用激光干涉仪(SP-S 120/500)测试样品的铁电性能和电致应变性能。采用荧光光谱仪(FLS920)对陶瓷的光致发光性能进行分析。

2 结果与讨论

图 1 为 $x\%\text{Dy}$ 和 $x\%\text{Eu}$ 陶瓷的 XRD 谱和表面 SEM 照片。由图 1a 和图 1b 可以看出,所有样品均具有单一的钙钛矿结构,无明显的第二相衍射峰,表明 Dy_2O_3 和 Eu_2O_3 均固溶到 $0.96\text{KNNS}-0.04\text{BNKZ}$ 基体中。从样品 $2\theta=44^\circ\sim 47^\circ$ 范围的 XRD 谱可以看出,低含量($x\leq 0.10$)掺杂样品在 $2\theta=46^\circ$ 附近具有(002)/(200)衍射双峰,表明具有 R-T 共存的相结构^[27]。当 $x\geq 0.20$ 时,(002)/(200)衍射双峰逐渐合并为单一的(200)衍射峰,表明此时样品结构为伪立方(P_c)相^[26]。上述结果说明 Dy、Eu 的掺杂提高了材料晶体结构对称性。另外,随着 Dy、Eu 掺杂量的提高,衍射峰整体向高角度偏移,说明 Dy、Eu 掺杂导致晶胞收缩。在陶瓷高温烧结过程中,组分中 K^+ 、 Na^+ 、 Bi^{3+} 等 A 位离子的挥发会形成 A 位空位。由于 Dy^{3+} ($r=1.08\text{ }\text{\AA}$, CN=9)和 Eu^{3+} ($r=1.12\text{ }\text{\AA}$, CN=9)具有与空位相近的离子半径与配位数,易于通过扩散占据 A 空位,进而形成均一的固溶体。同时,由于 Dy^{3+} 、 Eu^{3+} 的离子半径显著小于 K^+ ($r=1.64\text{ }\text{\AA}$, CN=12)、 Na^+ ($r=1.39\text{ }\text{\AA}$, CN=12)与 Bi^{3+} ($r=1.17\text{ }\text{\AA}$, CN=8)离子半径,导致材料晶胞体积极收缩。

由图 1c 可以看出,所有陶瓷均表现出较为致密的显微结构,采用阿基米德排水原理测其体积密度为 $4.48\sim 4.53\text{ g}/\text{cm}^3$,相对密度达 96%~97%,表明陶瓷烧结充分、致密性良好。随着 Dy/Eu 掺杂量的增加,陶瓷的平均晶粒尺寸逐渐减小,说明稀土掺杂有效抑制了晶粒生长。这主要归因于以下 2 方面:一是烧结过程中产生的空位缺陷在晶界处聚集,阻碍晶界迁移;二是稀土掺杂提高了体系的液相点,导致所需烧结温度升高,在固相烧结过程中进一步细化了晶粒^[28]。

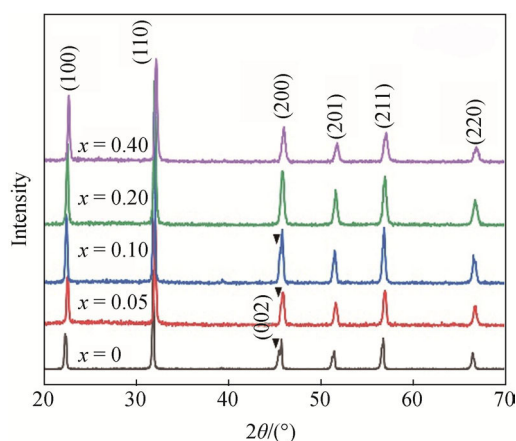
图 2 为 $x\%\text{Dy}$ 和 $x\%\text{Eu}$ 陶瓷的介电温谱、电滞回线与双向应变曲线。由图 2a 和图 2b 可以看出, $0.96\text{KNNS}-0.04\text{BNKZ}$ 基体在室温以上存在 2 个明

显的介电异常峰, 其中, 位于约 60°C 的峰对应于 R-T 相变($T_{\text{R-T}}$), 250°C 的峰对应于 T-C 相变(T_{C})。随着 Dy 和 Eu 掺杂含量的增加, $T_{\text{R-T}}$ 相变峰逐渐消失, 同时 T_{C} 相变峰明显展宽, 表明掺杂显著增强了体系的介电弛豫行为, 这一现象与陶瓷经掺杂后由 R-T 共存相转变为 P_{c} 相的结构演变密切相关。

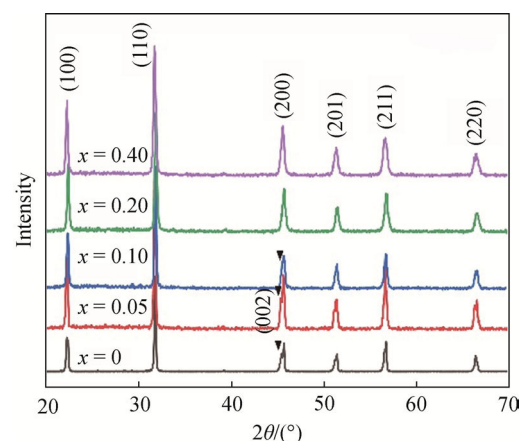
由图 2c 和图 2d 可见, 未掺杂样品($x=0$)呈现典型的铁电特性, 其电滞回线饱和良好, 具有较高的饱和极化强度(P_{max})与剩余极化强度(P_{r}), 且应变-电场(S - E)曲线呈“蝶”形并伴随明显的负向应变。适量掺杂(Dy, $x=0.10$; Eu, $x=0.05$)促使 P - E 曲线矩形度提高, P_{max} 与 P_{r} 同步上升, 表明材料的铁电性能进一步增强, 这与材料中 R-T 共存相的形成有关。然而, 过量掺杂($x \geq 0.20$)会明显削弱铁电性: P - E 曲线逐渐收缩为细长状, S - E 曲线则演变为回滞显著减小的“芽”状, 这源于 Dy/Eu 掺杂诱导晶体结构由 R-T 相向对称性更高的 P_{c} 相转变。当掺杂量达到 $x=0.40$ 时, 样品表现出近乎无负应变和低回滞的特征, 这与介电弛豫增强及电致伸缩效应主导应变

响应有关^[26]。

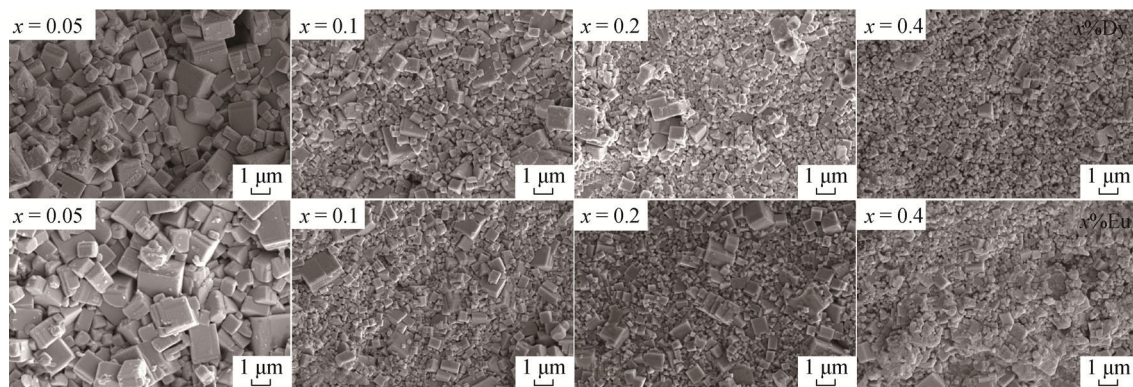
图 3 为 $x\%$ Dy 和 $x\%$ Eu 陶瓷的单向应变与压电应变系数。由图 3a 和图 3b 可见, 电致应变随掺杂量的变化规律与铁电性能密切相关: 适量的 Dy/Eu 掺杂通过增强铁电性提升了应变; 反之, 过量的掺杂会削弱铁电性, 从而导致应变性能下降。图 3c 为 $x\%$ Dy/Eu 陶瓷的 S_{uni} 与 d_{33}^* 随组分的变化。由图 3c 可见, S_{uni} 与 d_{33}^* 均随掺杂量 x 的增大先上升后下降, 并在一定掺杂量下取得最优值。其中, 0.10% Dy 和 0.05% Eu 掺杂的样品在 70 kV/cm 电场下的单向应变 S_{uni} 分别达 0.257% 和 0.241% , 对应的压电应变系数 $d_{33}^*(S_{\text{max}}/E_{\text{max}})$ 分别为 367 pm/V 和 344 pm/V , 这是由于适量掺杂 Dy/Eu 后, 材料发生一定程度的晶格畸变, 优化了材料内部的电畴结构, 从而使电畴更易响应外部电场, 进而增强了铁电性能和电致应变性能; 而过量掺杂 Dy/Eu 元素后, 会导致晶格畸变(氧八面体畸变)进一步增大, 进而钉扎电畴, 阻碍电畴在电场下的翻转和排列, 导致材料的铁电性能和电致应变性能降低。



(a) XRD patterns of $x\%$ Dy



(b) XRD patterns of $x\%$ Eu



(c) SEM images of $x\%$ Dy and $x\%$ Eu

图 1 $x\%$ Dy 和 $x\%$ Eu 陶瓷的 XRD 谱和表面 SEM 照片

Fig. 1 XRD patterns and SEM images of $x\%$ Dy and $x\%$ Eu ceramics

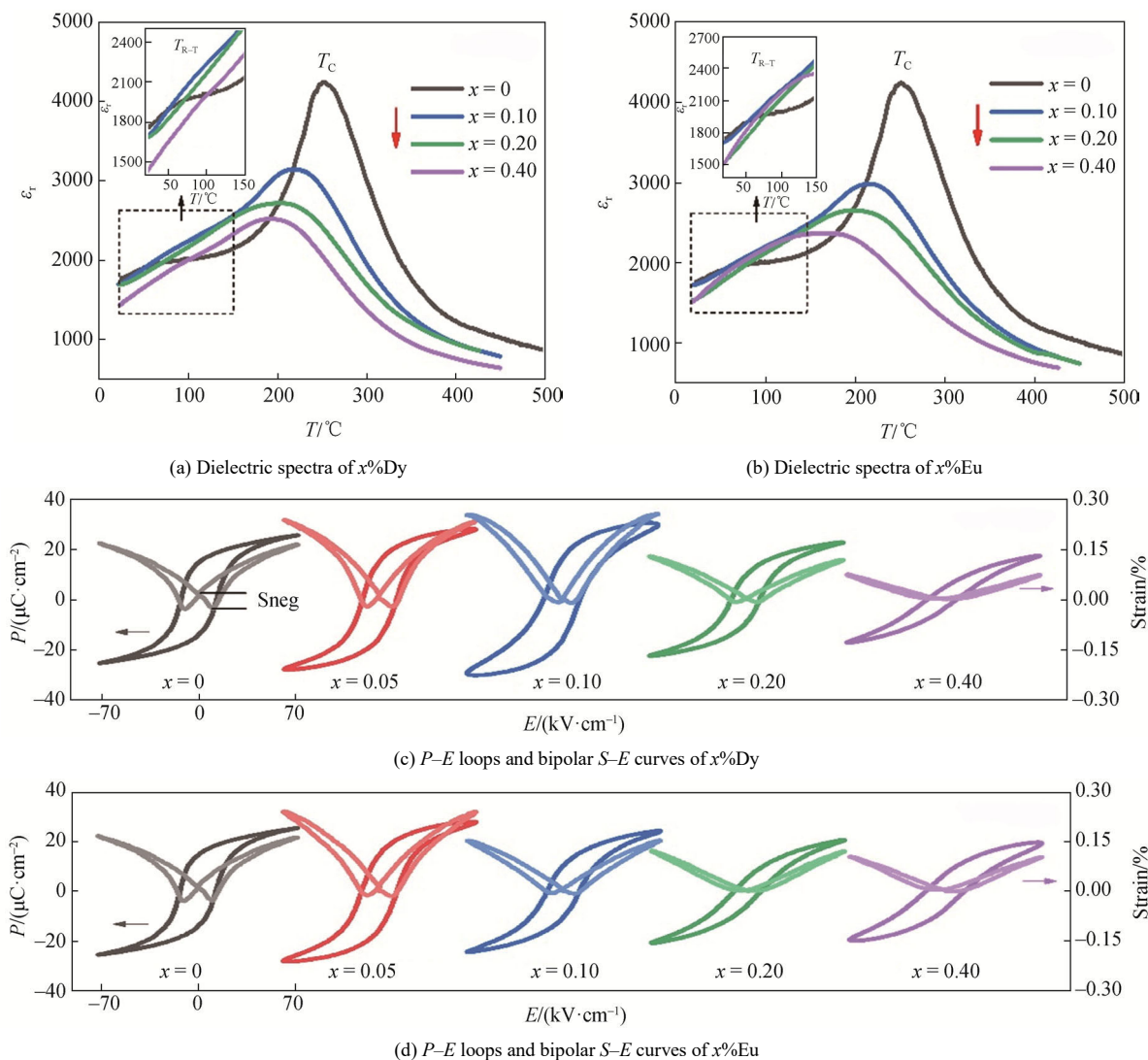


图 2 $x\% \text{Dy}$ 和 $x\% \text{Eu}$ 陶瓷的介电温谱、电滞回线与双向应变曲线
Fig. 2 Dielectric spectra, P - E loops and bipolar S - E curves of $x\% \text{Dy}$ and $x\% \text{Eu}$ ceramics

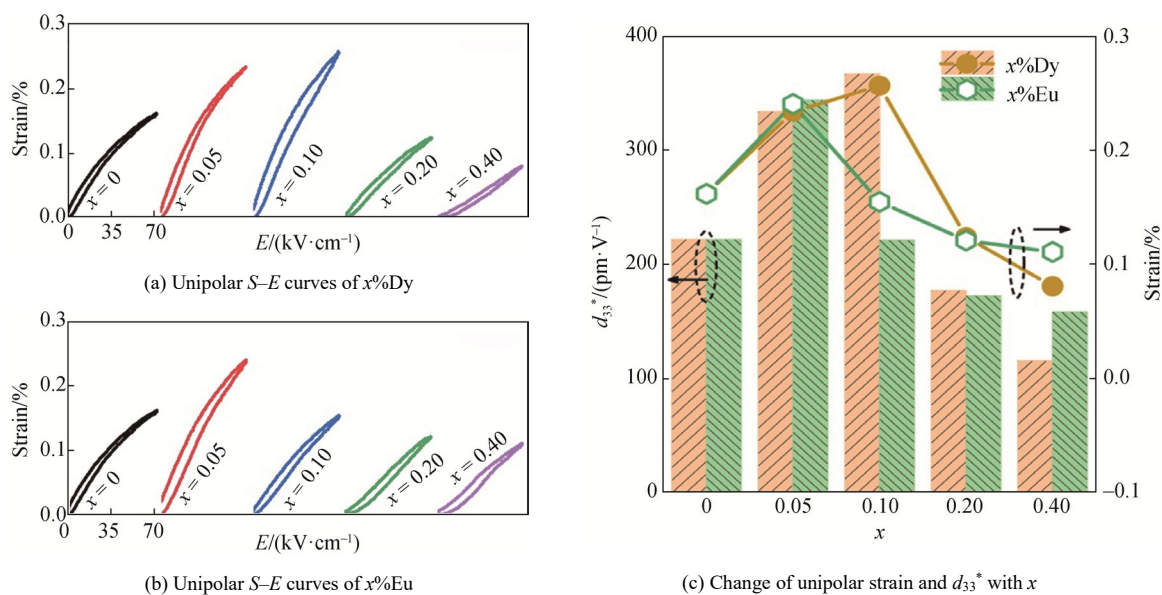


图 3 $x\% \text{Dy}$ 和 $x\% \text{Eu}$ 陶瓷的单向应变与压电应变系数
Fig. 3 Unipolar S - E curves and d_{33}^* values of $x\% \text{Dy}$ and $x\% \text{Eu}$ ceramics

图 4 为 0.05%Dy 和 0.05%Eu 陶瓷在不同温度下的单向应变与压电应变系数。由图 4 可以看出, 材料的应变值随温度升高虽略有降低, 但在 160 °C 时仍保持较高水平(>0.16%)。这表明陶瓷在宽温度区间内的电畴随电场的转向能力未随温度升高明显退化, 电致应变的热稳定性优异, 其中, 0.05%Dy 掺杂样品在 20~100 °C 范围内, d_{33}^* 始终高于 330 pm/V,

较室温值仅衰减 7.1%; 即使温度升至 160 °C, d_{33}^* 仍能保持在 292 pm/V, 衰减率为 17.5%。与此同时, 0.05%Eu 掺杂样品也展现出类似的高温稳定性, 其在 20~100 °C 区间的 d_{33}^* 维持在 327 pm/V 以上, 衰减率为 8.8%; 在 160 °C 时, d_{33}^* 为 280 pm/V, 较室温衰减 21.9%。0.05%Dy 和 0.05%Eu 陶瓷表现出优异的高温稳定性, 其稳定性与铅基 PZT 陶瓷相当^[1,29]。

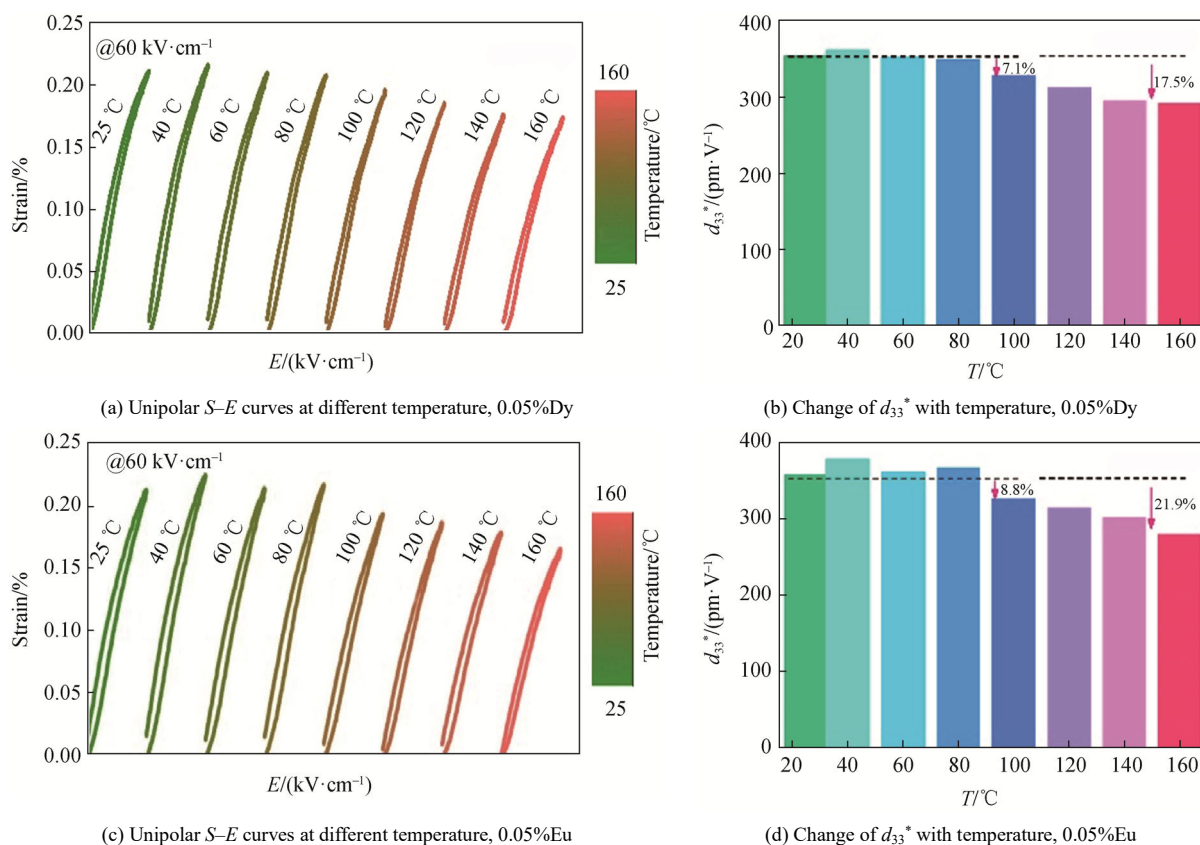


图 4 0.05%Dy 和 0.05%Eu 陶瓷的单向应变与压电应变系数
Fig. 4 Unipolar $S-E$ curves and d_{33}^* values of 0.05%Dy and 0.05%Eu ceramics

本工作通过 Dy/Eu 掺杂, 在优化 KNN 陶瓷电致应变性能的同时, 实现了材料的光致发光性能。图 5a 为 0.05%Dy 陶瓷的 PLE 光谱, 图 5b 为不同组分 $x\%$ Dy 陶瓷的 PL 光谱(激发波长 $\lambda_{ex}=452$ nm)。由图 5a 可以看出, PLE 光谱在 389、428、452 nm 和 474 nm 处有 4 个激发峰, 分别对应于从基态 $^6H_{15/2}$ 到激发态 $^4K_{17/2}$ 、 $^4G_{11/2}$ 、 $^4I_{15/2}$ 和 $^4F_{9/2}$ 的能级跃迁^[30,31]。由图 5b 可以看出, 在 452 nm 波长激发下, 样品产生 3 个发射峰, 位于 482、574 nm 和 662 nm 处, 分别对应于 $^4F_{9/2} \rightarrow ^6H_{15/2}$ 的弱蓝光发射、 $^4F_{9/2} \rightarrow ^6H_{13/2}$ 的强黄光发射和 $^4F_{9/2} \rightarrow ^6H_{11/2}$ 的弱红光发射^[30], 综合分析, 样品表现出强烈的黄色发光, 其 CIE 色度坐标位于黄色区域。增加 Dy 掺

杂量并未引起 PL 峰的显著位移, 但由于 Dy^{3+} 发光中心数量的直接贡献, 光致发光强度呈现持续增强的趋势。

由图 5c 和图 5d 可以看出, PLE 光谱在 465、526 nm 和 535 nm 处的激发峰, 分别对应于从基态 $^7F_0$ 到激发态 $^5D_2$ 、 $^5D_1$ 和 $^5D_0$ 的能级跃迁。在 526 nm 波长激发下, 样品产生 4 个发射; 位于 592 nm 和 615 nm 波长处的 $^5D_0 \rightarrow ^7F_j (j=1, 2)$ 能级跃迁, 为强橙光发射; 650~700 nm 范围的发射峰对应 $^5D_0 \rightarrow ^7F_j (j=3, 4)$ 能级跃迁, 为红光发射^[32]。所有样品均呈现强烈的红色发光, 其 CIE 色度坐标位于红色区域。此外, 随着 Eu^{3+} 掺杂量的增加, 光致发光强度呈现显著增强的趋势。

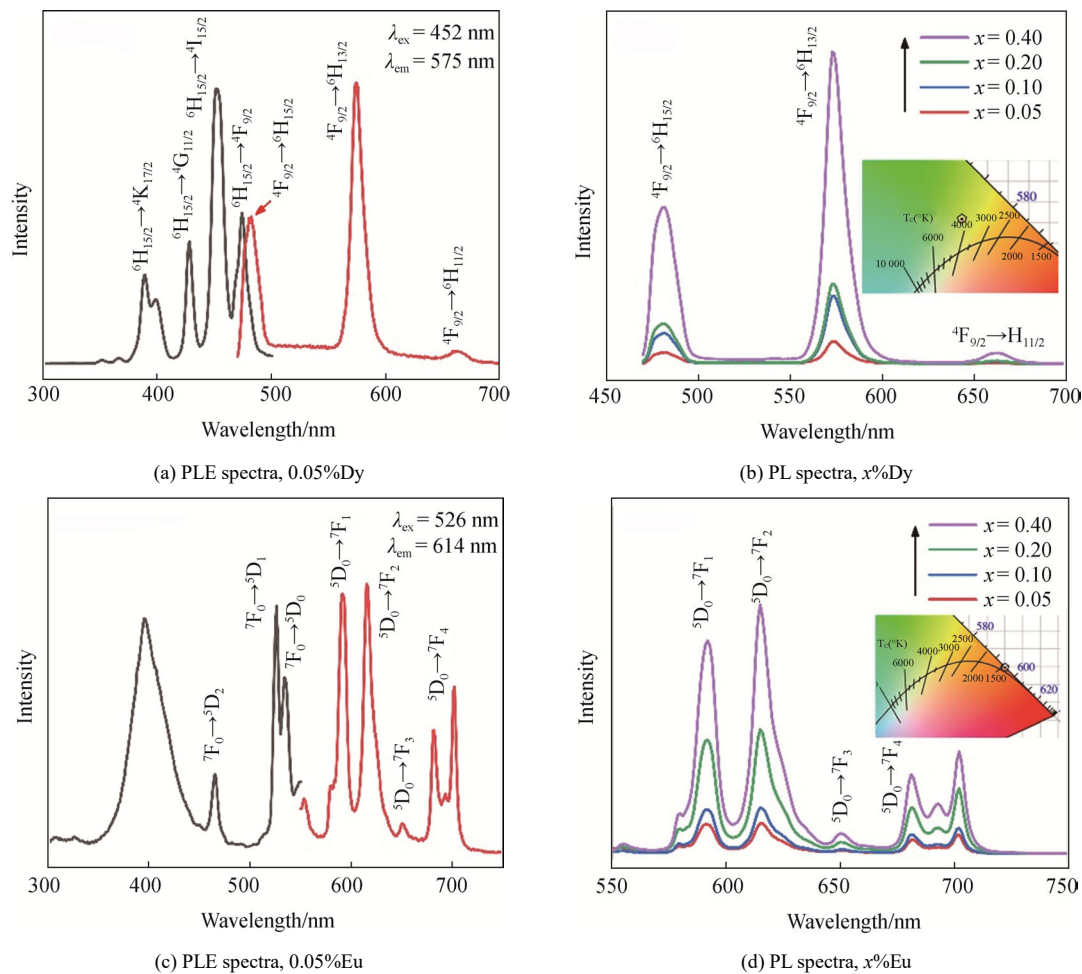


图5 $x\%$ Dy 和 $x\%$ Eu 陶瓷光致发光性能
Fig. 5 Photoluminescent properties of $x\%$ Dy and $x\%$ Eu ceramics

3 结论

Dy/Eu 的引入使 0.96KNNS–0.04BNKZ 陶瓷的相结构由 R–T 共存相向 P_r 相结构转变,促进了材料与铁电电致应变性能的提升。其中 0.10%Dy 和 0.05%Eu 掺杂的样品单向应变 S_{uni} 分别达 0.257% 和 0.241%, 对应的 d_{33}^* 分别为 367 pm/V 和 344 pm/V, 同时该样品展现出优异的温度稳定性, 在压电驱动器方面展现出良好应用前景。在光学性能方面, Dy/Eu 掺杂使陶瓷具备显著的光致发光特性: 在蓝光激发下, Dy^{3+} 掺杂样品呈现强黄光发射, 而 Eu^{3+} 掺杂样品则发出明亮的橙红色光。该材料兼具优异的电学性能与发光特性, 在未来光电耦合器件中具有潜在的应用价值。

参考文献:

- [1] SAITO Y, TAKAO H, TANI T, et al. Lead-free piezoceramics[J]. Nature, 2004, 432(7013): 84–87.
- [2] PUNETHA P, ADHIKARY G D, SENYSHYN A, et al. Short-Range Structural Correlations and Property Anomalies in Non-MPB Compositions of the Pb-Free Piezoelectric $Na_{0.5}Bi_{0.5}TiO_3$ – $K_{0.5}Bi_{0.5}TiO_3$ [J]. ACS Appl Mater Interfaces, 2025, 17(22): 32615–32624.
- [3] XI K B, WANG H Y, HUANG S C, et al. Thermally stable piezoelectric properties of lead-free ceramics featuring polar topological domains[J]. Acta Mater, 2025: 121152.
- [4] HAO J G, LI W, ZHAI J W, et al. Progress in high-strain perovskite piezoelectric ceramics [J]. Mater Sci Eng R, 2019, 135: 1–57.
- [5] WU J X, XIAO D Q, ZHU J G. Potassium-sodium niobate lead-free piezoelectric materials: past, present, and future of phase boundaries[J]. Chem Rev, 2015, 115(7): 2559–2595.
- [6] LV X, ZHU J G, XIAO D Q, et al. Emerging new phase boundary in potassium sodium–niobate based ceramics[J]. Chem Soc Rev, 2020, 49(3): 671–707.
- [7] HAO J G, Xu Z J, CHU R Q. et al. Bright reddish-orange emission and good piezoelectric properties of Sm_2O_3 -modified $(K_{0.5}Na_{0.5})NbO_3$ -based lead-free piezoelectric ceramics[J]. J Appl Phys, 2015, 117, 194104.
- [8] ZHOU J J, LI J F, CHENG L Q. et al. Addition of small amounts of $BiFeO_3$ to $(Li,K,Na)(Nb,Ta)O_3$ lead-free ceramics: Influence on phase structure, microstructure and piezoelectric properties[J]. J Eur Ceram Soc, 2012, 32(13), 3575–3582.

- [9] LIU H, YANG Z Q, Su B. et al. High temperature-insensitive electrostrain obtained in (K, Na)NbO₃-based lead-free piezoceramics[J]. *Small*, 2024, 20(51), 2407848.
- [10] LI R C, ZENG Y S, SUN X X, et al. Multidimensional synergy-induced high piezoelectricity and reliability KNN piezoceramics for high-frequency ultrasonic transducers[J]. *Sci China Mater*, 2023, 66(2): 686–695.
- [11] XIE Y N, XING J, TAN Z, et al. High mechanical quality factor and piezoelectricity in potassium sodium niobate ceramics[J]. *Ceram Int*, 2022, 48(5): 6565–6573.
- [12] CEN Z Y, CAO F Z, FENG M Y, et al. Simultaneously improving piezoelectric strain and temperature stability of KNN-based ceramics *via* defect design[J]. *J Eur Ceram Soc*, 2023, 43(3): 939–946.
- [13] WANG R P, WANG K, YAO F Z, et al. Temperature Stability of Lead-Free Niobate Piezoceramics with Engineered Morphotropic Phase Boundary[J]. *J Am Ceram. Soc*, 2015, 98(7): 2177–2182.
- [14] SUTAPUN M, MUANGHLUA R, VITTAYAKORN N. Phase transition, dielectric and piezoelectric properties of lead-free piezoelectric (K_{1/2}Na_{1/2})NbO₃-Bi(Zn_{2/3}Nb_{1/3})O₃ ceramics[J]. *Ferroelectrics*, 2016, 490(1): 1–12.
- [15] XIE L X, CHEN H, XIE Y N, et al. The roles of Sn⁴⁺ in affecting performance of potassium sodium niobate ceramics[J]. *J Alloys Compd*, 2022, 899: 163290.
- [16] HUAN Y, WANG X J, YANG W Y, et al. Optimizing energy harvesting performance by tailoring ferroelectric/relaxor behavior in KNN-based piezoceramics[J]. *J Adv Ceram*, 2022, 11(6): 935–944.
- [17] ZHANG M H, WANG K, DU Y J, et al. High and temperature-insensitive piezoelectric strain in alkali niobate lead-free perovskite[J]. *J Am Chem Soc*, 2017, 139(10): 3889–3895.
- [18] JIA P W, ZHENG Z S, LI Y L, et al. The achieving enhanced piezoelectric performance of KNN-based ceramics: decisive role of multi-phase coexistence induced by lattice distortion[J]. *J Alloys Compd*, 2023, 930: 167416.
- [19] ZHAO Z H, DAI Y J, HUANG F. The formation and effect of defect dipoles in lead-free piezoelectric ceramics: A review[J]. *Sustain Mater Technol*, 2019, 20: e00092.
- [20] 戚相成, 任鹏荣, 同向前. 铌酸钾钠基电工新型压电陶瓷电致应变及温度稳定性研究进展[J]. *高电压技术*, 2023, 49(7): 2831–2840.
- QI X C, REN P R, TONG X Q. High Volt Eng, 2023, 49(7): 2831–2840.
- [21] ZHAO Z H, LV Y K, DAI Y J, et al. Ultrahigh electro-strain in acceptor-doped KNN lead-free piezoelectric ceramics *via* defect engineering[J]. *Acta Mater*, 2020, 200: 35–41.
- [22] HUANGFU G, ZENG K, WANG B Q, et al. Giant electric field-induced strain in lead-free piezoceramics[J]. *Science*, 2022, 378(6624): 1125–1130.
- [23] 林奇发, 鲁齐铃, 高旻, 等. Er 掺杂(K_{0.5}Na_{0.5})NbO₃ 多功能结构陶瓷: 突破透明性和压电性的矛盾[J]. *硅酸盐学报*, 2025, 53(9): 2632–2642.
- LIN Q F, LU Q L, GAO M, et al. *J Chin Ceram Soc*, 2025, 53(9): 2632–2642.
- [24] GONG Z C, YUE H J, FANG K L, et al. Multifunctional energy storage and photoluminescence of Er-modified KNN-based transparent ferroelectric ceramics[J]. *J Materomics*, 2025, 11(4): 100993.
- [25] HUAN Y, GUI D Y, LI C X, et al. Simultaneously enhanced energy storage performance and luminance resistance in (K_{0.5}Na_{0.5})NbO₃-based ceramics *via* synergistic optimization strategy[J]. *J Adv Ceram*, 2024, 13(1): 34–43.
- [26] LIU Y, HAO J G, LI P, et al. Large electrostrictive effect and high optical temperature sensitivity in Er³⁺-modified (K_{0.5}Na_{0.5})NbO₃-based ferroelectric ceramics[J]. *Ceram Int*, 2024, 50(7): 12050–12058.
- [27] WANG X P, WU J G, XIAO D Q, et al. Giant piezoelectricity in potassium-sodium niobate lead-free ceramics[J]. *J Am Chem Soc*, 2014, 136(7): 2905–2910.
- [28] TAO H, WU W J, WU J G. Electrical properties of holmium doped (K, Na)(Nb, Sb)O₃-(Bi, Na)HfO₃ ceramics with wide sintering and poling temperature range[J]. *J Alloys Compd*, 2016, 689: 759–766.
- [29] WANG K, JO W, GOBELJIC D. et al. Temperature-insensitive (K,Na)NbO₃-based lead-free piezoactuator ceramics[J]. *Adv Funct Mater*, 2013, 23: 4079–4086.
- [30] PAWAR P P, MUNISHWAR S R, GAUTAM S, et al. Physical, thermal, structural and optical properties of Dy³⁺ doped lithium aluminoborate glasses for bright W-LED[J]. *J Lumin*, 2017, 183: 79–88.
- [31] WANG D, ZHAO J Q, LI Y, et al. Multifunctional BNT-based ferroelectric ceramics with large electrostrain and strong photoluminescence properties[J]. *J Adv Dielect*, 2024, 14(3): 2440009.
- [32] SUN H Q, ZHANG Q W, WANG X S, et al. Bi_{0.5}Na_{0.5}TiO₃: Eu³⁺: An intense blue converting red phosphor[J]. *Mater Lett*, 2014, 131: 164–166.

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孙静雯: 论文构思、设计研究方法/实验方案、撰写初稿
王佳蕊: 验证、绘制图表、分析/综合数据并推导结论
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Structure and Properties of Dy/Eu-Doped Potassium Sodium Niobate-Based Piezoelectric Ceramics

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Extended Abstract

Introduction Piezoelectric ceramics are critical components in sensors, actuators, energy converters, and micro-electromechanical systems. The lead-based compositions dominate in the existing market. However, the release of lead during their lifecycle poses

severe environmental and human-being health risks, which contradicts global sustainable development goals. Therefore, developing high-performance lead-free alternatives becomes a paramount research priority. Among lead-free alternatives, potassium sodium niobate ((K,Na)NbO₃, KNN)-based ceramics stand out due to their low driving voltage, large electrostrain, and minimal hysteresis, making them performance-competitive with conventional PZT for precision actuators. Their performance is typically enhanced by constructing polymorphic phase boundaries and regulating microstructure. However, the existing doping strategies inadvertently degrade thermal stability, which remains a key bottleneck for practical applications. Rare-earth ions act as effective modifiers in KNN-based piezoceramics. They enhance a relaxor behavior, and improve thermal stability by shifting rhombohedral–tetragonal (R–T) phase transition below room temperature, and introduce photoluminescence due to their abundant energy levels. The integration of electrostrain and luminescence in KNN-based systems is thus significant, paving a way for developing novel bimodal functional materials for next-generation optoelectronic devices. In this work, the 0.96(K_{0.48}Na_{0.52})(Nb_{0.95}Sb_{0.05})O₃–0.04Bi_{0.5}(Na_{0.82}K_{0.18})_{0.5}ZrO₃(0.96KNNs–0.04BNKZ) composition with a polymorphic phase transition characteristic was chosen as a matrix, and rare-earth oxides (Dy₂O₃ and Eu₂O₃) served as modifiers. The effect of rare-earth oxides doping on the microstructure, ferroelectric/electrostrain properties, and photoluminescence performance of the 0.96KNNs–0.04BNKZ ceramics was investigated.

Methods 0.96KNNs–0.04BNKZ–*x*%Dy/Eu (*x* = 0, 0.05, 0.10, 0.20, 0.40) lead-free ferroelectric ceramics were synthesized by a solid-state reaction method. The stoichiometric raw materials were weighed according to the formula. They were then ground in ethanol in a ball mill with zirconia balls for 24 h. The powders were calcined at 850 °C for 4 h, then ground again for 24 h. After drying, the powders were mixed with 10% polyvinyl alcohol (PVA) as a binder and then granulated. Subsequently, disc-shaped green compacts (with the sizes of 10 mm in diameter and 0.5 mm in thickness) were pressed and subjected to a debinding process at 550 °C. The ceramics were obtained after sintering at 1130–1200 °C for 2 h. After polishing, silver electrodes were fired at 650 °C for electrical testing. The ceramics were sintered at 1130 °C to 1200 °C for 2 h, depending on the doping levels. After polishing, silver electrodes were fired on the surfaces at 650 °C for electrical characterization. The phase structure was analyzed by an X-ray diffractometer (D8 advance). The surface morphology was determined by a field emission scanning electron microscope (Merlin compact, Carl Zeiss Co., Germany). The temperature-dependent dielectric constant was measured by a broadband dielectric spectrometer (Novocontrol concept 40). The ferroelectric and electric-field-induced strain were characterized by a ferroelectric analyzer (TF 2000) coupled with a laser interferometer (SP–S 120/500). The photoluminescence properties were evaluated by a fluorescence spectrometer (FLS920).

Results and discussion Dy/Eu–doped 0.96KNNs–0.04BNKZ ceramics exhibit a single perovskite structure. At low doping levels (*i.e.*, *x* ≤ 0.10%), the rhombohedral–tetragonal (R–T) coexisting phase maintains, while a higher doping (*i.e.*, *x* ≥ 0.20%) induces a transition to the pseudocubic (*P_c*) phase, with no secondary phases appears in all the samples. All the ceramics present dense and uniform microstructures. The average grain size gradually decreases with increasing Dy/Eu doping, indicating that rare-earth ions effectively inhibit grain growth. In terms of electrical properties, a moderate Dy/Eu doping (*i.e.*, Dy: *x*=0.10%; Eu: *x*=0.05%) enhances ferroelectricity, as reflected by improved *P*–*E* loop squareness and increased saturated polarization (*P*_{max}). The 0.10%Dy and 0.05%Eu samples achieve an optimal electrostrain performance, delivering unipolar strains (*S*_{uni}) of 0.257% and 0.241% at 70 kV/cm, which are accompanied by large piezoelectric strain coefficients (*d*₃₃^{*}) of 367 pm/V and 344 pm/V, respectively. An appropriate doping optimizes the domain structure and facilitates domain switching in an external electric field, thereby improving both ferroelectric and electrostrain properties. In contrast, excessive doping leads to a severe lattice distortion, notably octahedral tilting, which pins domain walls and hinders their reorientation in response to the electric field, ultimately compromising ferroelectric and electrostrain performance. Furthermore, the 0.05% Dy- and 0.05% Eu-doped ceramics exhibit excellent thermal stability, showing less than 10% variation in electrostrain at 25–100 °C, which demonstrates their great potential for use in piezoelectric actuators. In addition, Dy/Eu doping introduces a pronounced photoluminescence to the ceramics. Under blue-light excitation, Dy³⁺-doped samples yield an intense yellow emission, whereas Eu³⁺-doped samples produce a bright orange-red emission.

Conclusions The introduction of Dy/Eu could promote a phase transition from a mixed R–T phase to a *P_c* phase. An appropriate doping effectively enhanced the ferroelectric and electrostrain properties of the materials. Specifically, the 0.10% Dy- and 0.05% Eu-doped ceramics achieved unipolar strains (*S*_{uni}) of 0.257% and 0.241% at an electric field of 70 kV/cm, with corresponding piezoelectric strain coefficients (*d*₃₃^{*}) of 367 pm/V and 344 pm/V, respectively. Furthermore, the 0.05% Dy- and 0.05% Eu-doped samples exhibited excellent thermal stability, with a variation in electrostrain of less than 10% at 25–100 °C, demonstrating a great potential for piezoelectric actuator applications. In addition, Dy/Eu doping imparted outstanding photoluminescence properties to the ceramics. Under blue-light excitation, Dy³⁺-doped samples exhibited an intense yellow emission, while Eu³⁺-doped samples displayed a bright orange-red emission. The combination of electrical and luminescent characteristics could make this material a promising candidate for optoelectronic coupling devices.

Keywords lead-free piezoelectric ceramics; potassium sodium niobate; electrostrain; thermal stability