

不同掺杂量 $\text{Eu}_x\text{Lu}_{1.4-x}\text{Gd}_{0.6}\text{O}_3$ 透明陶瓷的制备与性能陈宇洋^{1,2}, 毕 愿^{1,3}, 朱丹阳^{1,2}, 贺宁桐^{1,4}, 胡 辰¹, 王雁斌^{1,4}, 张 芳³, 李 江^{1,2}

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摘 要: 为了满足高能射线成像对闪烁陶瓷的应用要求, 并探究 Eu^{3+} 掺杂量对陶瓷微观结构和光学性能的影响, 采用液相共沉淀法合成了不同 Eu^{3+} 掺杂量的 $\text{Eu}_x\text{Lu}_{1.4-x}\text{Gd}_{0.6}\text{O}_3$ ($x=0, 0.02, 0.06, 0.10, 0.14, 0.18$) 粉体并通过真空预烧结合热等静压烧结, 制备出 $\text{Eu}_x\text{Lu}_{1.4-x}\text{Gd}_{0.6}\text{O}_3$ 透明陶瓷。随着 Eu^{3+} 掺杂量的增加, 陶瓷直线透率先升高后降低, 在 $x=0.10$ 时达到最高(71.4%@611 nm)。 $\text{Eu}_x\text{Lu}_{1.4-x}\text{Gd}_{0.6}\text{O}_3$ 陶瓷的光致激发光谱和光致发光光谱证明了 Eu^{3+} 掺杂量的增加能够提升陶瓷的吸收峰和发射峰强度。陶瓷在 X 射线激发下的发光强度随着 Eu^{3+} 掺杂量的升高呈现先升高后降低的趋势, 在 Eu^{3+} 掺杂量(摩尔分数)为 3% 时达到最高。 $\text{Eu}_x\text{Lu}_{1.4-x}\text{Gd}_{0.6}\text{O}_3$ 陶瓷在可见光和 X 射线激发下都呈现强烈的红光发射, 与硅光电二极管光谱响应有着良好的耦合性。

关键词: 透明陶瓷; 闪烁陶瓷; 发光性能

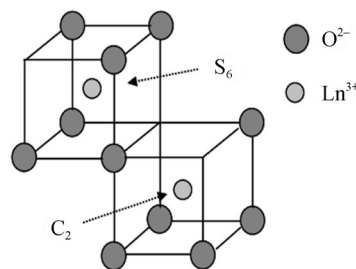
中图分类号: TB321/TQ174 文献标志码: A 文章编号: 0454-5648(2024)03-0828-08

网络出版时间: 2024-02-05



闪烁体是一种能将高能射线或粒子转换为紫外或可见光的功能材料。闪烁材料与光探测装置匹配构成闪烁探测器, 通过信号处理分析得到相关信息, 服务于人们的生活。闪烁材料广泛应用于医疗、空间探测、安全检查、无损检测等领域^[1-8]。在大型器件无损检测方面, 具有高能射线源的工业 CT 为了能够实现高分辨率成像, 对闪烁体提出了光产额高、衰减时间短、有效原子序数高和抗辐照能力强等要求^[9], 同时要求其具有高的 X 射线阻止能力和在发射波长较好的透过率^[10-13]。

2002 年, Lempicki 等就提出了 $\text{Eu}:\text{Lu}_2\text{O}_3$ 透明陶瓷可以作为红光闪烁体的设想^[14]。相较于 Ce^{3+} 、 Pr^{3+} 、 Tb^{3+} 等发光离子, Eu^{3+} 能够在 Lu_2O_3 基体中发出强烈的红色辐射发光, 与硅光二极管光谱响应有着良好的耦合性。 Lu_2O_3 基体为 c 型立方结构, Eu^{3+} 掺入 Lu_2O_3 基体会同时占据 Lu 离子所在的 C_2 格位和 S_6 格位^[15], 如图 1 所示。其中, C_2 格位 Eu^{3+} 的 $^5\text{D}_0 \rightarrow ^7\text{F}_2$ 能级跃迁是 $\text{Eu}^{3+}:\text{Lu}_2\text{O}_3$ 闪烁材料高强度的红色发射光(450~750 nm)的主要来源。

图 1 Ln_2O_3 晶体结构中不同 Ln 离子位置示意图^[15]Fig. 1 Schematic diagram of positions of different Ln^{3+} in Ln_2O_3 crystal structure^[15]

Seeley 等发现在 $\text{Eu}:\text{Lu}_2\text{O}_3$ 陶瓷中 Eu^{3+} 会在 Lu_2O_3 晶界处偏析, 影响陶瓷的光学质量, 限制光输出^[16]。引入 Gd^{3+} 后, 由于 Gd^{3+} 较大的离子半径(0.938 Å), 掺入到 Lu_2O_3 基体中拉伸了晶格, 减少 Eu^{3+} 从晶格内析出的可能性, 从而避免第二相的生成^[16], 从而提高材料的光学质量; 另一方面, Gd^{3+} 在 Lu_2O_3 中的掺入能够促进晶格内的 Eu^{3+} 重新排布, 使得 Eu^{3+} 更倾向于占据 C_2 格位, 敏化了 Eu^{3+} 的 4f-4f 发射, 从而优化材料的发光性能^[16]。Seeley

收稿日期: 2023-08-23。 修订日期: 2023-09-12。

基金项目: 中国科学院国际伙伴计划(121631KYSB20200039); 上海市“一带一路”国际合作项目(20520750200)。

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Received date: 2023-08-23. Revised date: 2023-09-12.

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等制备了 $\text{Eu:Lu}_{2-x}\text{Gd}_x\text{O}_3$ ($x=0.5$) 和 $\text{Eu:Lu}_2\text{O}_3$ 陶瓷, 发现 $\text{Eu:Lu}_{2-x}\text{Gd}_x\text{O}_3$ 透明陶瓷的荧光和闪烁特性要明显优于 $\text{Eu:Lu}_2\text{O}_3$ 陶瓷。Cherepy 等采用火焰喷雾法制备粉体, 分别采用真空烧结-热等静压法和两步烧结-热等静压法制备了高透明 $\text{Eu:Lu}_{2-x}\text{Gd}_x\text{O}_3$ 陶瓷, 所制备的陶瓷光产额达到了 57 000 ph/MeV。Seeley 等制备了 $\text{Eu}_x\text{Lu}_{1.4-x}\text{Gd}_{0.6}\text{O}_3$ ($x=0, 0.3, 0.6, 0.9, 1.0, 1.1$) 陶瓷, 研究发现 $\text{Eu}_{0.1}\text{Gd}_{0.6}\text{Lu}_{1.3}\text{O}_3$ 透明陶瓷具有优异的发光性能, 符合 MeV 量级 X 射线 CT 成像要求^[17]。

Eu^{3+} 掺杂 $\text{Gd}_2\text{O}_3\text{-Lu}_2\text{O}_3$ 固溶体陶瓷具有高密度和高有效原子系数, 能够提供高的 X 射线阻止能力和抗辐照能力; 有较高的光产额, 有利于产生清晰的图像; 且 Eu^{3+} 发光在红光区, 与硅光电二极管的光谱灵敏度有良好的匹配^[18-25]。综上所述, $\text{Eu}_x\text{Lu}_{1.4-x}\text{Gd}_{0.6}\text{O}_3$ 透明陶瓷在高能射线成像领域是一类极具应用前景的闪烁体。目前 LLNL 已完成高透明, 高光产额 $\text{Eu}_x\text{Lu}_{1.4-x}\text{Gd}_{0.6}\text{O}_3$ 透明陶瓷的商业化生产。而国内的研究仍处于较低水平, 陶瓷的光学质量有待提高, 无法满足实际应用需求^[26-30]。同时, 也缺乏对组分设计的相关研究。尤其是不同 Eu^{3+} 掺杂量对 $\text{Eu}_x\text{Lu}_{1.4-x}\text{Gd}_{0.6}\text{O}_3$ 陶瓷的结构和光谱性质的影响仍不明确^[31-37]。

本文针对不同 Eu^{3+} 掺杂量进行组分设计, 采用共沉淀法合成出了不同 Eu^{3+} 掺杂量的 $\text{Eu}_x\text{Lu}_{1.4-x}\text{Gd}_{0.6}\text{O}_3$ ($x=0, 0.02, 0.06, 0.10, 0.14, 0.18$) 粉体, 结合真空预烧和热等静压烧结制备出了 $\text{Eu}_x\text{Lu}_{1.4-x}\text{Gd}_{0.6}\text{O}_3$ 透明陶瓷, 并对其微观结构和光学性能进行了表征和分析。

1 实验

1.1 $\text{Eu}_x\text{Lu}_{1.4-x}\text{Gd}_{0.6}\text{O}_3$ 粉体制备

将适量的 Eu_2O_3 [纯度为 99.995% (质量分数)]、 Lu_2O_3 (纯度为 99.995%)、 Gd_2O_3 (纯度为 99.999%) 分别溶于稀硝酸中, 得到 $\text{Eu}(\text{NO}_3)_3$ 、 $\text{Lu}(\text{NO}_3)_3$ 、 $\text{Gd}(\text{NO}_3)_3$ 溶液。按照相应的化学计量比配制 500 mL 浓度为 0.25 mol/L 的金属混合溶液, 加入 125 mL 的 1 mol/L 的 $(\text{NH}_4)_2\text{SO}_4$ 溶液, 通过滴加稀硝酸调节混合溶液初始 pH=1.3, 充分搅拌后以 3 mL/min 的速率将 600 mL 的 1 mol/L 的 NH_4HCO_3 溶液滴入金属混合溶液, 滴定结束后搅拌 10 min, 陈化 3 h。获得的沉淀用乙醇和水的混合液 (无水乙醇: 水=1:4) 洗涤 2 次, 再用醇洗涤 2 次, 离心后 70 °C 干燥 18 h, 将粉体进行 200 目筛网 (筛孔尺寸为 75 μm)

过筛, 1 100 °C、空气气氛条件下保温 4 h 煅烧, 最后得到 $\text{Eu}_x\text{Lu}_{1.4-x}\text{Gd}_{0.6}\text{O}_3$ ($x=0, 0.02, 0.06, 0.10, 0.14, 0.18$) 的粉体。

1.2 陶瓷制备

将合成的纳米粉体在 $\phi 18\text{ mm}$ 的模具中以 40 MPa 的压力成型, 再通过 250 MPa 冷等静压获得陶瓷素坯。将素坯放入真空钨丝炉进行 1 600 °C、真空条件下保温 2 h 预烧, 再通过 1 750 °C、176 MPa 的 Ar 气氛条件下保温 2 h 的热等静压烧结 (HIP) 烧结和 1 100 °C、空气气氛条件下保温 20 h 退火获得不同 Eu^{3+} 掺杂量的 $\text{Eu}_x\text{Lu}_{1.4-x}\text{Gd}_{0.6}\text{O}_3$ 透明陶瓷。

1.3 样品表征

采用场发射扫描电镜 SU9000 电子显微镜 (日本日立公司) 拍摄样品的显微形貌。XRD 谱由 D8/DISCOVER DAVINCIX 射线衍射仪 (德国布鲁克公司) 检测, 测试条件: Cu 靶, 工作电压为 40 kV, 电流为 30 mA, $\text{Cu } K_{\alpha}=0.154\,06\text{ nm}$, 测试角度 2θ 区间为 $10^{\circ}\sim 80^{\circ}$, 扫描速率为 $2(^{\circ})/\text{min}$ 。陶瓷的光致发光光谱 (PLE) 和光致发光光谱 (PL) 由 FLS-980 型荧光光谱仪测试 (英国爱丁堡仪器公司)。X 射线辐射发光光谱 (XEL) 由自搭的 X 射线激发发射光谱仪对闪烁陶瓷进行性能表征, 使用 QE65000 型光谱仪 (美国海洋光学公司) 对测试样品的发光信号收集分析, 测试条件为 X 射线光管电压 70 kV, 电流为 1.5 mA。透过率曲线使用 Cary-5000 紫外-可见-近红外分光光度计 (美国 Varian 公司) 测试。样品密度根据 Archimedes 原理, 其计算公式为:

$$\rho = m_0 \rho_0 / (m_0 - m_1) \quad (1)$$

其中: m_0 为干燥试样在空气中的质量; m_1 为试样经充分吸水后完全浸没在水中的质量; ρ_0 为蒸馏水的密度 1 g/cm^3 , 样品的相对密度为 $\rho_1 = (\rho / \rho_{\text{th}}) \times 100\%$; ρ_{th} 为样品的理论密度。

2 结果与讨论

2.1 $\text{Eu}_x\text{Lu}_{1.4-x}\text{Gd}_{0.6}\text{O}_3$ 粉体的形貌与结构

图 2 是 $\text{Eu}_x\text{Lu}_{1.4-x}\text{Gd}_{0.6}\text{O}_3$ 粉体 SEM 微观形貌照片。由图 2 可见, 随着 Eu^{3+} 掺杂量的提升, 粉体形貌差异不明显, 所合成的粉体均为纳米级颗粒且存在一定程度团聚。这是因为粉体颗粒尺寸小, 表面能较大, 颗粒之间发生吸附导致团聚。

图 3 是 $\text{Eu}_x\text{Lu}_{1.4-x}\text{Gd}_{0.6}\text{O}_3$ 粉体的 XRD 谱。从图 3a 可以看出, 所制备的粉体都为立方晶系 (Lu_2O_3 PDF 12-0728), 且随着 Eu^{3+} 掺杂量的提升, 衍射峰位向低角度移动, 这是由于 Eu^{3+} 的离子半

径 (0.950 Å) 和 Gd^{3+} 的离子半径 (0.938 Å) 比 Lu^{3+} (0.848 Å) 的要大, 随着 Eu^{3+} 的掺入, 晶格参数变大。根据 Scherrer 公式计算得到随着 Eu^{3+} 掺杂量

增加, 粉体的平均晶粒尺寸逐步降低, 由 63.7 nm 降低到 55.0 nm, 材料的理论密度由 8.83 g/cm^3 降低到 8.64 g/cm^3 。

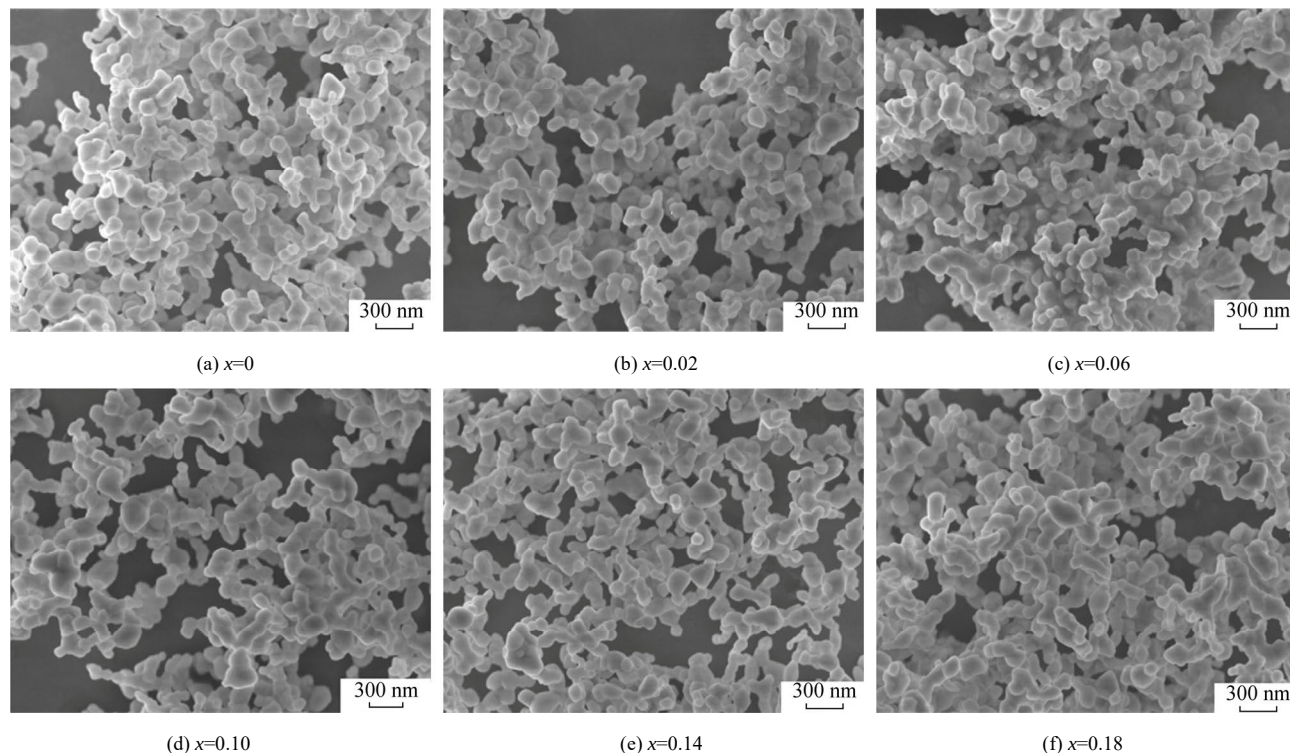


图 2 $\text{Eu}_x\text{Lu}_{1.4-x}\text{Gd}_{0.6}\text{O}_3$ 粉体的 SEM 照片
Fig. 2 SEM images of $\text{Eu}_x\text{Lu}_{1.4-x}\text{Gd}_{0.6}\text{O}_3$ powders

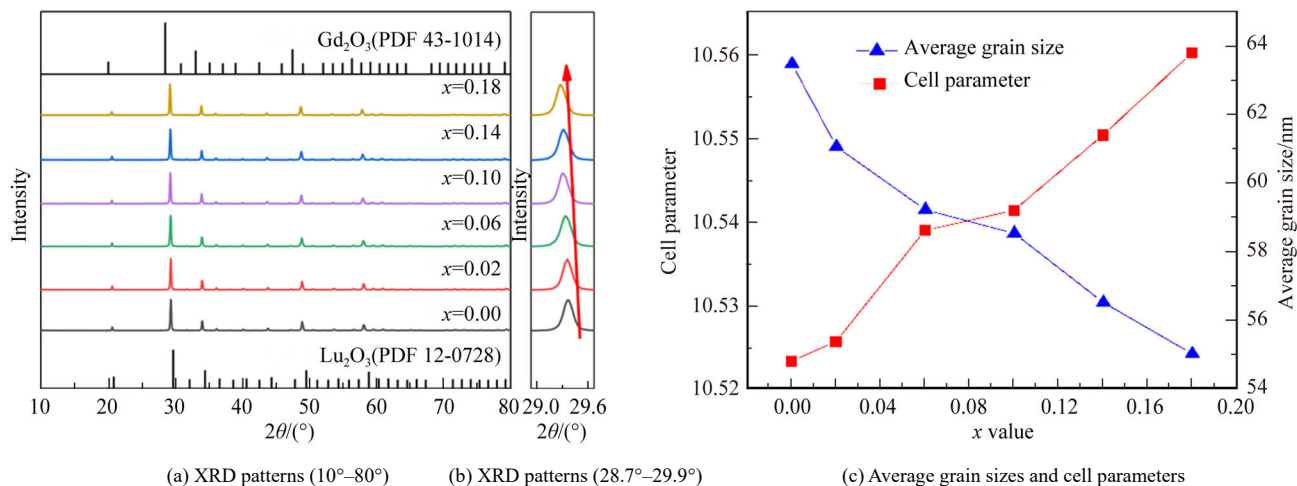


图 3 $\text{Eu}_x\text{Lu}_{1.4-x}\text{Gd}_{0.6}\text{O}_3$ 粉体的 XRD 谱、晶胞参数和平均晶粒尺寸
Fig. 3 XRD patterns, average grain sizes and cell parameters of $\text{Eu}_x\text{Lu}_{1.4-x}\text{Gd}_{0.6}\text{O}_3$ powders

2.2 $\text{Eu}_x\text{Lu}_{1.4-x}\text{Gd}_{0.6}\text{O}_3$ 透明陶瓷的微观结构

图 4 是 $\text{Eu}_x\text{Lu}_{1.4-x}\text{Gd}_{0.6}\text{O}_3$ 素坯经过 1600°C 、真空条件下保温 2 h 烧结的预烧体相对密度。由图 4 可见, 所有陶瓷的相对密度均在 95% 以上, 且随着 Eu^{3+} 掺杂量的增加, 陶瓷的相对密度有增大的趋势。

图 5 是 $\text{Eu}_x\text{Lu}_{1.4-x}\text{Gd}_{0.6}\text{O}_3$ 预烧陶瓷的 SEM 微观

形貌图。由图 5 可见, 所制备的陶瓷预烧体晶粒尺寸均匀, 观察不到明显的气孔, 且没有第二相。

图 6 是对应陶瓷通过截线法测得陶瓷平均晶粒尺寸。由图 6 可见, 随着 Eu^{3+} 掺杂量增加, 晶粒尺寸从 $1.0 \mu\text{m}$ 减小到 $0.9 \mu\text{m}$ 。这是由于 Eu^{3+} 的掺杂使得晶格发生了畸变, 从而抑制了陶瓷晶粒在烧结过程中的长大。

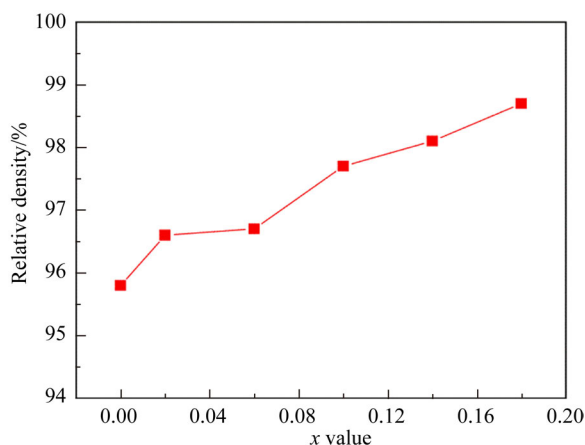
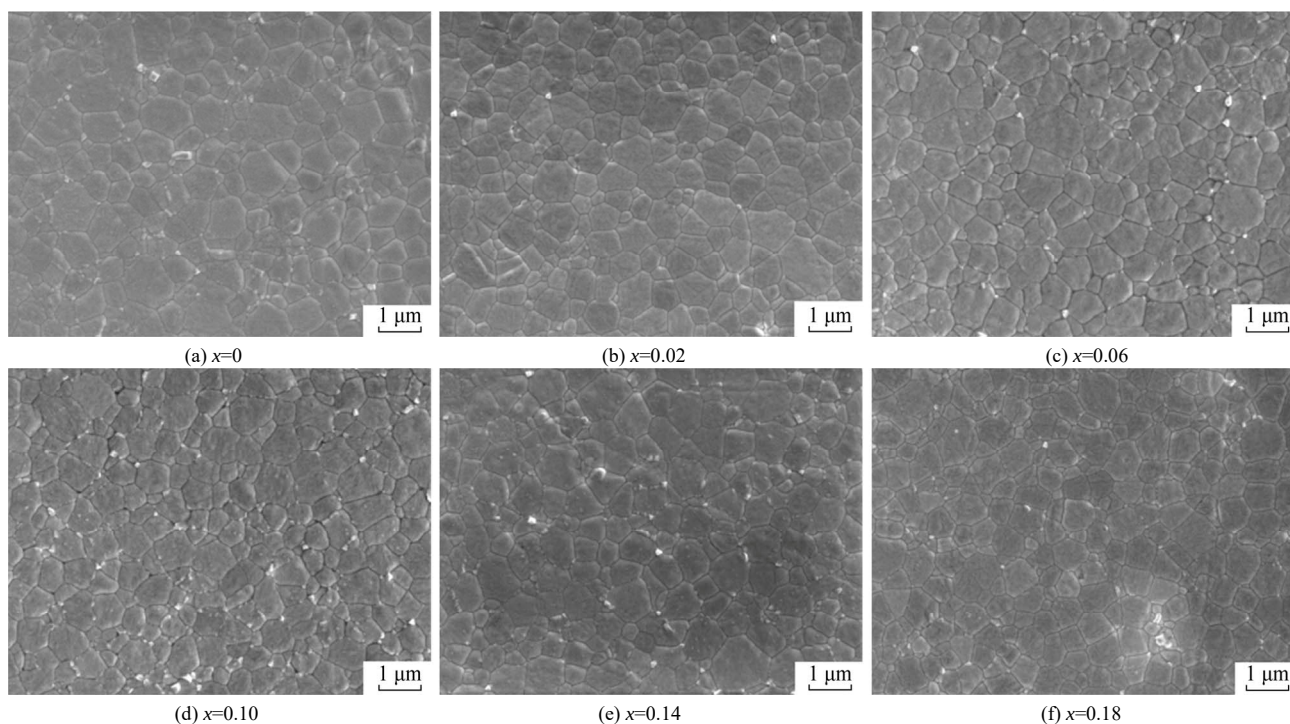
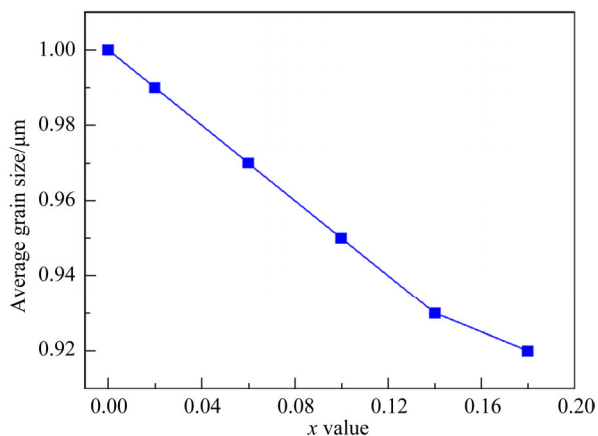
图 4 真空烧结 $\text{Eu}_x\text{Lu}_{1.4-x}\text{Gd}_{0.6}\text{O}_3$ 陶瓷的相对密度Fig. 4 Relative densities of vacuum sintered $\text{Eu}_x\text{Lu}_{1.4-x}\text{Gd}_{0.6}\text{O}_3$ ceramics图 5 真空烧结 $\text{Eu}_x\text{Lu}_{1.4-x}\text{Gd}_{0.6}\text{O}_3$ 陶瓷的 SEM 照片Fig. 5 SEM images of vacuum sintered $\text{Eu}_x\text{Lu}_{1.4-x}\text{Gd}_{0.6}\text{O}_3$ ceramics图 6 $\text{Eu}_x\text{Lu}_{1.4-x}\text{Gd}_{0.6}\text{O}_3$ 陶瓷预烧体的平均晶粒尺寸Fig. 6 Average grain sizes of pre-sintered ceramics $\text{Eu}_x\text{Lu}_{1.4-x}\text{Gd}_{0.6}\text{O}_3$ ceramics

图 7 是 $\text{Eu}_x\text{Lu}_{1.4-x}\text{Gd}_{0.6}\text{O}_3$ 陶瓷经过 HIP 处理后的 SEM 照片, 图 8 是对应陶瓷的平均晶粒尺寸。由图 7~图 8 可见, 相较预烧体, HIP 后陶瓷的晶粒发生了明显的长大。随着 Eu^{3+} 掺杂量从 0 增加到 9%, HIP 后陶瓷通过截线法测得的陶瓷平均晶粒尺寸从 $76.5 \mu\text{m}$ 降低到 $30.1 \mu\text{m}$, 逐渐减小。这是由于 Eu^{3+} 的掺杂使得晶格发生了畸变, 从而抑制了陶瓷晶粒在 HIP 过程中的长大。

2.3 $\text{Eu}_x\text{Lu}_{1.4-x}\text{Gd}_{0.6}\text{O}_3$ 透明陶瓷的光学性能

图 9 是真空烧结结合 HIP 后处理制备的 $\text{Eu}_x\text{Lu}_{1.4-x}\text{Gd}_{0.6}\text{O}_3$ 陶瓷(厚度为 1.4 mm)的直线透过率曲线和实物照片。从图 9a 可以看出, 陶瓷的直线透过率随着 Eu^{3+} 掺杂量的增加而呈现先上升后下降的

趋势, 当 $x=0.1$ 时, 陶瓷的直线透过率在 611 nm 处最高达到了 71.4% 。当 Eu^{3+} 掺杂量较高时, 由于 Eu^{3+} 的离子半径($0.950 \text{ \AA}$)与 Lu^{3+} 的离子半径($0.848 \text{ \AA}$)有一定差距, 此时随着 Eu^{3+} 掺杂量的增加, 陶瓷内部晶格畸变加剧, 导致陶瓷的直线透过率下降。此外陶瓷透过率曲线还包含 Gd^{3+} 和 Eu^{3+} 的特征吸收峰, 分别是位于 308 nm 处和 314 nm 处 Gd^{3+} 的特征吸收峰, 对应 Gd^{3+} 的 $^8\text{S}_{7/2} \rightarrow ^6\text{P}_J$ 跃迁; 323 、 363 、 382 、 394 、 414 、 468 、 533 、 580 nm 处的吸收峰为 Eu^{3+} 的特征吸收峰, 分别对应 Eu^{3+} 基态 $^7\text{F}_0$ 能级到 $^5\text{L}_8$ 、 $^5\text{D}_4$ 、 $^5\text{L}_7$ 、 $^5\text{L}_6$ 、 $^5\text{D}_3$ 、 $^5\text{D}_2$ 、 $^5\text{D}_1$ 、 $^5\text{D}_0$ 能级的跃迁。

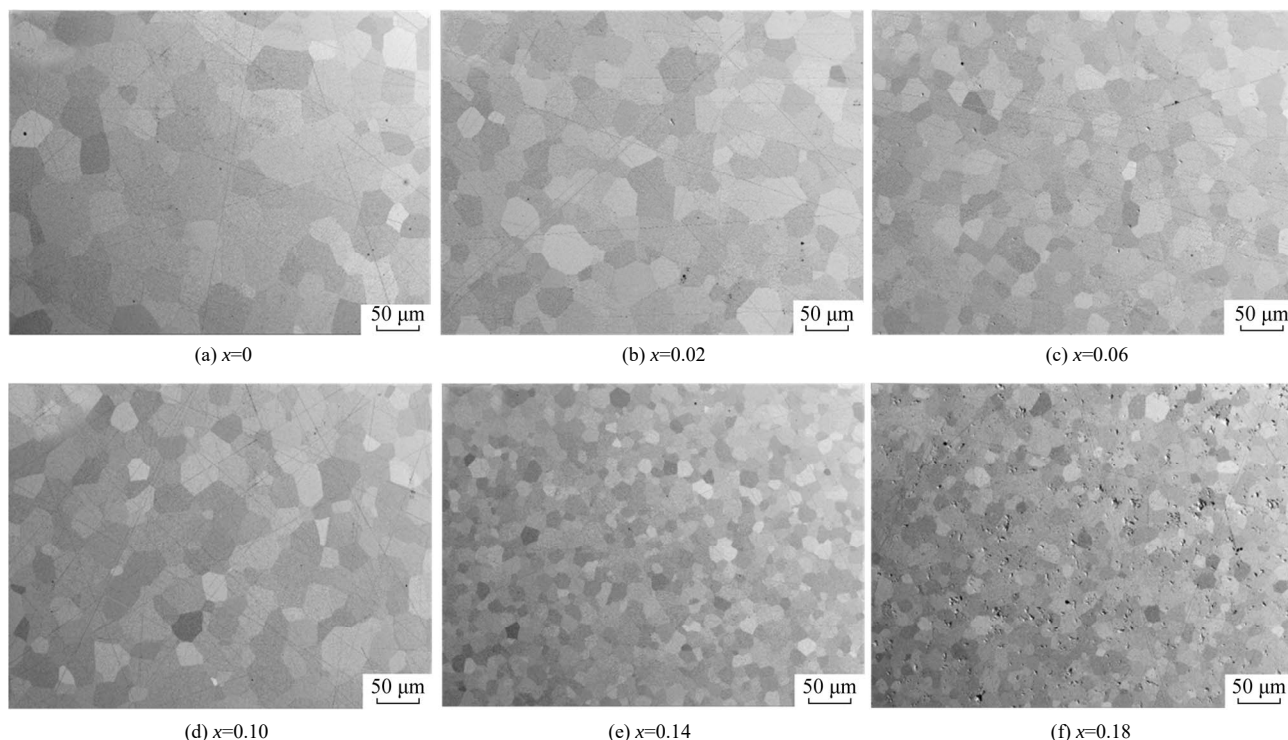
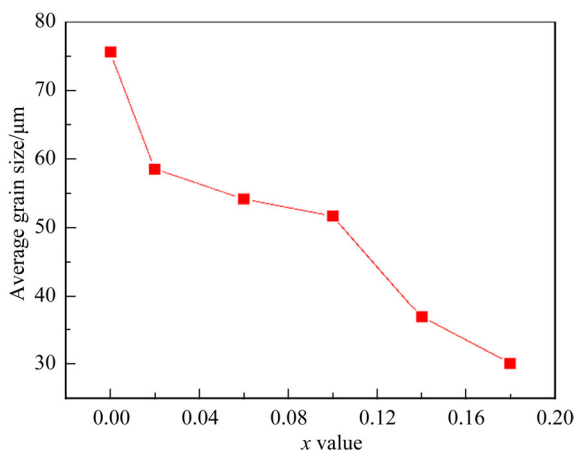
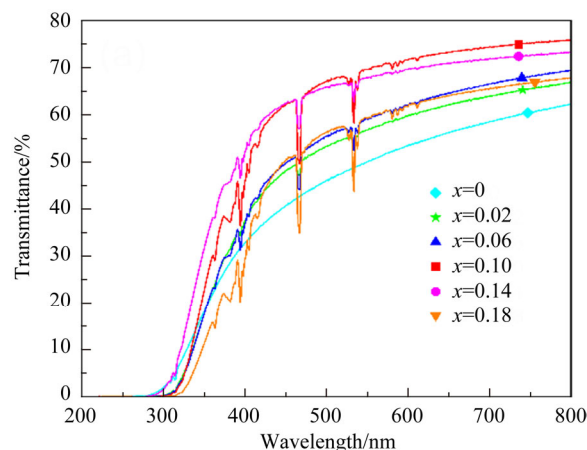
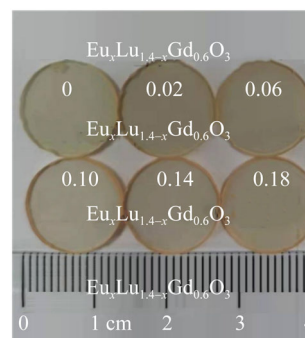
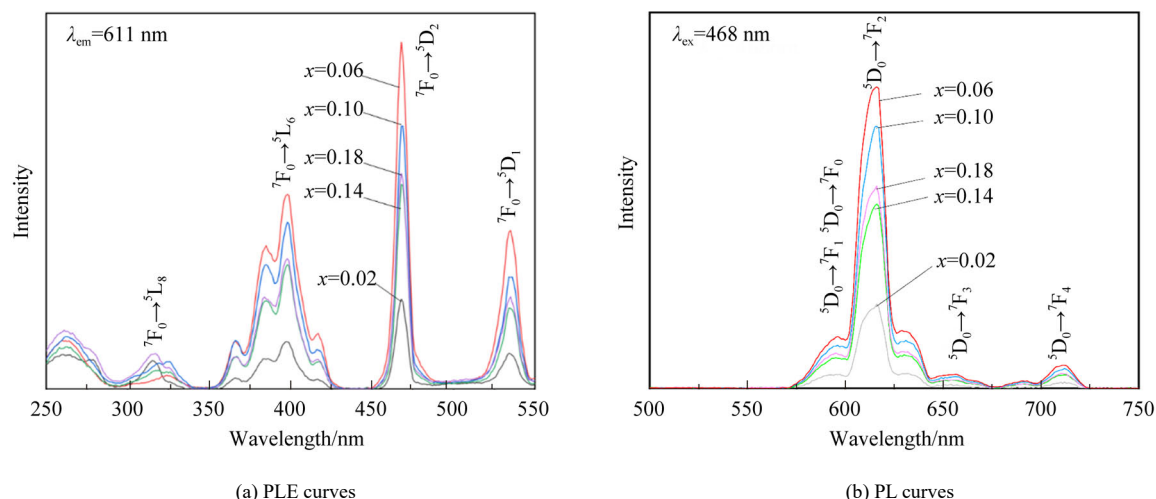
图 7 HIP 后处理 $\text{Eu}_x\text{Lu}_{1.4-x}\text{Gd}_{0.6}\text{O}_3$ 陶瓷的 SEM 照片Fig. 7 SEM images of HIP post-treated $\text{Eu}_x\text{Lu}_{1.4-x}\text{Gd}_{0.6}\text{O}_3$ ceramics图 8 $\text{Eu}_x\text{Lu}_{1.4-x}\text{Gd}_{0.6}\text{O}_3$ 陶瓷 HIP 后的平均晶粒尺寸Fig. 8 Average grain sizes of HIP post-treated $\text{Eu}_x\text{Lu}_{1.4-x}\text{Gd}_{0.6}\text{O}_3$ ceramics

图 10 是 $\text{Eu}_x\text{Lu}_{1.4-x}\text{Gd}_{0.6}\text{O}_3$ 陶瓷的光致激发光谱 (PLE) 和光致发光光谱 (PL)。由图 10a 可以看出, 陶瓷的激发峰分别对应 Eu^{3+} 的能级跃迁吸收峰, 其中, 323 nm 对应 $^7\text{F}_0 \rightarrow ^5\text{L}_8$; 394 nm 处对应 $^7\text{F}_0 \rightarrow ^5\text{L}_6$; 468 nm 处对应 $^7\text{F}_0 \rightarrow ^5\text{D}_2$; 533 nm 处对应 $^7\text{F}_0 \rightarrow ^5\text{D}_1$ 。由光致发光光谱可以看出, 陶瓷的主发射峰位于 611 nm 处, 对应于 Eu^{3+} 的 $^5\text{D}_0 \rightarrow ^7\text{F}_2$ 能级跃迁吸收峰。陶瓷的大部分激发峰和全部发射峰强度都随着 Eu^{3+} 掺杂量的增加而呈现上升的趋势, 对应陶瓷内部发光中心的逐渐增多。在图 10a 中, 323 nm 的吸收峰对应 Eu^{3+} 的 $^7\text{F}_0 \rightarrow ^5\text{L}_8$ 的能级跃迁, 而位于 308 nm 和 314 nm



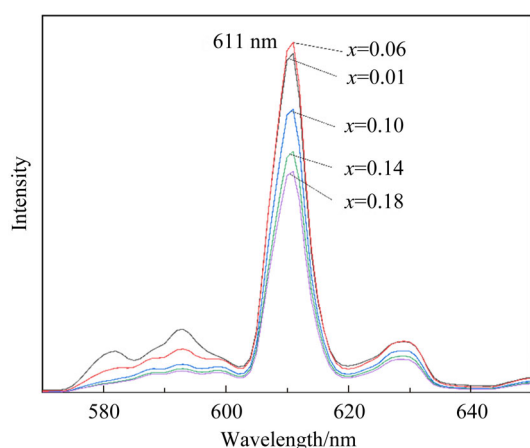
(a) In-line transmittance curves

(b) Photographs of $\text{Eu}_x\text{Lu}_{1.4-x}\text{Gd}_{0.6}\text{O}_3$ ceramics图 9 真空烧结结合 HIP 后处理制备的 $\text{Eu}_x\text{Lu}_{1.4-x}\text{Gd}_{0.6}\text{O}_3$ 陶瓷的直线透过率曲线和实物照片Fig. 9 In-line transmittance curves and photographs of $\text{Eu}_x\text{Lu}_{1.4-x}\text{Gd}_{0.6}\text{O}_3$ ceramics prepared by vacuum sintering combined with hot isostatic pressing (HIP) post-treatment

图 10 $\text{Eu}_x\text{Lu}_{1.4-x}\text{Gd}_{0.6}\text{O}_3$ 陶瓷的光致激发光谱和光致发光光谱Fig. 10 Hotoluminescence excited spectra (PLE) curves and photoluminescence (PL) curves of $\text{Eu}_x\text{Lu}_{1.4-x}\text{Gd}_{0.6}\text{O}_3$ ceramics

的吸收峰对应 Gd^{3+} 的 $^8\text{S}_{7/2} \rightarrow ^6\text{P}_J$ 跃迁, 这部分能量吸收主要源于 Gd^{3+} , 激发峰强度并未随 Eu^{3+} 变化呈现出明显的变化规律。

图 11 是 $\text{Eu}_x\text{Lu}_{1.4-x}\text{Gd}_{0.6}\text{O}_3$ 陶瓷的 XEL 谱。从图 11 可以看出, $\text{Eu}_x\text{Lu}_{1.4-x}\text{Gd}_{0.6}\text{O}_3$ 陶瓷的发光光谱是由 Eu^{3+} 特征发射峰组成, 主发射峰位于 611 nm 处, 是 $^5\text{D}_0 \rightarrow ^7\text{F}_2$ 跃迁发射出的强烈红光, 当 Eu^{3+} 掺杂量较低时, 随着发光中心数量的增加, 陶瓷的发光强度逐渐升高; 当 Eu^{3+} 掺杂量超过 3% 时, 发光中心的间距减小, 同时由于激发源的能量较高, Eu^{3+} 之间的能量传递增多, 同时 Eu^{3+} 和缺陷等之间的跃迁几率增加, 从而导致闪烁发光强度下降, 而光致发光强度不下降。陶瓷整体呈现出强烈的红光发射, 此波段适配于对红光敏感的硅光二极管。

图 11 $\text{Eu}_x\text{Lu}_{1.4-x}\text{Gd}_{0.6}\text{O}_3$ 陶瓷的 XEL 谱Fig. 11 XEL patterns of $\text{Eu}_x\text{Lu}_{1.4-x}\text{Gd}_{0.6}\text{O}_3$ ceramics

3 结论

通过液相共沉淀法合成了具备优良烧结活性的

纯立方相 $\text{Eu}_x\text{Lu}_{1.4-x}\text{Gd}_{0.6}\text{O}_3$ 纳米粉体, 并采用真空预烧结合热等静压烧结后处理制备出了 $\text{Eu}_x\text{Lu}_{1.4-x}\text{Gd}_{0.6}\text{O}_3$ 透明陶瓷。在 Eu^{3+} 掺杂量为 5% 时陶瓷的直线透过率最高, 在主发射峰 611 nm 处达 71.4%。 $\text{Eu}_x\text{Lu}_{1.4-x}\text{Gd}_{0.6}\text{O}_3$ 陶瓷的光致激发光谱和光致发光光谱证明了 Eu^{3+} 掺杂量的增加能够提升陶瓷的吸收峰和发射峰强度。在 Eu^{3+} 掺杂量为 3% 时, 陶瓷在 X 射线激发下红光发射最强, 发射主峰位于 611 nm, 对应 Eu^{3+} 的 $^5\text{D}_0 \rightarrow ^7\text{F}_2$ 跃迁。高透过率和高红光发射强度对实现高分辨率 X 射线成像具有重大意义。

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Preparation and Performance of $\text{Eu}_x\text{Lu}_{1.4-x}\text{Gd}_{0.6}\text{O}_3$ Transparent Ceramics

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Extended Abstract

Introduction In non-destructive testing of large devices, industrial computed tomography (CT) with high-energy radiation sources requires scintillators with a high performance of light yield, short decay time, high effective atomic number, and strong radiation

resistance to achieve high-resolution imaging. Eu^{3+} doped $\text{Gd}_2\text{O}_3\text{--Lu}_2\text{O}_3$ solid solution ceramics have a high density and an effective atomic number, having high X-ray stopping power and radiation resistance. The ceramics have a high light yield that is beneficial to improving imaging quality. Moreover, Eu^{3+} emits a light in the red region, which matches well with the spectral sensitivity of silicon photodiodes. $\text{Eu}_x\text{Lu}_{1.4-x}\text{Gd}_{0.6}\text{O}_3$ transparent ceramics are one of scintillators with great application prospects in the field of X-ray imaging. A recent study managed to prepare commercial products of $\text{Eu}_x\text{Lu}_{1.4-x}\text{Gd}_{0.6}\text{O}_3$ transparent ceramics with a high transparency and a high light output. However, such a research is still at the initial stage, and the optical quality of ceramics needs to be improved to meet practical application needs. There is also a lack of research on component design. Especially, the effect of Eu^{3+} concentration on the structure and spectral properties of $\text{Eu}_x\text{Lu}_{1.4-x}\text{Gd}_{0.6}\text{O}_3$ ceramics is still unclear. In this paper, $\text{Eu}_x\text{Lu}_{1.4-x}\text{Gd}_{0.6}\text{O}_3$ ($x=0, 0.02, 0.06, 0.10, 0.14, 0.18$) ceramics with different Eu^{3+} concentrations were prepared *via* coprecipitation and subsequent vacuum sintering/hot isostatic pressing (HIP), and their microstructure and optical properties were analyzed.

Methods In the synthesis of nano-powder, the obtained precursor was calcined in air at 1 100 °C for 4 h to obtain $\text{Eu}_x\text{Lu}_{1.4-x}\text{Gd}_{0.6}\text{O}_3$ ($x=0, 0.02, 0.06, 0.10, 0.14, 0.18$) powders. The synthesized powders were molded in a 18 mm mold at 40 MPa, and then the ceramic green bodies were obtained by cold isostatic pressing at 250 MPa, pre-sintered in vacuum at 1 600 °C for 2 h and then sintered in argon atmosphere under 176 MPa at 1 750 °C for 2 h. The fabricated $\text{Eu}_x\text{Lu}_{1.4-x}\text{Gd}_{0.6}\text{O}_3$ ceramics were annealed in air at 1 100 °C for 20 h to remove oxygen vacancies introduced by sintering in a reducing atmosphere.

The microstructure of the sample was characterized by a model SU9000 field emission scanning electron microscope (Hitachi Co., Japan). The XRD pattern was detected by a model D8/DISCOVER DAVINCIX X-ray diffractometer (Brooke Co., Germany). The photoluminescence spectra (PL) and photoluminescence excited spectra (PLE) of ceramics were tested by a model FLS-980 fluorescence spectrometer (Edinburgh Instruments Ltd., UK). The performance of scintillating ceramics was characterized by an X-ray excitation emission spectrometer. The emission signals of the test samples were analyzed by a model QE65000 spectrometer (Ocean Optics Co., USA) excited by an X-ray tube operating at a voltage of 70 kV and a current of 1.5 mA. The transmittance curve was tested by a model Cary-5000 ultraviolet visible near-infrared spectrophotometer (Varian Co., USA).

Results and discussion The $\text{Eu}_x\text{Lu}_{1.4-x}\text{Gd}_{0.6}\text{O}_3$ ($x=0, 0.02, 0.06, 0.10, 0.14, 0.18$) powders are all cubic crystalline, and the diffraction peak position shifts towards a lower angle as Eu^{3+} doping concentration increases because the ion radius of Eu^{3+} (i.e., 0.950 Å) or Gd^{3+} (i.e., 0.938 Å) is larger than that of Lu^{3+} (i.e., 0.848 Å). According to Scherrer's formula, the average grain size of the powders gradually decreases from 63.7 nm to 55.0 nm as the concentration of Eu^{3+} increases. The $\text{Eu}_x\text{Lu}_{1.4-x}\text{Gd}_{0.6}\text{O}_3$ ceramics have uniform grain sizes, no obvious pores occur, and there is no second phase. The grain size measured by a linear intercept method decreases from 1.0 μm to 0.9 μm as the Eu^{3+} doping concentration increases. This is because the lattice distortion caused by Eu^{3+} doping suppresses the growth of ceramic grains in sintering. Compared to the prepared ceramics, the grain sizes of the ceramics after HIP increase. The average grain size of the ceramics after HIP decreases from 76.5 μm to 30.1 μm as the Eu^{3+} doping concentration increases from 0 to 9%.

The in-line transmittance of ceramics firstly increases and then decreases with the increase of Eu^{3+} concentration. When $x=0.1$, the in-line transmittance of ceramics reaches a maximum of 71.4% at 611 nm. When the concentration of Eu^{3+} is high, the lattice distortion inside the ceramic intensifies, leading to a decrease in the in-line transmittance. In the XEL patterns of $\text{Eu}_x\text{Lu}_{1.4-x}\text{Gd}_{0.6}\text{O}_3$ ceramics, the emission spectrum is composed of Eu^{3+} characteristic emission peaks. The main emission peak is located at 611 nm, which is an intense red light emitted from the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition. When the Eu^{3+} concentration is low, the emission intensity of the ceramic gradually increases with the increase of the number of emission centers. When the concentration of Eu^{3+} exceeds 3%, the distance between the emission centers decreases. Also, the energy transfer between Eu^{3+} increases and the transition probability between Eu^{3+} and defects increases due to the high energy of the excitation source, resulting in a decrease in scintillation luminescence intensity. The ceramic exhibits an intense red light emission matching well with silicon photodiodes.

Conclusions The maximum in-line transmittance of the ceramic could be obtained at the Eu^{3+} doping concentration of 5%, reaching 71.4% at 611 nm. The photoluminescence and photoluminescence excited spectra of $\text{Eu}_x\text{Lu}_{1.4-x}\text{Gd}_{0.6}\text{O}_3$ ceramics demonstrated that increasing the concentration of Eu^{3+} could enhance the absorption and emission peak intensities of the ceramics. At the concentration of Eu^{3+} of 3%, the ceramic exhibited the most intense red light emission under X-ray excitation with the main emission peak located at 611 nm, corresponding to the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition of Eu^{3+} . High transmittance and high red light emission intensity were of great significance for achieving a high-resolution X-ray imaging.

Keywords transparent ceramics; scintillation ceramics; luminescence performance