Controlled processing of (Gd, Ln)$_2$O$_3$:Eu (Ln = Y, Lu) red phosphor particles and compositional effects on photoluminescence

Bin Lu$^{1,2}$, Ji-Guang Li$^1$ and Yoshio Sakka$^{1,2}$

$^1$ Materials Processing Unit, National Institute for Materials Science, Tsukuba, Ibaraki 305-0047, Japan
$^2$ Department of Materials Science and Engineering, Graduate School of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Ibaraki 305-0047, Japan

E-mail: LJJiguang@nims.go.jp

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Abstract

Synthesis of (Gd$_{0.95-x}$Ln$_x$Eu$_{0.05}$)$_2$O$_3$ (Ln = Y and Lu, x = 0–0.95) powders via ammonium hydrogen carbonate (AHC) precipitation has been systematically studied. The best synthesis parameters are found to be an AHC/total cation molar ratio of 4.5 and an ageing time of 3 h. The effects of Y$^{3+}$ and Lu$^{3+}$ substitution for Gd$^{3+}$, on the nucleation kinetics of the precursors and structural features and optical properties of the oxides, have been investigated. The results show that (i) different nucleation kinetics exist in the Gd–Y–Eu and Gd–Lu–Eu ternary systems, which lead to various morphologies and particle sizes of the precipitated precursors. The (Gd, Y)$_2$O$_3$:Eu precursors display spherical particle morphologies and the particle sizes increase along with more Y$^{3+}$ addition. The (Gd, Lu)$_2$O$_3$:Eu precursors, on the other hand, are hollow spheres and the particle sizes increase with increasing Lu$^{3+}$ incorporation, (ii) the resultant oxide powders are ultrafine, narrow in size distribution, well dispersed and rounded in particle shape, (iii) lattice parameters of the two kinds of oxide solid solutions linearly decrease at a higher Y$^{3+}$ or Lu$^{3+}$ content. Their theoretical densities linearly decrease with increasing Y$^{3+}$ incorporation, but increase along with more Lu$^{3+}$ addition and (iv) the two kinds of phosphors exhibit typical red emissions at ∼613 nm and their charge-transfer bands blue shift at a higher Y$^{3+}$ or Lu$^{3+}$ content. Photoluminescence/photoluminescence excitation intensities and external quantum efficiency are found to decrease with increasing value of x, and the fluorescence lifetime mainly depends on the specific surface areas of the powders.

Keywords: red phosphor, yttria, lutetium oxide, gadolinia, Eu$^{3+}$ doping, photoluminescence, lifetime, quantum efficiency

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1. Introduction

Eu\(^{3+}\)-activated Gd\(_2\)O\(_3\), Y\(_2\)O\(_3\) and Lu\(_2\)O\(_3\) as three kinds of well-known red phosphors are widely applied in various lighting and display systems. The three phosphors present typical red photoluminescence (PL) at ∼612 nm upon UV excitation into the charge-transfer (CT) band (electron transfer from O\(^2-\) to Eu\(^{3+}\)) [1–8]. Improved performance of displays requires high-quality phosphors for sufficient brightness, high resolution and long-term stability. Phosphor particles of spherical shape, ultrfine size, good dispersion and narrow size distribution are desired for three reasons: (i) spherical shape not only allows the formation of a denser phosphor layer by close packing, but also minimizes the light scattering on particle surface to increase the efficiency of luminescence and brightness [9], (ii) ultrafine powders provide small pixel sizes for improved resolution [10–13] and (iii) well-dispersed and narrow size-distributed particles produce uniform luminescence over the whole phosphor screen [14, 15].

The (Gd, Ln)\(_2\)O\(_3\):Eu (Ln = Y, Lu) solid solution systems were studied based on the following three major considerations:

1. Compared with Y\(_2\)O\(_3\):Eu and Lu\(_2\)O\(_3\):Eu, Gd\(_2\)O\(_3\):Eu phosphor displays relatively strong PL and CT bands due to the low electronegativity for Gd\(^{3+}\). In general, the PL intensity of Ln\(_2\)O\(_3\):Eu can be significantly enhanced at an elevated synthesis temperature. However, Gd\(_2\)O\(_3\):Eu will undergo a transformation from a cubic to a monoclinic (or hexagonal) phase upon heating (>1250 °C), by which its PL intensity would be sharply lowered.

2. The ionic radius of Y\(^{3+}\) (0.0900 nm) is close to that of Ho\(^{3+}\) (0.0901 nm) [16], leading to similar chemical properties, and thus Y is generally regarded as a member of the lanthanide family, Y\(_2\)O\(_3\) is cost-effective, and hence Y\(^{3+}\)-doped Gd\(_2\)O\(_3\):Eu red phosphor not only owns low-cost advantage but also exhibits relatively high emission intensity. In addition, Y\(^{3+}\) doping can effectively suppress the phase transformation of Gd\(_2\)O\(_3\) through solid-solution formation. (Gd, Y)\(_2\)O\(_3\):Eu is a promising material to be used in the fields of fluorescent lamp, white LEDs, and can also be densified into transparent ceramic scintillator by high-temperature sintering [17, 18].

3. Lu\(^{3+}\) has smaller ionic radius than Y\(^{3+}\), and thus its doping is more effective in stabilizing the cubic structure of Gd\(_2\)O\(_3\). Moreover, Lu\(^{3+}\) possesses high absorption of x-rays to reduce the multiple scattering of light because of its high density and high effective atomic number. It has been proved suitable as an x-ray-stopping powder in ceramic scintillators [19–21].

The commercial Ln\(_2\)O\(_3\):Eu phosphors are classically yielded by high-temperature solid-phase reaction and ball-milling treatment, which often gives rise to large particle size, considerable agglomeration and broad particle size distribution. Therefore, wet chemical methods are necessary in the synthesis of fluorescent powders. Based on previous reports [10–12, 14, 22–30], urea-based homogeneous precipitation (UBHP) technique is found to be a good tool for acquiring uniform and monodispersed particles. Compared with the UBHP, ammonium hydrogen carbonate (AHC) precipitation is relatively time-efficient, cost-effective, operation-simple and high-yield. In this work, (Gd, Ln)\(_2\)O\(_3\):Eu (Ln = Y, Lu) red phosphors were studied for their synthesis, formation mechanism, compositional impacts and PL behaviors.

2. Experimental procedures

The starting materials were Gd(NO\(_3\))\(_3\)·6H\(_2\)O (>99.95% pure, Kanto Chemical Co., Inc., Tokyo, Japan), Y(NO\(_3\))\(_3\)·6H\(_2\)O (>99.99% pure, Kanto Chemical) and Eu(NO\(_3\))\(_3\)·6H\(_2\)O (>99.95% pure, Kanto Chemical). Lu(NO\(_3\))\(_3\) was prepared by dissolving a Lu\(_2\)O\(_3\) powder (>99.95% pure, Kanto Chemical) in an excessive amount of nitric acid at ∼90°C.

Precipitated precursors for (Gd\(_{0.95–x}\).Ln\(_x\)Eu\(_{0.05}\))O\(_3\), which has 80 atoms per unit cell, x-ray density was prepared by dissolving a Lu\(_2\)O\(_3\) powder (>99.95% pure, Kanto Chemical) in an excessive amount of nitric acid at ∼90°C.

Precipitated precursors for (Gd\(_{0.95–x}\).Ln\(_x\)Eu\(_{0.05}\))O\(_3\) were synthesized by dripping AHC (ultrahigh purity, Kanto Chemical) solution (1.5 M) into a stoichiometric amount of mother liquor (0.15 M for total cationic concentration) at selected AHC/total cation molar ratio (R) under magnetic stirring at room temperature. For typical synthesis, the x value was selected from 0 to 0.95 and the molar ratio of Eu\(^{3+}\) to total cations was fixed at 5 at.% because the concentration quenching of luminescence was found at 5 at.% for Y\(_2\)O\(_3\):Eu [12, 31] and 5–7 at.% for Gd\(_2\)O\(_3\):Eu [32–35]. The resultant suspension, after ageing for different times, was filtered and repeatedly washed with distilled water to remove the byproducts. Then it was rinsed with anhydrous alcohol to remove water and dried at 80 °C. The dried precursors were lightly crushed with an alumina mortar and a pestle, and finally calcined in a tube furnace under flowing oxygen gas (250 ml min\(^{-1}\)) at selected temperatures for 4 h with a heating rate of 5 °C min\(^{-1}\).

Compositions of the precursors were determined by chemical analysis. Cation contents were detected by the inductively coupled plasma spectroscopic approach with an accuracy of 0.01 wt% (Model SPSS3520, SII Nanotechnology Inc., Tokyo, Japan), carbon contents were assayed on a carbon/sulfur determinator with an accuracy of 0.01 wt% (Model SPS3520, SII Nanotechnology Inc., Tokyo, Japan), and NH\(_4\)\(^+\) contents were determined by the standard distillation-titrimetric method with an experimental error of ±0.1 wt%. The precursors and their oxides were characterized using thermogravimetry (TG; Model 6200, SII Nanotechnology Inc.), x-ray diffractometry (XRD; Model RINT2200, Rigaku Corporation, Japan), Brunauer–Emmett–Teller analysis (BET; Model Autosorb-iQ, Quantachrome Instruments, Florida, USA), field-emission scanning electron microscopy (FE-SEM; Model S-5000, Hitachi, Tokyo), laser diffraction particle size analysis (LDPSA, Model Horiba LA-920, Kyoto, Japan) and fluorescence spectroscopy (Model FP-6500, JASCO, Tokyo).

For the cubic-structured C-type sesquioxide lattice, which has 80 atoms per unit cell, x-ray density was
3. Results and discussion

3.1. AHC/total cation molar ratio (R) impact on (Gd_{0.75}Y_{0.2}Eu_{0.05})_2O_3 precursors and their oxides

R has significant effects on the nature of precipitated precursors, and the impact of R on the morphologies of the (Gd_{0.75}Y_{0.2}Eu_{0.05})_2O_3 precursors is shown in figure 1.

Figure 1 shows the morphologies of the (Gd_{0.75}Y_{0.2}Eu_{0.05})_2O_3 precipitated precursors obtained at R = 1–15 and an ageing time of 1 h. At R = 1–4.5, the colloidal precursors appear spherical and are composed of ultrafine primary particles (figures 1(a)–(d)), whereas those acquired at R = 7.5–15 display non-uniform mixtures and consist of very large and small platelike particles (figures 1(e) and (f)). In particular, at low R (1–2), the precursor powders strongly agglomerate, which is probably because the low pH is close to their isoelectric points.

Ln^{3+} ions are hydrated to [Ln(H_2O)_6]^{3+} and then undergo hydrolysis to form [Ln(OH)_x(H_2O)_{6-x}]^{3-x} species in water solution (equations (3) and (4)). However, the AHC solution contains many kinds of ionic species, such as HCO_3^-, CO_3^{2-}, OH^-, H^+ and NH_4^+. Compositions of the precursors formed from the reaction systems depend on the competition of the ionic species that combine with Ln^{3+} (equations (5)–(7)):

\[
\text{Ln}^{3+} + 6\text{H}_2\text{O} \rightarrow [\text{Ln}(\text{H}_2\text{O})_6]^{3+},
\]

\[
[\text{Ln}(\text{H}_2\text{O})_6]^{3+} + x\text{H}_2\text{O} \rightarrow [\text{Ln}(\text{OH})_x(\text{H}_2\text{O})_{6-x}]^{3-x} + x\text{H}_3\text{O}^+.
\]

\[
[\text{Ln}(\text{OH})_x(\text{H}_2\text{O})_{6-x}]^{3-x} + 3\text{HCO}_3^- + (x + n - 7)\text{H}_2\text{O} \rightarrow \text{Ln}(\text{OH})\text{CO}_3 \cdot n\text{H}_2\text{O} + 2\text{CO}_2 + x\text{OH}^-.
\]

\[
2\text{Ln}(\text{OH})\text{CO}_3 \cdot n\text{H}_2\text{O} + \text{HCO}_3^- \rightarrow \text{Ln}_2(\text{CO}_3)_3 \cdot n\text{H}_2\text{O} + \text{OH}^- + \text{H}_2\text{O},
\]

\[
\text{Ln}_2(\text{CO}_3)_3 \cdot n\text{H}_2\text{O} + \text{CO}_3^{2-} + 2\text{NH}_4^+ \rightarrow 2\text{NH}_4\text{Ln}(\text{CO}_3)_2 \cdot n\text{H}_2\text{O}.
\]

The XRD patterns of the (Gd_{0.75}Y_{0.2}Eu_{0.05})_2O_3 precursors obtained at R = 1–15 and an ageing time of 1 h are shown in figure S1 (available from stacks.iop.org/STAM/14/064202/mmedia) of the supporting information. The precursor powders produced at R = 1–4.5 exhibit the amorphous phases corresponding to their spherical particle shapes (figures 1(a)–(d)). As R increases above 7.5, the precursor powders improve their crystallinities and exhibit the characteristics of layered rare-earth carbonate structures.
Table 1. Elemental content (wt%) of precursor powders prepared under typical synthesis conditions.

| R     | Ageing (h) | Gd  | Y    | Eu  | C     | N     | Approx. formula |
|-------|------------|------|------|-----|-------|-------|----------------|
| 1     | 1          | 47.2 | 4.9  | 3.4 | 6.4   |       | (Gd₃₀Yo.1₂Eu₀.₈₀)₂(CO₃)₂·5 UINavigationController.0₂·2.₄H₂O |
| 4.5   | 1          | 44.8 | 6.7  | 2.8 | 7.₃   |       | (Gd₃₀Yo.2Eu₀.₀₅)₂(CO₃)₂·₄H₂O |
| 4.₅   | 10         | 45.₈ | 7.₂  | 2.₉ | 7.₃   | 0.₉₂  | (NH₄)₀.₅[Gd₃₀Yo.₂Eu₀.₀₅]₂(CO₃)₂·₃H₂O |
| 7.₅   | 1          | 3₇.₈ | 5.₆  | 2.₄ | 7.₄   | 3.₁   | (NH₄)₀.₇[Gd₃₀Yo.₂Eu₀.₀₅]₂(CO₃)₃·₇.₅·₆H₂O |

Figure 2. FE-SEM micrographs of the (Gd₀.₇₅Y₀.₃Eu₀.₀₅)₂O₃ oxides calcined at 1100 °C for 4 h, obtained from the precursors of R = 1 (a), R = 2 (b), R = 3 (c), R = 4.₅ (d), R = 7.₅ (e) and R = 15 (f).

3.2. Ageing-time effect on the (Gd₀.₇₅Y₀.₃Eu₀.₀₅)₂O₃ precursors and their oxides

Figure 3 displays the impact of ageing time on the properties of the (Gd₀.₇₅Y₀.₃Eu₀.₀₅)₂O₃ precursors and their oxides. At R = 4.₅, the ageing time was selected from 1 to 10 h. With an ageing time of 3 h, the precursor also exhibits spherical shape (figure 3(a)) and its oxide is well dispersed (figure 3(d)). As the ageing time increases to 6 h, the precursor and its oxide transform into a platelike morphology (figures 3(b), (e)). When the ageing time is over 10 h, the precursor also keeps the layered structure, but may consist of two phases of the hydrated carbonate and the hydrated ammonium rare-earth carbonate, as shown by the combined results of the element analysis (table 1) and the XRD analysis (figure S3 in the supporting information).

3.3. Synthesis and characterization of (Gd, Ln)₂O₃:Eu compounds

A series of (Gd₀.₉₅₋ₓLnₓEu₀.₀₅)₂O₃ (Ln = Y and Lu, x = 0–0.₉₅) powders were synthesized under the optimized conditions of R = 4.₅ and an ageing time of 3 h.

Figures 4(a)–(c) show the morphologies of (Gd₀.₉₅₋ₓYₓEu₀.₀₅)₂O₃ (x = 0, 0.₆ and 0.₉₅) precursors. It can be seen that all of the precursor powders exhibit spherical shapes corresponding to their amorphous phases (figure S4 in the supporting information) and the particle sizes increase with greater Y³⁺ addition (~50, 68 and 78 nm...
Figure 3. FE-SEM micrographs showing morphologies of the $(\text{Gd}_{0.75}\text{Y}_{0.2}\text{Eu}_{0.05})_2\text{O}_3$ precursors and their oxides: the precursors synthesized at an ageing time of 3 h (a), 6 h (b) and 10 h (c); and (d)–(f) for their oxides, respectively.

Figure 4. FE-SEM micrographs of $(\text{Gd}_{0.95-x}\text{Ln}_x\text{Eu}_{0.05})_2\text{O}_3$ precursor powders with Ln = Y, $x = 0$ (a), $x = 0.6$ (b) and $x = 0.95$ (c); Ln = Lu, $x = 0.1$ (d), $x = 0.6$ (e) and $x = 0.95$ (f).

for $x = 0$, 0.6 and 0.95, respectively, as measured from the FE-SEM micrographs). The composition-dependent particle size is closely related with the nucleation and particle growth processes, while the occurrence of precipitation depends on supersaturation given by the following equation [36]:

$$S = a_A a_B / K_{sp},$$

where $a_A$ and $a_B$ are the activities of partially hydrolyzed cation $[\text{Ln(OH)}_x(\text{H}_2\text{O})_{6-x}]^{3-x}$ and anion $(\text{CO}_3^{2-})$, and $K_{sp}$ is the solubility product constant. Nucleation starts only when $S$ reaches the critical supersaturation $S^\ast$. The solubility of a lanthanide basic carbonate increases with decreased ionic radius of Ln$^{3+}$ [12]. According to the lanthanide contraction law, the $K_{sp}$ value increases in the order $\text{Eu(OH)CO}_3 < \text{Gd(OH)CO}_3 < \text{Y(OH)CO}_3$. Thus, $\text{Eu(OH)CO}_3$ and $\text{Gd(OH)CO}_3$ are formed in priority to act as crystal nuclei (equation (8)). As the Ln$^{3+}$ cation and AHC concentration are fixed, more Gd$^{3+}$ leads to a higher nucleation density and thus smaller particle size. The deviating chemical composition of the precursor powder prepared at $R = 1$ for 1 h also supports our interpretations (table 1).

Figures 4(d)–(f) are FE-SEM micrographs showing the morphologies of $(\text{Gd}_{0.95-x}\text{Lu}_x\text{Eu}_{0.05})_2\text{O}_3$ ($x = 0.1, 0.6, 0.95$) precursors. It can be observed that a higher Lu$^{3+}$ content leads to much larger particles ($\sim 56$, 78 and 101 nm for $x = 0.1$, 0.6 and 0.95, respectively, as measured from the FE-SEM micrographs) of frequently empty interiors. This phenomenon can be interpreted from the nucleation kinetics among...
exhibits the XRD patterns of the rare-earth cations with high degrees of hydrolysis, such as Sc-containing compounds. Although the $K_{sp}$ increases in the order Eu(OH)CO$_3$ < Gd(OH)CO$_3$ < Lu(OH)CO$_3$, the relatively high degree of hydrolysis for Lu$^{3+}$ may dominate here. The higher hydrolysis degree of Lu$^{3+}$ induces a higher activity of [Lu(OH)$_6$]$_{x}$; therefore Lu(OH)CO$_3$ is produced in priority in the Gd–Lu–Eu ternary system. Meanwhile, the high degree of hydrolysis also causes a low pH value of the nitrate solution (equation (4)). Thus, when the AHC is added, a fair amount of small bubbles would be generated via chemical decomposition of AHC (equation (9)), some of which provide crystal nuclei to form the hollow structures. According to our previous studies [37, 38], such a phenomenon is also observed for other rare-earth cations with high degrees of hydrolysis, such as Sc-containing compounds.

$$\text{H}^+ + \text{HCO}_3^- \rightarrow \text{CO}_2 + \text{H}_2\text{O.} \quad (9)$$

Figure 5 exhibits the morphologies of the (Gd$_{0.95-\text{x}}$Eu$_{\text{x}}$)$_2$O$_3$ ($\text{x} = 0, 0.6, 0.95$) and (Gd$_{0.95-\text{x}}$Lu$_{\text{x}}$Eu$_{0.05}$)$_2$O$_3$ ($\text{x} = 0.1, 0.6, 0.95$) powders calcined at 1100°C for 4h. The resultant oxide particles are ultrafine, uniform in size, well-dispersed and rounded in particle shape. The particle size distribution curve is given out in figure S5 of the supporting information (available from stacks.iop.org/STAM/14/064202/mmedia) by taking the (Gd$_{0.95}$Eu$_{0.05}$)$_2$O$_3$ powder as an example. This sample shows a narrow and unimodal particle size distribution.

Tables 2 and 3 show the $S_{\text{BET}}$ value, the grain size calculated by XRD, the statistical particle-size data from the FE-SEM micrographs obtained with the WinRoof image analysis software, and the particle size measured via LDPSA of the (Gd, Ln)$_2$O$_3$:Eu oxides.

The grain sizes of the oxide powders generally decrease with increasing $Y^{3+}$ or $Lu^{3+}$ incorporation, since the lattice constants of (Y$_{0.95}$Eu$_{0.05}$)$_2$O$_3$ (10.61 Å, figure 7) and (Lu$_{0.95}$Eu$_{0.05}$)$_2$O$_3$ (10.40 Å) are much smaller than that of (Gd$_{0.95}$Eu$_{0.05}$)$_2$O$_3$ (10.80 Å). Mass diffusion in (Y$_{0.95}$Eu$_{0.05}$)$_2$O$_3$ and (Lu$_{0.95}$Eu$_{0.05}$)$_2$O$_3$ may be slower than that in (Gd$_{0.95}$Eu$_{0.05}$)$_2$O$_3$ upon calcination and, therefore, smaller grain sizes result at a higher $Y^{3+}$ or $Lu^{3+}$ content. The SEM sizes of the oxides also generally decrease along with more $Y^{3+}$ or $Lu^{3+}$ addition. LDPSA is effective in detecting agglomerates [39]. Some relatively small particle sizes detected by LDPSA indicate less agglomeration and higher dispersion of the powders.

Figure 6 exhibits the XRD patterns of the (Gd, Ln)$_2$O$_3$:Eu oxide powders calcined at 1100°C for 4h. The XRD peaks of the two kinds of solid solutions shift

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**Table 2.** $S_{\text{BET}}$, crystallite size, SEM size and particle size of (Gd, Y)$_3$O$_2$:Eu oxides.

| Y$^{3+}$ content (%) | $S_{\text{BET}}$ (m$^2$ g$^{-1}$) | XRD (nm) | SEM (nm) | LDPSA (nm) |
|----------------------|-------------------------------|----------|----------|------------|
| 0                    | 6.8                           | 46.3     | 187      | 288        |
| 10                   | 12.3                          | 46.3     | 165      | 303        |
| 20                   | 12.7                          | 41.6     | 156      | 216        |
| 40                   | 14.5                          | 46.3     | 153      | 218        |
| 60                   | 19.4                          | 38.0     | 120      | 182        |
| 80                   | 21.7                          | 41.7     | 115      | 145        |
| 95                   | 15.4                          | 41.7     | 116      | 142        |

**Table 3.** $S_{\text{BET}}$, crystallite size, SEM size and particle size of (Gd, Lu)$_2$O$_3$:Eu oxides.

| Lu$^{3+}$ content (%) | $S_{\text{BET}}$ (m$^2$ g$^{-1}$) | XRD (nm) | SEM (nm) | LDPSA (nm) |
|----------------------|-------------------------------|----------|----------|------------|
| 10                   | 15.4                          | 46.3     | 126      | 199        |
| 20                   | 18.3                          | 38.0     | 106      | 173        |
| 40                   | 19.2                          | 38.0     | 105      | 216        |
| 60                   | 19.7                          | 34.8     | 87       | 154        |
| 80                   | 16.8                          | 34.8     | 78       | 224        |
| 95                   | 15.4                          | 34.8     | 80       | 328        |
toward the high-angle side along with more Y\(^{3+}\) or Lu\(^{3+}\) incorporation. Apparently, Y\(^{3+}\) and Lu\(^{3+}\) doping leads to a gradual contraction in the unit cell of the cubic crystal owing to the smaller ionic radius of Y\(^{3+}\) and Lu\(^{3+}\) than that of Gd\(^{3+}\) and Eu\(^{3+}\).

The calculated lattice constants and theoretical densities of the (Gd\(_{0.95-x}\)Ln\(_x\))\(_2\)O\(_3\):Eu solid solutions are shown in figure 7. The cell parameters linearly decrease along with increasing \(x\) value, which observes Vegard’s law, implying that homogeneous solid solutions have been formed. The theoretical densities calculated with the cell parameters linearly decrease with more Y\(^{3+}\) addition due to its atomic number which is lower than Gd\(^{3+}\), whereas the theoretical densities increase at a higher Lu\(^{3+}\) content since it is much heavier than Gd\(^{3+}\).

Figure 8 shows the PL spectra of (Gd, Ln\(_x\))\(_2\)O\(_3\):Eu phosphors. Both (Gd, Y\(_{0.95-x}\))\(_2\)O\(_3\):Eu and (Gd, Lu\(_{0.95-x}\))\(_2\)O\(_3\):Eu oxide powders calcined at 1100°C exhibit the characteristic emissions of Eu\(^{3+}\) from \(^5\text{D}_0 \rightarrow ^7\text{F}_J\) (\(J = 0, 1, 2, 3, 4\)) transitions. The sharpest emission peak at 613 nm and that at 630 nm are associated with the \(^5\text{D}_0 \rightarrow ^7\text{F}_2\) transitions of Eu\(^{3+}\). The group of emission peaks at 587, 592 and 598 nm derives from \(^5\text{D}_0 \rightarrow ^7\text{F}_1\) of Eu\(^{3+}\), while those at 582, 652 and 708 nm are assigned to the \(^5\text{D}_0 \rightarrow ^7\text{F}_6, ^5\text{D}_0 \rightarrow ^7\text{F}_3\) and \(^5\text{D}_0 \rightarrow ^7\text{F}_2\) transitions, respectively.

The excitation spectra of (Gd, Ln\(_x\))\(_2\)O\(_3\):Eu particles obtained with the emission at 613 nm are shown in figure 9. The main bands at 248–258 nm are due to the transition by CT, viz., electronic transition from the 2p orbital of O\(^2-\) to the 4f orbital of Eu\(^{3+}\), the peaks at 217–235 nm as the left shoulder of the broad CT bands are ascribed to the absorption of rare-earth-oxide host lattice, and the right ones at 276 nm are assigned to the \(^8\text{S}_7/2 \rightarrow ^6\text{I}_J\) internal f–f transition of Gd\(^{3+}\) [6]. The overlapped bands from 300 to 335 nm arise from the \(^8\text{S}_7/2 \rightarrow ^6\text{P}_J\) of Gd\(^{3+}\) and \(^7\text{F}_{0,1} \rightarrow ^5\text{H}_J\) transitions of Eu\(^{3+}\). The two types of bands can be distinguished by comparing with the non-Gd\(^{3+}\)-containing samples, that is, the peaks at 308 and 314 nm are only for the \(^5\text{S}_7/2 \rightarrow ^5\text{P}_J\) transition of Gd\(^{3+}\). The other weak peaks beyond 350 nm are assignable to the f–f Eu\(^{3+}\) transition.

The PL and photoluminescence excitation (PLE) intensities of (Gd, Ln\(_x\))\(_2\)O\(_3\):Eu powders mainly depend on the amount of Gd\(^{3+}\), since the differences in electronegativities among Gd\(^{3+}\), Y\(^{3+}\) and Lu\(^{3+}\) result in diverse abilities to attract electrons and even shifted-peak locations of CT bands [12, 22] (6 nm for (Gd, Y\(_2\))\(_2\)O\(_3\):Eu and 10 nm for
Figure 8. PL behaviors of the (Gd, Ln)₂O₃:Eu phosphors with the composition (Gd₀.₉₅₋ₓYₓEu₀.₀₅)O₃ (a) and (Gd₀.₉₅₋ₓLuₓEu₀.₀₅)O₃ (b). The PL spectra were obtained under excitations with the peak wavelengths of the CT bands shown in figure 9.

Figure 9. PLE spectra of the (Gd, Ln)₂O₃:Eu phosphors with the composition (Gd₀.₉₅₋ₓYₓEu₀.₀₅)O₃ (a) and (Gd₀.₉₅₋ₓLuₓEu₀.₀₅)O₃ (b). The PLE spectra were obtained by monitoring the 613 nm emissions of Eu³⁺.

(Gd, Lu)₂O₃:Eu. The low electronegativity for Gd³⁺ (1.20) leads to easy electron transfer, and thus PL intensity is enhanced, although the larger particle size of its oxide also contributes to the relatively strong emission. For (Gd, Y)₂O₃:Eu and (Gd, Lu)₂O₃:Eu powders of the same Gd³⁺ concentration, the PL and PLE intensities are in the order (Gd, Lu)₂O₃: Eu < (Gd, Y)₂O₃: Eu. This is also owing to the lower electronegativity of Y³⁺ (1.22) than that of Lu³⁺ (1.27). In this work, the (Gd₀.₉₅Eu₀.₀₅)O₃ phosphor exhibits PL intensity at 613 nm, about 1.7 times that of the (Y₀.₉₅Eu₀.₀₅)O₃ phosphor and 2.9 times that of the (Lu₀.₉₅Eu₀.₀₅)O₃ phosphor, which is similar to the relative CT band intensity ratios.

Calcination temperature also plays an important role in the luminescence of the resultant phosphors and the results are shown in figure 10 with the (Gd₀.₇₅Y₀.₂Eu₀.₀₅)O₃ sample as an example. The PL intensity increases with increasing calcination temperature owing to the more homogeneous component distribution among Gd³⁺, Y³⁺ and Eu³⁺, which alleviates localized concentration quenching of Eu³⁺. Improved crystallinity (figure S6 in the supporting information (available from stacks.iop.org/STAM/14/064202/mmedia)) and larger particle size are another two important reasons. The phosphor particles calcined at 500 °C exhibit low emission intensity probably because of the combined effects of disordered coordination between Ln³⁺ and O²⁻ in the amorphous structure (figure S6 in the supporting information) and the
presence of CO$_2^-$ in the intermediate calcination product (figure S2 in the supporting information), which may raise the non-radiative relaxation rate. The PL intensity is significantly improved as the temperature increases to 600 °C, due to the phase transformation from an amorphous to a cubic phase. A linear increase in PL intensity is observed at a higher calcination temperature from 600 to 1300 °C (the inset in figure 10).

Figure 11 shows the fluorescence lifetime of the (Gd, Ln)$_2$O$_3$:Eu phosphors, which was obtained from the fluorescence decay curves (figure S7 in the supporting information) by a single exponential equation

$$I = A \exp (-t/\tau_R) + B,$$

(10)

where $\tau_R$, $t$ and $I$ denote the fluorescence lifetime, delay time and relative intensity, respectively, and $A$ and $B$ are constants. The lifetimes of Eu$^{3+}$-doped Y$_2$O$_3$, Gd$_2$O$_3$ and Lu$_2$O$_3$ phosphors vary in the range of 1.1–2.6 ms [6, 32, 40–44]. In this work, the fluorescence lifetime is observed at 1.48–2.23 ms for the (Gd, Y)$_2$O$_3$:Eu and 1.48–2.52 ms for the (Gd, Lu)$_2$O$_3$:Eu phosphors, which are close to each other and are in good agreement with the reported values. The fluorescence lifetime decreases at a higher calcination temperature largely due to the smaller specific surface area (larger particle size) and improved crystallinity (figure S8 in the supporting information) [45, 46].

The external quantum efficiency was reported to be in the wide range of 8.0–91.9% for the Y$_2$O$_3$:Eu [47–49], 4.6–23.6% for the Gd$_2$O$_3$:Eu [50, 51] and 30–90% for the Lu$_2$O$_3$:Eu phosphors [44, 52, 53]. Such significant deviation can be ascribed to varied particle sizes, particle morphologies and crystal defects, etc. As shown in figure 12, the $\varepsilon_{ex}$ is found in this study to be 63–100% for (Gd, Y)$_2$O$_3$:Eu and 46–100% for (Gd, Lu)$_2$O$_3$:Eu, and depends on the Gd$^{3+}$ concentration, which may be attributed to the sensitization effect of Gd$^{3+}$ [33]. In addition, the $\varepsilon_{ex}$ dramatically increases with increasing calcination temperature of the sample (figure S9 in the supporting information). A 700 °C increase from 600 to 1300 °C improves the $\varepsilon_{ex}$ by ~83.3%, mainly owing to the crystal perfection.

**Figure 11.** Fluorescence lifetime of the (Gd, Ln)$_2$O$_3$:Eu phosphors.

**Figure 12.** External quantum efficiency of the (Gd, Ln)$_2$O$_3$:Eu phosphors.

4. Conclusions

Well-dispersed (Gd, Ln)$_2$O$_3$:Eu powders have been synthesized via AHC precipitation under optimized conditions of $R = 4.5$ and an ageing time of 3 h. The nucleation kinetics between Gd–Y–Eu and Gd–Lu–Eu systems are different. For the Gd–Y–Eu ternary system, the nucleation order is found to be Y$^{3+} < $ Gd$^{3+} < $ Eu$^{3+}$. On the other hand, the nucleation density increases in the order of Gd$^{3+} < $ Eu$^{3+} < $ Lu$^{3+}$ in the Gd–Lu–Eu system. The grain sizes of the resultant oxides generally decrease with increasing Y$^{3+}$ or Lu$^{3+}$ addition. The lattice parameters of the two kinds of oxide solid solutions linearly shrink at a higher Y$^{3+}$ or Lu$^{3+}$ content. The theoretical densities of the (Gd, Ln)$_2$O$_3$:Eu phosphor linearly decrease with increasing Y$^{3+}$ incorporation, but increase along with more Lu$^{3+}$ addition. The (Gd, Ln)$_2$O$_3$:Eu phosphor particles exhibit typical red emissions at 613 nm upon UV excitation into the CT band at 248–258 nm. The center of the CT bands red shifts at a higher Gd$^{3+}$ content. The PL/PLE intensities and $\varepsilon_{ex}$ of the (Gd, Ln)$_2$O$_3$:Eu phosphors improve at a higher Gd$^{3+}$ concentration. Elevated calcination temperature enhances the PL intensity and the $\varepsilon_{ex}$, however, lowers the lifetime of the (Gd, Ln)$_2$O$_3$:Eu phosphors. The two kinds of materials made in this work may find potential applications in luminescence and scintillation fields.

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**References**

[1] Park C-S, Kwak M-G, Choi S-S, Song Y-S, Hong S-J, Han J-I and Lee D Y 2006 J. Lumin. 118 199

[2] Williams D K, Yuan H and Tissue B M 1999 J. Lumin. 83–84 297
