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Synthesis and Fluorescence Quantum Yield of $Gd_{1-x}Eu_xOOH$ Crystals

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Abstract

Eu^{3+}-doped gadolinium oxyhydroxide $Gd_{1-x}Eu_xOOH$ crystals were synthesized by the flux method. The X-ray diffraction data for the crystals were well refined assuming a monoclinic structure with the $P2_1/m$ space group. $Gd_{1-x}Eu_xOOH$ ($x \le 0.2$) crystals showed strong red emission, and the highest fluorescence quantum yield (Φ_f) was 0.27, obtained for $x = 0.10$. Φ_f decreased rapidly as the Eu^{3+} content x increased above 0.2, owing to concentration quenching. Analysis with a percolation model indicated three-dimensional energy transfer between the Eu^{3+} ions.

Keywords

Gadolinium Oxyhydroxide; Fluorescence Quantum Yield; Percolation Model

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1. Introduction

Some rare-earth compounds have excellent optical properties and hence are widely used in high-performance luminescence devices and as catalyst supports. Trivalent rare-earth ions such as Eu^{3+}, Tb^{3+}, and Tm^{3+}-doped in a suitable host material show strong emission based on electron transition between the 4*f* orbitals. The luminescence properties depend strongly on the chemical composition and crystal structure of the host material. One of the Gd(III) compounds, gadolinium oxyhydroxide (GdOOH), which has a monoclinic structure with the $P2_1/m$ space group, can be obtained as a stable phase by the thermal dehydration of hydroxide $Gd(OH)_3$ [1]-[4]. Although this compound can function as a host material for phosphors, there are very few reports on its photoluminescence properties [5] [6]. Fluorescence quantum yield, Φ_f, which is defined as the ratio of the number of emitted photons to the number of absorbed photons, is a fundamental parameter that decides the photoluminescence efficiency of a compound/phosphor [7]. Hence, evaluation of the activator content dependence of Φ_f using high-quality single-crystal specimens is important.

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In this study, we synthesized $Gd_{1-x}Eu_xOOH$ crystals and evaluated their luminescence properties, including Φ_f. In addition, we evaluated the critical Eu^{3+} concentration in the $Gd_{1-x}Eu_xOOH$ system by using a percolation model.

2. Experimental

Crystals of Eu^{3+}-doped gadolinium oxyhydroxide, $Gd_{1-x}Eu_xOOH$ (x = 0, 0.02, 0.04, 0.06, 0.08, 0.1, 0.15, 0.2, 0.3, 0.4, 0.5, 0.6, 0.8, 1), were synthesized by the flux method. Appropriate amounts of Gd_2O_3 powder (99.9%) and Eu_2O_3 powder (99.9%) were mixed in an agate mortar for 1 h. Then, the Gd_2O_3/Eu_2O_3 mixture was placed in a 20-mL Zr crucible and covered by a layer of a NaOH (15 g)/KOH (5 g) mixture. The crucible was placed in an alumina container, covered with an alumina lid, and heated in an electric furnace at 330˚C for 72 h in ambient atmosphere. Subsequently, the flux was dissolved in large excess of water; the obtained crystals were washed thoroughly in distilled water to remove any residual flux and dried on a hot plate at 80˚C for 1 h.

The chemical composition of the crystals was measured using an inductively coupled plasma optical emission spectrometer (ICP-OES; Seiko Instruments Inc., SPS1700HVR) and an energy-dispersive X-ray spectrometer (EDS; JEOL, EX-23000 BU). The crystal structures were identified by powder X-ray diffraction (XRD; Rigaku, RINT2000). The diffraction data were acquired using CuKα radiation generated at 40 kV and 20 mA, in the 2θ range 10~80˚ at room temperature, and refined by the Rietveld method [8]. Thermogravimetric analysis (TG) and differential thermal analysis (DTA) were carried out in air, at temperatures between 30 and 785˚C at a heating rate of 10˚C /min (Seiko Instruments Inc., TG/DTA6300). The fluorescence excitation and emission spectra were measured at room temperature using a fluorescence spectrophotometer (Hitachi, F-7000). The excitation spectra were corrected for the spectral distribution of the lamp intensity by the Rhodamine B method, and the emission spectra were corrected for the spectral response of the instrument by using a substandard light source. The Φ_f values were measured using an absolute photoluminescence quantum yield measurement system (Hamamatsu, C9920-02), at room temperature [7].

3. Results and Discussion

$Gd_{1-x}Eu_xOOH$ crystallized at the bottom of the crucible. As shown in **Figure 1**, the as-grown GdOOH crystals were transparent and had a plate-like shape with flat surfaces, which could be attributed to the growth in a liquid phase. The maximum length of the crystal was about 1.2 mm. The external surface of the crystals remained largely unchanged through the entire composition range. No trace of Zr, Na, and K impurities was detected by ICP-OES measurements, although these elements were expected to be incorporated into the crystals because of the use of the Zr crucible and NaOH/KOH mixture. The Gd/Eu ratio in the grown crystals, which was measured by EDS, was in good agreement with the molar ratios of Gd_2O_3 and Eu_2O_3, indicating that $Gd_{1-x}Eu_xOOH$ crystals with different compositions could be obtained by simply changing the molar ratio of the starting materials.

Figure 2 shows the powder XRD profiles of $Gd_{1-x}Eu_xOOH$ and the result of data refinement by the Rietveld method. The black squares show the experimental data, and the red and blue solid lines show the calculated profile and the difference between the experimental and calculated profiles, respectively. All the diffraction data were well refined assuming a monoclinic structure with the $P2_1/m$ space group, and no structural change was observed over the entire composition range considered. The lattice parameters for GdOOH (a = 0.4339 nm, b = 0.3717 nm, c = 0.6072 nm, β = 108.79˚) and EuOOH (a = 0.4346 nm, b = 0.3744 nm, c = 0.6107 nm, β = 108.62˚) agreed with those reported in previous studies [9] [10]. When Gd^{3+} (ionic radius: 0.0935 nm) in GdOOH was replaced by Eu^{3+} (ionic radius: 0.0947 nm), the lattice constants showed a slight increase, in accordance with Vegard' law. $Gd_{1-x}Eu_xOOH$ had low rare-earth site symmetry and a layered structure in which the rare earth layers were sandwiched between an O layer and an OH layer [11] [12].

The TG curve of the as-grown crystals indicated no apparent weight loss in the temperature range 30~400˚C, indicating that the as-grown crystals did not include $Gd(OH)_3$, which normally decomposes at 270˚C [4]. In the TG profile, the first large weight loss was observed at 445˚C, with a corresponding endothermic effect, attributable to the removal of water molecules from GdOOH crystals. The experimental weight loss of 4.5% agreed well with the theoretical value of 4.7% calculated assuming the following thermal decomposition: $2GdOOH \rightarrow Gd_2O_3 + H_2O$. The XRD profiles of the specimens subjected to TG/DTA measurements showed a single phase, Gd_2O_3. These results indicated that the as-grown crystals comprised a single phase of GdOOH and did not contain Gd_2O_3 and $Gd(OH)_3$ at all.

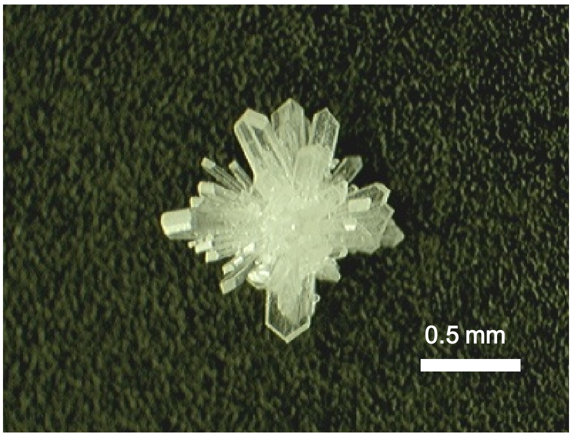


Figure 1. Photograph of as-grown GdOOH crystals synthesized at 330˚C for 72 h.

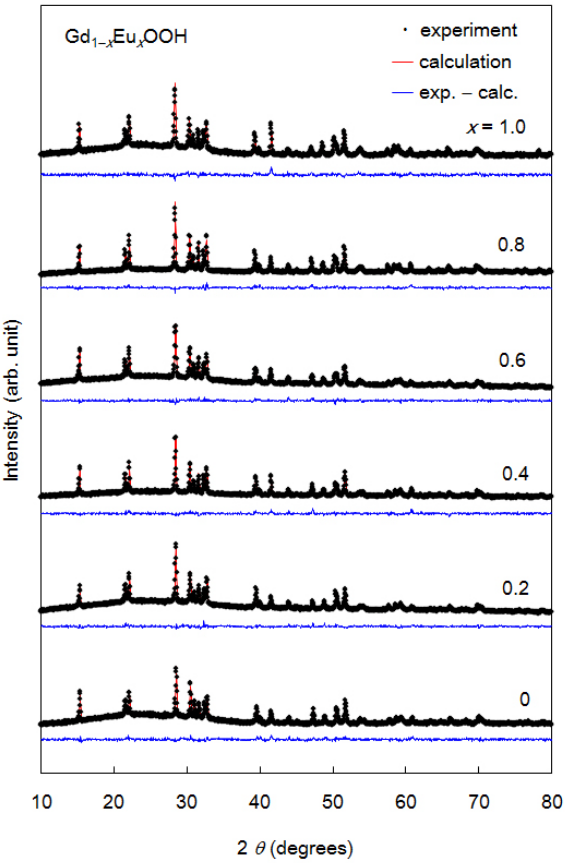


Figure 2. Powder X-ray diffraction profiles of $Gd_{1-x}Eu_xOOH$ crystals and results of data refinement by the Rietveld method.

Figure 3 shows the excitation spectra of the $Gd_{1-x}Eu_xOOH$ crystals; spectral measurements were performed at 617 nm, which is the maximum emission wavelength of Eu^{3+} in this system ($^5D_0 \rightarrow {}^7F_2$ transition). The excitation spectra showed sharp peaks between 300 nm and 550 nm, which were attributed to the direct intraconfigurational 4*f*-4*f* transitions from the $^7F_0$ and $^7F_1$ levels of Eu^{3+}. The intensity of these peaks increased as the Eu^{3+} content increased up to $x = 0.1$. The wide peak between 200 nm and 300 nm, which was attributed to the overlapping of

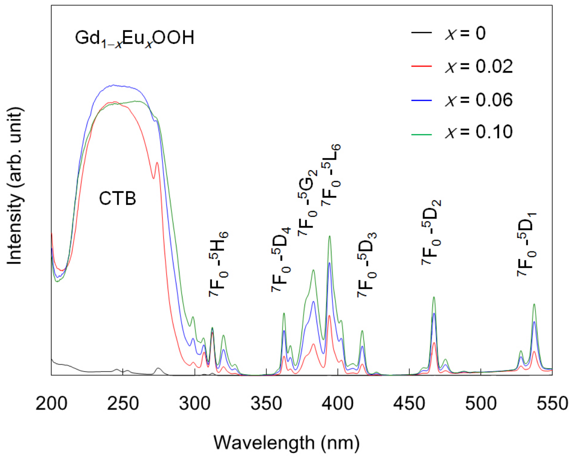


Figure 3. Excitation spectra of $Gd_{1-x}Eu_xOOH$ crystals.

the O^{2-} to Eu^{3+} charge transfer band (CTB) and the band due to energy transfer from Gd^{3+} to Eu^{3+} [13], indicated energy transfer from the oxyhydroxide host to Eu^{3+}. The intensity of the sharp peaks appearing at wavelengths longer than 300 nm changed with the Eu^{3+} content, but that of the wide peak at wavelengths below 300 nm did not change much.

Figure 4 shows the emission spectrum of the $Gd_{0.9}Eu_{0.1}OOH$ crystals under 243 nm illumination. Strong red luminescence from Eu^{3+} was observed in the visible range. These peaks could be attributed to the transition from the lowest exited level $^5D_0$ to the $^7F_{0-4}$ levels of the ground term. The most intense transition was $^5D_0 \rightarrow {}^7F_2$, the allowed electric dipole transition, at 617 nm. The other electric dipole transition, $^5D_0 \rightarrow {}^7F_4$, was observed near 710 nm. In addition to electric dipole transitions, a strong magnetic dipole transition, $^5D_0 \rightarrow {}^7F_1$, was observed near 595 nm. A $^5D_0 \rightarrow {}^7F_0$ transition, which is normally forbidden by the free-ion selection rules, occurred at around 580 nm, as the selection rules are broken by the low symmetry of the rare-earth sites.

Figure 5 shows the Eu^{3+} content dependence of Φ_f for the $Gd_{1-x}Eu_xOOH$ crystals under excitation at 243, 258, and 394 nm (Eu^{3+}: $^7F_0 \rightarrow {}^5L_6$), with the former two wavelengths being close to the peak maxima in the excitation spectra. The highest Φ_f of 0.27 was obtained when the Eu^{3+} content was around 0.1. The decrease in Φ_f for $x < 0.1$ was attributed to the small amount of Eu^{3+}, which is the photoactivator, in the system. At all excitation wavelengths, Φ_f decreased rapidly as the Eu^{3+} content increased beyond 0.2, because of concentration quenching caused by the transfer of excitation energy between the Eu^{3+} ions.

The critical Eu^{3+} concentration was evaluated by using the percolation model, which has been used to explain energy transfer in the solid state [14]-[16]. In this study, the aforesaid model was applied to the system under the following assumptions: energy transfer between the Eu^{3+} ions occurs only among the neighbor sites in the rare-earth sublattice. When the Eu^{3+} concentration was below the critical value, the Eu^{3+} ions showed emission individually, and the Φ_f values were high. When the Eu^{3+} concentration exceeded the critical value P_c, Φ_f decreased rapidly because of energy transfer from the percolating cluster to the killer center, which consists of vacancies and impurities. V. A. Vyssotsky *et al.* suggested the following expression for calculating the critical concentration in the percolation model:

$$P_c = d/z(d-1) \tag{1}$$

where P_c, z, and d are the critical concentration, number of neighbor sites, and number of dimensions, respectively [16]. When energy transfer between the Eu^{3+} ions occurs only in the inner layers of the rare-earth sublattice, the number of dimensions is considered to be 2 (pseudo-two-dimensional energy transfer). When energy transfer occurs in the interlayers, the number of dimensions is considered to be 3 (three-dimensional energy transfer). **Figure 6** shows the percolation model and the P_c value calculated using Equation (1). In this figure, only the rare-earth sublattice is depicted, and the Eu^{3+} ions between which energy transfer occurs are bonded by gray cylinders. Energy transfer between the Eu^{3+} ions is assumed to occur within 0.363 nm for (a), 0.373 nm for (b), 0.404 nm for (c), and 0.435 nm for (d). The experimental result agrees well with the calculated value of P_c (0.19) estimated for Eu^{3+}-Eu^{3+} interactions within 0.404 nm (c). In this case, the Eu^{3+} ions have eight neighbors

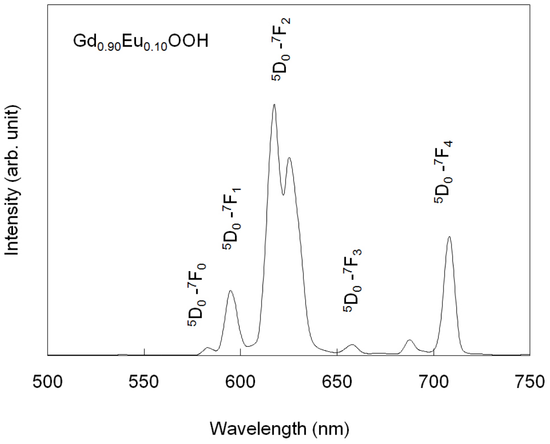


Figure 4. Emission spectrum of $Gd_{0.9}Eu_{0.1}OOH$ crystals.

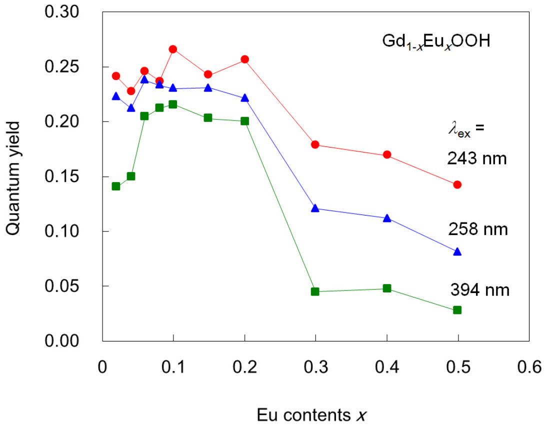
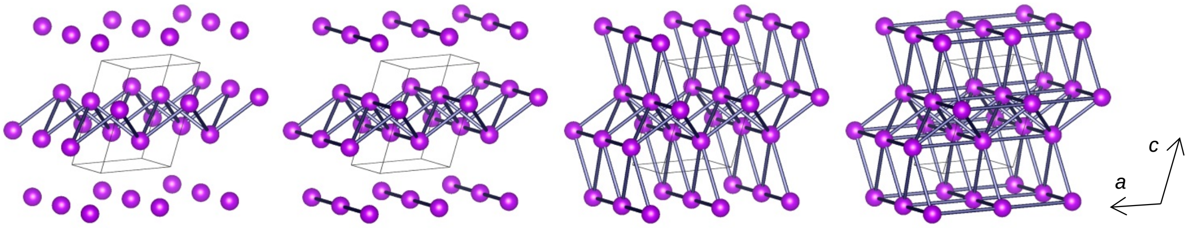


Figure 5. Eu^{3+} content dependence of the fluorescence quantum yield Φ_f of $Gd_{1-x}Eu_xOOH$ crystals.



(a) Eu-Eu within 0.363 nm $P_c = 0.50$ ($d = 2$, $z = 4$)

(b) Eu-Eu within 0.373 nm $P_c = 0.33$ ($d = 2$, $z = 6$)

(c) Eu-Eu within 0.404 nm $P_c = 0.19$ ($d = 3$, $z = 8$)

(d) Eu-Eu within 0.435 nm $P_c = 0.15$ ($d = 3$, $z = 10$)

Figure 6. Percolation model of the $Gd_{1-x}Eu_xOOH$ system.

with three-dimensional energy transfer. This result indicates three-dimensional energy transfer occurs between the Eu^{3+} ions in this system.

To improve the luminescence properties of the crystals, it is necessary to increase the critical concentration of Eu^{3+}. In general, compounds with a low-dimensional arrangement of rare-earth ions show a high critical concentration. On the basis of the results obtained using the percolation model in this study, we state that two-dimensional models have a higher critical concentration (0.50 and 0.33) than do three-dimensional models. When the increase in the distance between the rare-earth layers restrains interlayer energy transfer, the critical concentration of Eu^{3+} in this system can increase. Therefore, excellent luminescence properties can be obtained by co-doping larger ions in the rare-earth sublattice with a high level of Eu^{3+} doping. The high alkali durability of the $Gd_{1-x}Eu_xOOH$ crystals is confirmed by the fact that they are stable in NaOH/KOH solution at 330˚C.

4. Conclusion

$Gd_{1-x}Eu_xOOH$ crystals with a maximum length of 1.2 mm were synthesized by the flux method. The $Gd_{1-x}Eu_xOOH$ ($x \leq 0.2$) crystals showed strong red emission, with the maximum Φ_f of 0.27 for $x = 0.10$. The critical Eu^{3+} content was 0.2, because Φ_f decreased rapidly beyond this level owing to concentration quenching. This critical content was the closest to that estimated by a percolation model for Eu^{3+}-Eu^{3+} interactions within 0.404 nm, wherein Eu^{3+} had eight neighbors, indicating three-dimensional energy transfer between the Eu^{3+} ions in the rare-earth sublattice. The synthesized crystals showed excellent alkali durability and hence may be used as a high-efficiency host material in unique photomedical applications such as photochemical internalization and photodynamic therapy.

Acknowledgements

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