Photoluminescence

DOI: 10.1002/anie.200806206

Oriented Monolayer Film of Gd_2O_3:0.05 Eu Crystallites: Quasi-Topotactic Transformation of the Hydroxide Film and Drastic Enhancement of Photoluminescence Properties**

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With the rapid developments in nanotechnology, inorganic functional films have become an important line of research owing to their large variety of potential applications, such as display units, catalytic films, solar cells, chemical sensors, thin-film transistors, and essential components in microelectronic devices.[1] Inorganic monolayer and multilayer films constructed from nanoparticles,[2] exfoliated nanosheets,[3] one-dimensional nanotubes/nanowires,[4] layered double hydroxides,[5] and zeolite platelet crystallites[6] have been fabricated by various chemical methods, such as sequential adsorption and Langmuir–Blodgett deposition.

Recently, a series of new rare-earth-based layered hydroxides with a typical composition of $[RE_8(OH)_{20}(H_2O)_7][A^{n-}]_{4/n}$ (RE = Sm, Eu, Gd, Tb, Dy, Ho, Er, Y; A^{n-} = the interlayer anion) has been synthesized, which display platelet morphology with uniform rectangular shape.[7] A photoluminescence activator, such as Eu^{3+}, can be incorporated into this layered structure. For example, as-prepared $Eu(OH)_{2.5}Cl_{0.5}\cdot 0.9\,H_2O$ exhibits characteristic photoluminescence properties resulting from Eu^{3+} 4f–4f transitions. Most recently, we achieved self-assembly of $Eu(OH)_{2.5}Cl_{0.5}\cdot 0.9\,H_2O$ platelet crystallites at the hexane/water interface and then transferred them to a substrate to form monolayer and multilayer films that had red-emission photoluminescence.[8]

In general, the photoluminescence behavior of rare-earth oxides is better than that of hydroxides because of the absence of nonradiative relaxation channels provided by high-energy vibration of hydroxy (OH) species.[9] For example, Eu^{3+}-activated rare-earth oxides are promising phosphor materials for optical and electro-optical devices.[10] Among the Eu^{3+}-activated rare-earth oxides, Gd_2O_3:Eu is an important red-emitting phosphorescent material as a result of its high luminescent efficiency.[10] Gd_2O_3:Eu nanoparticles,[11,12] one-dimensional nanorods,[13] and monodispersed colloidal spheres[14] have been synthesized in the past few years. It has also been reported that Gd_2O_3:Eu phosphors prepared by a spray pyrolysis method show higher photoluminescence intensity compared to commercially available Y_2O_3:Eu.[15] Therefore, it is of interest to develop a film of Gd_2O_3:Eu platelet crystallites and study its photoluminescence properties.

The ionic radii of Gd^{3+} (1.053 Å) and Eu^{3+} (1.066 Å) ions are very similar. This inspired us to consider that the photoluminescence active element Eu and non-active element Gd could possibly be simultaneously incorporated into the layered $[RE_8(OH)_{20}(H_2O)_7][A^{n-}]_{4/n}$ structure, that is, a rare-earth hydroxide solid solution. Gd_2O_3:Eu crystallites might be obtained by annealing of these precursor hydroxide platelets. The conversion from rare-earth hydroxide into oxide without evident morphological changes by annealing at suitable conditions has been reported,[16] thus this route might provide Gd_2O_3:Eu crystallites with two-dimensional platelet morphology. Furthermore, a high-quality oriented film of Gd_2O_3:Eu platelet crystallites may conveniently be fabricated by transformation from the corresponding hydroxide film.

An optimal 5% Eu^{3+} (molar percent) was doped in the layered $Gd(OH)_{2.5}Cl_{0.5}\cdot 0.9\,H_2O$.[17] Subsequently, an oriented film of these hydroxide solid-solution crystallites was fabricated by a self-assembling method as previously reported.[8] After heat treatment, the precursor hydroxide film was found to transform into an oriented Gd_2O_3:0.05 Eu monolayer film with platelet morphology of the crystallites retained (as shown in Scheme 1). Most importantly, the photoluminescence properties were greatly enhanced during the conversion from the precursor hydroxide into oxide film.

Figure 1a shows the X-ray diffraction (XRD) pattern of powder samples for the precursor hydroxide. All the diffraction peaks can be indexed as a layered rare-earth hydroxide structure reported in our previous study.[7a,b] No peaks of impurities were detected, indicating that Eu^{3+} ions were successfully incorporated into the host lattice to form a homogeneous solid solution. Based on chemical analysis, the composition of the hydroxide precursor was estimated to be $Gd_{0.95}Eu_{0.05}(OH)_{2.42}Cl_{0.48}(CO_3)_{0.05}\cdot 0.86\,H_2O$ (calcd (%): Eu 3.25, Gd 63.94, OH^- 17.61, Cl^- 7.29, C 0.26, H_2O 6.63; found: Eu 3.2, Gd 64.1, OH^- 17.5, Cl^- 7.3, C 0.23, H_2O 6.7), which was simplified as $Gd(OH)_{2.5}Cl_{0.5}\cdot 0.9\,H_2O$:0.05 Eu. The XRD pattern of the precursor hydroxide film is given in Figure 1b. Sharp 00l diffraction peaks and the absence of other diffraction peaks, in comparison with that of the powder

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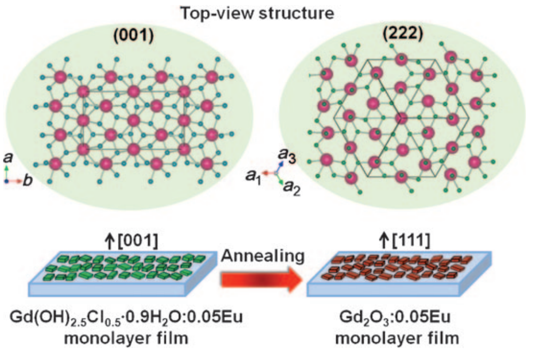
[**] This work was supported by CREST of the Japan and Technology Agency (JST) and World Premier International Center Initiative (WPI Initiative) on Materials Nanoarchitectonics, MEXT (Japan). Hydroxide film = $Gd(OH)_{2.5}Cl_{0.5}\cdot 0.9\,H_2O$:0.05 Eu.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200806206.



Scheme 1. Top-view structure of the crystal plane of layered $Gd(OH)_{2.5}Cl_{0.5}\cdot 0.9\,H_2O$:0.05 Eu (001) and cubic Gd_2O_3:0.05 Eu (222) (rare-earth (red), OH (blue), and O (green)) and schematic illustration of structural transformation from $Gd(OH)_{2.5}Cl_{0.5}\cdot 0.9\,H_2O$:0.05 Eu film into Gd_2O_3:0.05 Eu film.

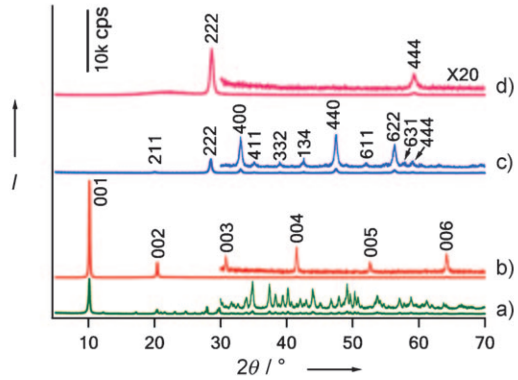


Figure 1. XRD patterns of a) $Gd(OH)_{2.5}Cl_{0.5}\cdot 0.9\,H_2O$:0.05 Eu powder samples, b) $Gd(OH)_{2.5}Cl_{0.5}\cdot 0.9\,H_2O$:0.05 Eu film, c) Gd_2O_3:0.05 Eu powder sample transformed at 800 °C for 2 h, d) Gd_2O_3:0.05 Eu film transformed at 800 °C for 2 h.

sample, were attributed to the preferential crystallite orientation in the film.[8] It was found that annealing of the precursor hydroxide monolayer at a temperature lower than 600 °C did not transform the precursor hydroxide into oxide (see the Supporting Information, Figure S1). By annealing at 600–800 °C, a film of cubic Gd_2O_3:0.05 Eu phase (whose diffraction peaks corresponded well with JCPDS 43-1014) was obtained. Annealing at 800 °C resulted in a film that gave sharper diffraction peaks than that formed at 600 °C, suggesting improved crystallinity for the as-transformed oxide film. When the treatment temperature reached 1000 °C, the intensity of diffraction peaks for the cubic Gd_2O_3:0.05 Eu phase decreased considerably and some impurity was detected. All these results clearly demonstrate that a pure Gd_2O_3:0.05 Eu film of high crystallinity could be synthesized by annealing at an optimal temperature of 800 °C. As a comparison, the powder sample of precursor hydroxide was annealed under the same conditions. Corresponding XRD pattern was also characteristic of pure cubic Gd_2O_3:0.05 Eu phase (Figure 1 c). In contrast to the powder sample, the oxide film showed only 222 and 444 reflections (Figure 1 d), indicating the formation of a highly oriented film along the [111] direction of the Gd_2O_3:0.05 Eu crystallites. As illustrated in Scheme 1, the projections in the [001] direction for precursor hydroxide crystal and in the [111] direction for cubic Gd_2O_3:0.05 Eu crystal present close similarities in terms of rare-earth atomic configuration, which suggested a quasi-topotactic transformation from the hydroxide film to the oxide film and could account for the preferential [111] orientation for the Gd_2O_3:0.05 Eu film.

Figure 2 shows the scanning electron microscopy (SEM) images of precursor hydroxide film and quasi-topotactic transformed oxide film, respectively. Both the hydroxide and oxide films are semitransparent (Figure 2 insets). For the precursor hydroxide film, the substrate was densely covered by micrometer-sized rectangular crystallites with the same orientation. The close contact between adjacent crystallites led to a uniform monolayer film with a high coverage area ratio (Figure 2 a,b). After annealing at 800 °C, no obvious morphological changes in the Gd_2O_3:0.05 Eu crystallites were observed compared with the precursor hydroxide crystallites. The high coverage area ratio and preferred orientation of the crystallites in the as-transformed film were still apparent, indicating that a high-quality Gd_2O_3:0.05 Eu monolayer film was obtained (Figure 2 c,d). Our previous study demonstrated an average height of 101 ± 33 nm for the hydroxide crystallites.[8] Thus the as-transformed film is rather thin. Moreover, the crystallites in the oxide film were not easily removed by scraping, and they were more tightly immobilized on the substrate compared to those of the precursor film. The adhesion force of the crystallites on the substrate increased during the annealing process, which is desirable for device applications. Annealing at higher temperature, such as 1000–1100 °C, resulted in a rough surface of the crystallites, although the rectangular shape was retained (see the Supporting Information, Figure S2e,f).

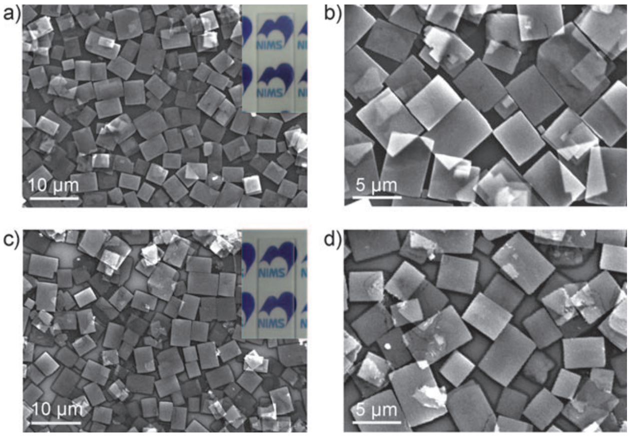


Figure 2. SEM images of the oriented a),b) $Gd(OH)_{2.5}Cl_{0.5}\cdot 0.9\,H_2O$:0.05 Eu film and c,d) Gd_2O_3:0.05 Eu film transformed at 800 °C. Inserts in (a) and (c) are photographs of the semitransparent hydroxide and oxide films, respectively.

Figure 3 a and b depict the photoluminescence spectra of the precursor hydroxide film and quasi-topotactic transformed oxide film, respectively. For the precursor hydroxide film, the excitation spectrum has only one sharp peak at

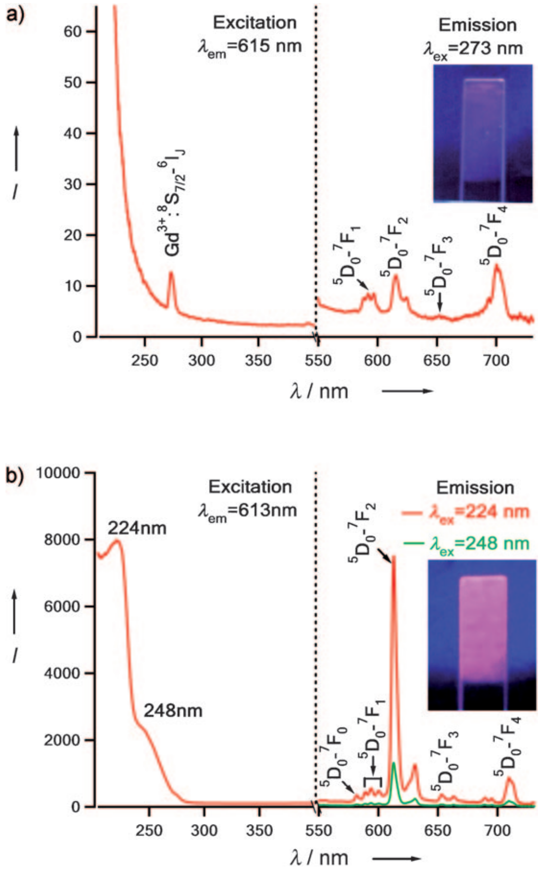


Figure 3. Excitation and emission spectra of a) $Gd(OH)_{2.5}Cl_{0.5}\cdot 0.9\,H_2O$:0.05 Eu film and b) Gd_2O_3:0.05 Eu film transformed at 800 °C. The inset shows the red-light emission of the precursor hydroxide film and oxide film under UV irradiation.

273 nm, which could be assigned to the Gd^{3+} transition from the ground level $^8S_{7/2}$ to excited level ^6I_J.[18] No f–f transition lines of Eu^{3+} in the longer wavelength region were detected because of their very weak intensity compared with the Gd^{3+} $^8S_{7/2}$-^6I_J transition. The presence of the Gd^{3+} transitions in the excitation spectrum indicated efficient energy transfer from Gd^{3+} to doped Eu^{3+}, which may be attributed to the strong interaction between Gd^{3+} and Eu^{3+} in the host layer of the layered hydroxide crystal. The emission spectrum for the precursor hydroxide film displayed typical $^5D_0$–^7F_J ($J = 0, 1, 2, 3, 4$) transitions of Eu^{3+}, which were consistent with those in previous work.[8]

For the oxide film, the excitation spectrum consisted a broad intense band with a maximum at 224 nm and a shoulder at around 248 nm, which could be attributed to the Gd_2O_3 host excitation band and the charge-transfer band (CTB) between O^{2-} and Eu^{3+}, respectively.[19] These results provided evidence that the observed emission was dominated by the host band-gap excitation of Gd_2O_3 rather than the direct excitation of the Eu^{3+}. All the emission lines at 582, 589–601, 613, 654, and 709 nm were assigned to $^5D_0$–^7F_J ($J = 0, 1, 2, 3, 4$) transitions of Eu^{3+}, respectively. The highest emission intensity was from the hypersensitive forced electric dipole $^5D_0$–$^7F_2$ transition peak of Eu^{3+}, suggesting that Eu^{3+} was located at a site with no inversion symmetry.[13,14] The annealing temperature played a crucial role in the luminescent intensity of as-transformed film. The film transformed at 400 °C exhibited very weak emission (see the Supporting Information, Figure S3). The emission intensity improved steadily with increased annealing temperature and reached a maximum at 800 °C. Further increase in the temperature led to considerable decrease in luminescence intensity, which might be caused by the impurity and defects in the film. This effect of the annealing temperature on photoluminescence properties was consistent with the observation of impurity phases in the XRD data at high temperature.

It is surprising that the emission maximum of the oxide film annealed at 800 °C is 527 times higher than that of the hydroxide film (Table 1, enhanced ratio $R_{en} = 527$, $R_{en} = I_{\text{Oxide max}}/I_{\text{Hydro max}}$, where $I_{\text{Hydro max}}$ and $I_{\text{Oxide max}}$ are the emission maximum intensity of hydroxide form excited at 273 nm and oxide form excited at 224 nm, respectively), indicating that photoluminescence properties of the film were remarkably enhanced by the phase transformation. The dramatically enhanced luminescence intensity could also be visualized by the photographs of the hydroxide and oxide films under UV irradiation (Figure 3, insets). The faint red emission of the precursor hydroxide film is hardly visible. In contrast, the oxide film emitted intense red light. The enhancement of luminescence may be attributed to the removal of OH groups and water molecules located in the intralayer and interlayer of the layered hydroxide crystal, respectively, which yield nonradiative quenching by energy transfer to OH vibration and thus decrease the emission intensity.[20]

Table 1: Maximum emission intensity (I_{max}) and enhanced ratio (R_{en}) of the oriented films and powder samples.

	I_{max} hydroxide (at 701 nm)	I_{max} oxide (at 613 nm)	R_{en}
Film	14	7511	527
Powder	24	1575	65

More interestingly, some apparent differences in photoluminescence properties between the oriented film and powder sample were observed for the oxide form after the annealing. For the oriented film, the intensity by Gd_2O_3 host excitation was 3.8 times higher than that by charge-transfer band excitation. For the powder sample, the former was slightly lower than the latter (see the Supporting Information, Figure S4b). Moreover, the enhanced ratio of emission intensity from the hydroxide to the oxide was much smaller for the powder sample than that of the oriented film (Table 1). These findings revealed that the oriented film showed more prominent photoluminescence properties than the powder sample. During the experiment, the annealing of the precursor hydroxide film and the powder was carried out under the same conditions. There were no differences in crystal structure or morphology of the crystallites in the film and the powder sample after annealing, which might significantly affect the photoluminescence properties.[21] Although the reason for the prominent luminescence of the oxide film is not yet clear, we speculate that the preferential orientation of the crystallites may be responsible. Recently, Ida et al. prepared a series of luminescent perovskite nanosheets, and observed that the emission intensity derived from the host excitation was very different when the orientation of the nanosheets in solution was changed.[22] This result revealed that photoluminescence properties were strongly influenced by orientation. In the present study, all the (222) crystal planes of the Gd_2O_3 crystallites in the film were parallel to the substrate surface, which may lead to much higher absorption of excited energy and more efficient energy transfer from Gd_2O_3 host to Eu^{3+} compared to that of randomly stacked crystallites in the powder sample. Furthermore, the flat surface of the oriented film may reduce scattering of the excitation UV light, also resulting in higher emission intensity compared to the powder sample.

In summary, we have proposed a novel approach to fabricating a high-quality monolayer film of oriented Gd_2O_3:0.05 Eu platelet crystallites by a quasi-topotactic transformation from hydroxide film. The photoluminescence properties of the oxide film are greatly improved compared with the precursor hydroxide film, and are also much more prominent than that of the corresponding powder sample. This Gd_2O_3:0.05 Eu monolayer film is semitransparent with a flat surface and strong adhesion, and is very promising for applications such as optical/display devices and luminescence probes, because of its superior photoluminescence properties.

Experimental Section

The $Gd(OH)_{2.5}Cl_{0.5}\cdot 0.9\,H_2O$:0.05 Eu solid solution was synthesized by the homogeneous precipitation method.[7] Then a monolayer film of $Gd(OH)_{2.5}Cl_{0.5}\cdot 0.9\,H_2O$:0.05 Eu crystallites was self-assembled at the hexane/water interface using a similar process to that described previously.[8] The $Gd(OH)_{2.5}Cl_{0.5}\cdot 0.9\,H_2O$:0.05 Eu film was heated at the desired temperature (at one temperature in the range 200–1100 °C) for 2 h in air to transform it into Gd_2O_3:0.05 Eu monolayer film. For comparison, $Gd(OH)_{2.5}Cl_{0.5}\cdot 0.9\,H_2O$:0.05 Eu powder was heated at 800 °C for 2 h to obtain the Gd_2O_3:0.05 Eu powder sample (see the Supporting Information for details). XRD patterns of the hydroxide and oxide films were recorded on a Rigaku RINT-2000 diffractometer ($Cu_{K\alpha}$, $\lambda = 0.15405$ nm). The films were examined using a Keyence VE8800 scanning electron microscope at an accelerating voltage of 10 kV. The photoluminescence excitation and emission spectra were measured on a Hitachi F-7000 fluorescence spectrophotometer at room temperature.

Received: December 19, 2008

Keywords: hydroxides · lanthanides · luminescence · oxides · thin films

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