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To cite this article: Shintaro Ida et al 2009 IOP Conf. Ser.: Mater. Sci. Eng. 1 012014

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Synthesis and photoluminescence properties of layered oxides intercalated with Eu$^{3+}$ ions by electrostatic self-assembly method using oxide nanosheets

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Abstract. Layered oxides intercalated with Eu$^{3+}$ ions were prepared by self-assembly deposition method based on the electrostatic interaction between negative charged oxide nanosheets and Eu$^{3+}$ ions. The layered oxides were composed of two-dimensional host nanosheet layer with guest Eu$^{3+}$ ions and gave Eu$^{3+}$ emission based on an energy transfer from bandgap excitation of the host oxide nanosheets to the Eu$^{3+}$ ions. The photoluminescence properties of the Eu$^{3+}$ ions were influenced by the type of nanosheet and the intercalated water molecules. Relatively-strong emission of Eu$^{3+}$ was observed from Eu$^{3+}$-intercalated titanate layered oxide. The intensity of Eu$^{3+}$ emission increased with increasing the amount of intercalated water molecules. This indicates that the energy transfer from TiO$_2$-$\delta$ nanosheet to Eu$^{3+}$ is promoted by the intercalated water molecules. In addition, the intensity of Eu$^{3+}$ emission was stronger at high pH than at low pH. This emission change is presumably due to two phenomena. One is a fine hydration state change of Eu$^{3+}$ in the interlayer, and the other is a change in energy transfer from the TiO$_2$-$\delta$ nanosheet to Eu$^{3+}$.

1. Introduction
Layered oxides composed of two-dimensional host oxide layers with guest cations have various interesting properties such as superconducting [1], ferroelectric [2] and photocatalytic properties [3]. These properties strongly depend on the combination between the host layers and the guest cations. Therefore, controlling the combination of layer structure is an important technique for material developing. Generally, two main soft-solution processes are utilized for the preparation of layered structure with desired guest cation into the interlayer. One is the ion-exchange technique carried out in an aqueous solution of a cation of interest, which is substituted for an alkaline cation of the starting layered oxide [4-7]. The other one is the direct assembly of a host oxide nanosheet and a cation of interest in a solution due to the electrostatic interaction. The latter technique is superior to the former in terms of easy and optimal intercalation of the guest cation. In the latter technique, two methods such as the electrostatic self-assembly deposition (ESD) [8] and layer-by-layer assembly (LBL) techniques [9-11] are available to prepare the desired layered oxides. Various kinds of intercalated layered oxides can be easily prepared under controlled pH in a solution by the ESD method, while the LBL method allows us to control the number of layers deposited on a substrate.

Nanosheets can be prepared by exfoliation of layered compounds [12-18]. For instance, TiO$_2$-$\delta$-type nanosheets [12], perovskite-type nanosheets [13-15] and hydroxide-type nanosheets [16, 17] have been reported. The layered compounds prepared by ESD and LBL techniques have been studied in
various fields such as photocatalyst, electrode for Li cell and luminescent material. As for luminescent material, it has been reported that several types of layered oxides and TiO$_2$ nanoparticles doped with lanthanide cations show strong emission by an energy transfer process from the host matrix excited by band gap illumination to the in-matrix lanthanide cations [19-21]. This behavior suggests that lanthanide cations in the interlayer of the TiO$_{2.8-}\delta$-type nanosheets might result in strong emission under the excitation of TiO$_{2.8-}\delta$-type nanosheets. Actually, several reports on luminescence properties of the nanosheet-based layered oxides have been reported [22-24].

In the present work, we demonstrate a successful preparation of layered oxides intercalated with Eu$^{3+}$ ions by electrostatic self-assembly method using oxide nanosheets and investigate the photoluminescence behavior of these films under several thermal, humidity and pH conditions in detail.

2. Experimental section

Cs$_{0.76}$Ti$_{1.81}$O$_4$ and K$_4$Nb$_6$O$_{17}$ were prepared as parent materials of nanosheets by a complex polymerization method and conventional solid-state reaction, respectively. Exfoliation of these layered oxides was carried out according to the previous reported method [8, 25]. Nanosheets derived from Cs$_{0.76}$Ti$_{1.81}$O$_4$ and K$_4$Nb$_6$O$_{17}$ are abbreviated as TiO$_{2.8-}\delta$ nanosheet and Nb$_6$O$_{17}$ nanosheets, respectively.

Preparation of layered oxide intercalated with Eu$^{3+}$ was carried out using two methods: electrostatic self-assembly deposition (ESD) and layer-by-layer self-assembly deposition (LBL). The ESD method was simply done by adding 10 mL of colloidal solution having nanosheets into 0.01 M Eu(CH$_3$COO)$_3$ aqueous solution. The pH of the colloidal solution was carefully adjusted to 7.5-8 with 0.1 M HCl solution. Mixing two solutions resulted in an immediate precipitation, which consists of a single phase of the layered oxide intercalated with Eu$^{3+}$ formed by electrostatic interaction between a negatively charged nanosheet and positively charged Eu$^{3+}$. The precipitation was rinsed with pure water in order to remove excess Eu$^{3+}$ and other undesired ions. To prepare films of the layered oxides, precipitate was simply applied on a Pt substrate after extracting with a pipet and was allowed to dry at room temperature. Deposition of the films by the LBL method was carried out as follows. Si was used as a substrate in this study. Substrates were primed in aqueous polyethyleneimine (PEI) 2.5 g/L solution for 20 min to charge the surface of the substrate positively. Primed substrates were dipped into the colloidal solution having negatively charged nanosheets and then 0.01 M Eu(CH$_3$COO)$_3$ aqueous solution for 10 min under ultrasonic treatment, repeatedly with rinsing and drying under a N$_2$ stream. The sequence was carried out $n$ times.

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The crystal structure and orientation of the films were analyzed from X-ray diffraction patterns (using Cu Kα radiation, Rigaku RINT-2500VHF). The compositions of the deposited films were analyzed by an inductively coupled plasma (ICP) spectrophotometer (Seiko Instruments, SPS7800). The ICP was carried out after dissolving the films in acid solution. EXAFS spectra of the Ln L$_{III}$-edge were recorded on a BL-7C instrument at the Photon Factory with a Si(111) double crystal monochromator of the High Energy Accelerator Research Organization at Tsukuba, Japan (Proposal #2007G519). Excitation and emission spectra were analyzed by a Jasco FP-6500 spectrofluorometer with a 150 W Xe lamp source. Excitation and emission spectra were taken at room temperature. pH dependence of Eu$^{3+}$ emission was investigated as follows. The sample films prepared by LBL technique were put in triangle quartz cell filled with pH-controlled aqueous solution, and then pH-dependence of the Eu$^{3+}$ emission was measured keeping the film unchanged. HCl and NaOH were used as reagents for pH control. The emission decay curves of the films were plotted on the basis of the time-resolved emission spectra, which were obtained by using a Perkin-Elmer LS 45 fluorescence spectrometer. In addition, in order to investigate the hydration condition of Eu$^{3+}$, the luminescence life times were calculated on the basis of the emission decay curves obtained from light and heavy water.

3. Results and discussion

Figure 1 shows the XRD pattern of as-deposited layered oxides intercalated with Eu$^{3+}$ prepared by ESD method. The Eu$^{3+}$-intercalated layered oxide prepared from TiO$_{2.8}$ nanosheets and Nb$_6$O$_{17}$
nanosheets are abbreviated as Eu/TiO and Eu/NbO, respectively. The diffraction peaks at 5-10 degree are based on layered structure in which Eu$^{3+}$ ions are sandwiched between nanosheets. Figure 2 shows TG curves of Eu/TiO and Eu/NbO powders, respectively. The main weight loss appeared to be a result of removal of the intercalated water. The weight loss takes place in two main steps. The first step between RT and 100 °C stands for the removal of relatively free water and is followed by the removal of hydrate water coordinating Eu$^{3+}$, which occurs in the range 100-500 °C. From ICP and thermal analyses, the composition with water content was determined to be Eu$_{0.31}$Ti$_{1.81}$O$_4$$\cdot$2.1H$_2$O and Eu$_{1.36}$Nb$_6$O$_{17}$$\cdot$11.9H$_2$O, respectively. This indicates that the intercalated Eu$^{3+}$ ions exist as aqua ions and are coordinated with 7-10 water molecules under ambient conditions. Calculations were performed under the assumption that a significant portion of the intercalated water molecules surrounds the lanthanide cations in the interlayer because lanthanides have a high tendency of hydration in an aqueous environment. Theoretically, in the case of Eu/TiO, the negative charge of the TiO$_{2-\delta}$ nanosheets layers may be neutralized only if 0.25 mol of Eu$^{3+}$ is present in the interlayer of 1 mol of layered oxide according to the chemical composition of the original layered compound (Eu/Ti = 0.25/1.81). In the case of Eu/NbO, the theoretical composition of Eu/Nb = 1.33/6. These values are in close agreement with the above composition derived from the ICP measurement.

The XRD patterns of heat-treated samples at different temperatures are given in Figure 3. Typically, heat treatment results in the shift of the peak assigned to layered structure to higher degrees, which is an indication of contraction in the interlayer distance as a result of the consecutive removal of free and hydrate water. As the temperature increases, the number of coordinated water molecules decreases, and finally, the layer distance represents a value close enough to accommodate a bare lanthanide cation, which has a radius of around 1.1 Å.

Emission spectra of Eu$^{3+}$-intercalated layered oxide prepared by the ESD method is given in Figure 4, where excitation was carried out at 300 nm. Emission intensity of Eu/NbO was much weaker than that of Eu/TiO. The peaks at 593.2 and 614.4 nm in the emission spectra were assigned to the $^5$D$_0$ - $^7$F$_1$ and $^5$D$_0$ - $^7$F$_2$ transitions, respectively. The peak represents red emission, which also could be seen with the naked eye under illumination with a UV light source at a wavelength of 254 nm. The excitation spectra of the Eu$^{3+}$-intercalated layered oxide at room temperature is obtained by monitoring at 614 nm (Figure 4). The broad peak (270-370 nm) on the excitation spectrum of Eu/TiO, which is

![Figure 1. XRD patterns of as-deposited layered oxides intercalated with Eu$^{3+}$ prepared by ESD method.](image1)

![Figure 2. TG/DTA curves of Eu/TiO and Eu/NbO powders.](image2)
Figure 3. Effect of heat treatment on the XRD pattern of Eu/TiO films.

Figure 4. Excitation and emission spectra of as-prepared Eu/TiO and Eu/NbO films ($\lambda_{\text{ex}}$:614 nm, $\lambda_{\text{em}}$:300 nm).

Figure 5. Effect of heat treatment on excitation spectra of Eu/TiO films ($\lambda_{\text{ex}}$:614 nm).

Figure 6. Effect of humidity on excitation and emission spectra of Eu/TiO films ($\lambda_{\text{ex}}$:614 nm, $\lambda_{\text{em}}$:300 nm).

the same as the UV absorption spectrum, clearly provides evidence that the observed emission is mainly contributed by band gap excitation in the TiO$_{2.5}$ nanosheet layer. Thus, electrons and holes produced by the band gap excitation migrate in the host layer and easily move into the interlayer to be trapped by the Eu$^{3+}$ cations. The conduction band level of TiO$_{2.5}$ nanosheet is lower than that of Nb$_6$O$_{17}$ nanosheets [24], and higher than the light-emitting level of Eu$^{3+}$[22, 23]. Thus, the light-emitting level of Eu$^{3+}$ is closer to the conduction band level of TiO$_{2.5}$ nanosheet than that of Nb$_6$O$_{17}$ nanosheets. The weak emission intensity of Eu/NbO is presumably due to the large energy gap between conduction band level and light-emitting level of Eu$^{3+}$.

Figure 5 shows the effects of heat treatment on the excitation spectra of the Eu/TiO films, respectively. The intensity of the excitation peak at 350-250 nm due to the host TiO$_{2.5}$ bandgap excitation is dramatically diminished, which reveals that the contribution of the host band gap
excitation to the emission decreases. Since heat treatment helps in removing water from the interlayer only, it is obvious that coordinating water molecules to the intercalated Eu$^{3+}$ cation play a supplementary role in the energy transfer from host TiO$_2$ to intercalated Eu$^{3+}$ ions. Humidity controlled experiments confirm this mechanism, as Figure 6 clearly shows. The as-deposited Eu/TiO film gave a high intensity peak on emission and excitation spectra at 100% RH, while the film conditioned at 5% RH produced much lower intensity peaks. In addition, films conditioned in different humidity environments resulted in different XRD diffraction patterns. The layer distance of the film kept at 100% RH decreased by about 2 nm at 5% RH as a result of the release of water in the interlayer. Thus, the surrounding water molecules around Eu$^{3+}$ in the interlayer promote the energy transfer process to the Eu$^{3+}$. There are several reports on the state of the hydrogen bonds on the surface of the nanosheet and TiO$_2$ using $^1$H NMR [26-30]. Takagaki and Domen et al. reported that there are several types of OH groups in the exfoliated HTiNbO$_5$ [26, 27]. Nosaka et al. reported that the H$_2$O molecules with high mobility were increased on the TiO$_2$ surface by UV irradiation [28-30]. Thus, it is possible that water molecules in the interlayer of Eu/TiO exist with special condition compared to free water. Presumably, when the interlayer Eu$^{3+}$ cations are coordinated with water molecules, the crystal field strength applied on the Eu$^{3+}$ cations is stronger. Thus, electrons and holes migrating in the host layer move simultaneously through the surrounding water molecules to interlayer lanthanide cations to yield emission rather than giving radiation-less quenching via energy transfer to OH vibration on water molecules. Probably, water molecules in the interlayer will be fixed via hydrogen bonding, as in ice, leading to a decrease the radiation-less quenching.

Figure 7 shows the photoluminescence spectra of Eu/TiO films, measured in various H$_2$O and D$_2$O solutions of differing pH. The emission spectra were obtained under an excitation wavelength of 260 nm. The red emission intensity of Eu/TiO in 0.01 M NaOH aqueous solution was stronger than the emission in 0.01 M HCl aqueous solution. Two phenomena may help explain the mechanism for the observed emission change of Eu/TiO. One is the change in the efficiency of energy transfer in different pH conditions. In our previous study, the photodeposited quantity of Ag and MnO$_2$ on TiO$_x$ nanosheet surface was strongly dependent on pH, and the deposits were relatively small at low pH [31]. We concluded that photoproduced electrons in TiO$_x$ nanosheets more easily recombine with photoproduced holes at low pH than at high pH. In Eu/TiO, this recombination will reduce the efficiency of energy transfer from TiO$_x$ nanosheets to Eu$^{3+}$, resulting in low emission intensity from Eu$^{3+}$ at low pH. The other factor is a change in the hydration state of Eu$^{3+}$ in Eu/TiO, as we will discuss in a later section.

The emission intensities in D$_2$O were stronger than those in H$_2$O (Fig. 7). It is known that, in general, the excited states relax via two competitive paths. One is by light emission and the other is by...

**Figure 7.** Excitation and emission spectra of Eu/TiO films measured in various H$_2$O and D$_2$O solutions. (a) 0.01 M NaOH (solvent: H$_2$O) and 0.01 M NaOD (solvent: D$_2$O), (b) 0.01 M NaCl (solvent: H$_2$O) and 0.01 M NaCl (solvent: D$_2$O), and (c) 0.01 M HCl (solvent: H$_2$O) and 0.01 M DCl (solvent: D$_2$O). $\lambda_{em}$: 614 nm, $\lambda_{ex}$: 260 nm.
phonon emission (quenching), and the latter path applies to the present case. The rate of phonon emission, \( \omega \), depends on phonons, simultaneously emitted to bridge the energy gap, and is expressed as:

\[
\omega \propto \exp(-k\Delta E/h\nu_{\text{max}}),
\]

where \( \Delta E \) is the energy gap to the nearest lower level and \( h\nu \) is the maximum energy of phonons coupled to the emitting state [32, 33]. The phonon emission rate, \( \omega \), decreases rapidly with increasing \( \Delta E \), so that the competitive light emission or radiative process becomes dominant. Large values of \( h\nu_{\text{max}} \) also quench light emission. Therefore, in general, the photoluminescence of \( \text{Eu}^{3+} \) strongly depends on the chemical environment of the ions, and \( \text{Eu}^{3+} \) ions exhibit a stronger luminescence in \( \text{D}_2\text{O} \) than in \( \text{H}_2\text{O} \) because of the smaller phonon energy of \( \text{D}_2\text{O} \) (\( \nu_{\text{O-D stretch MAX}} \sim 2800 \text{ cm}^{-1} \)) compared to that of \( \text{H}_2\text{O} \) (\( \nu_{\text{O-H stretch MAX}} \sim 3600 \text{ cm}^{-1} \)) [34]. This indicates that the general quenching effect of \( \text{Eu}^{3+} \) emission by \( \text{H}_2\text{O} \) occurs in the interlayer of \( \text{Eu/TiO} \). Thus, the photoluminescence properties of \( \text{Eu/TiO} \)-films are dependent on the hydration state of the water molecules surrounding the \( \text{Eu}^{3+} \) ions in the interlayer, as occurs in general with \( \text{Eu}^{3+} \) ions in aqueous solution.

The emission response of the \( \text{Eu/TiO} \) film to changing pH is presumed to be based on the change in hydration state of \( \text{Eu}^{3+} \). The luminescence lifetimes for \( \text{Eu}^{3+} \) obtained under different pH conditions are gathered in Table 1, which calculated from the fluorescence decay carves. From the lifetimes of \( \text{Eu}^{3+} \) in \( \text{H}_2\text{O} \) and \( \text{D}_2\text{O} \), it is possible to evaluate the number of water molecules directly coordinated to interlayer \( \text{Eu}^{3+} \), \( q_{\text{Eu}} \), by the following equation:

\[
q_{\text{Eu}} = 1.2 [(1/\tau_H) – (1/\tau_D) – 0.25] \quad (2)
\]

where \( \tau_H \) and \( \tau_D \) are luminescence lifetimes of \( \text{Eu}^{3+} \) in \( \text{H}_2\text{O} \) or \( \text{D}_2\text{O} \), respectively [35-38]. Thus, the \( \text{Eu/TiO} \) film at \( \text{pH}=2 \) has 7.6 inner-sphere water molecules, while at \( \text{pH}=12 \) it has 1.9 inner-sphere molecules. \( \text{Eu}^{3+} \) ions are known to be coordinated with nine water molecules [\( \text{Eu(H}_2\text{O})_9 \)] in aqueous solution. This value is close to that of \( \text{Eu}^{3+} \) in \( \text{Eu/TiO} \) film at \( \text{pH}=2 \). This may indicate that the \( \text{Eu}^{3+} \) ions in \( \text{Eu/TiO} \) film at low \( \text{pH} \) exist in the same hydration state as free \( \text{Eu}^{3+} \) ions in aqueous solution. As a result, the \( \text{Eu}^{3+} \) emission intensity at low \( \text{pH} \) is weak because the \( \text{Eu}^{3+} \) ions have 7.6 water molecules quenching their emissions. At high \( \text{pH} \), the value of the inner-sphere water molecules of \( \text{Eu}^{3+} \) is smaller than at low \( \text{pH} \). Having less inner water molecules may lead to the high emission intensity because of \( \text{H}_2\text{O} \) phonon quenching. However, the presence of water always causes quenching. As mentioned above, the emission intensity of \( \text{Eu}^{3+} \) from the interlayer of \( \text{TiO}_x \) nanosheets increases with increasing amount of interlayer water molecules.

In order to evaluate the interlayer conditions directly, the local environment of \( \text{Eu}^{3+} \) in \( \text{Eu/TiO} \) was investigated by EXAFS. Figure 8 shows a typical Fourier transform of \( k^2 \)-weighted \( \text{Eu L}_{\text{III}} \)-edge EXAFS spectra for \( \text{Eu/TiO} \) powder in 0.1 \( \text{M NaOH} \) solution. In the FT-EXAFS spectra, a strong peak appeared at atomic distances of around 2.0 \( \text{Å} \). To obtain detailed structural parameters on the basis of

<table>
<thead>
<tr>
<th>Solution</th>
<th>( \tau / \text{ms} )</th>
<th>Number of inner-sphere water molecules of ( \text{Eu}^{3+} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01 M HCl (in ( \text{H}_2\text{O} ))</td>
<td>0.13</td>
<td>7.6</td>
</tr>
<tr>
<td>0.01 M DCl (in ( \text{D}_2\text{O} ))</td>
<td>0.84</td>
<td></td>
</tr>
<tr>
<td>0.01 M NaCl (in ( \text{H}_2\text{O} ))</td>
<td>0.17</td>
<td>5.5</td>
</tr>
<tr>
<td>0.01 M NaCl (in ( \text{D}_2\text{O} ))</td>
<td>0.87</td>
<td></td>
</tr>
<tr>
<td>0.01 M NaOH (in ( \text{H}_2\text{O} ))</td>
<td>0.34</td>
<td>1.9</td>
</tr>
<tr>
<td>0.01 M NaOH (in ( \text{D}_2\text{O} ))</td>
<td>0.89</td>
<td></td>
</tr>
</tbody>
</table>
the model, a curve-fitting analysis of the Eu L_{III}-edge EXAFS spectrum was conducted in an r-range including the observed strong Fourier peaks. As the model structure, EXAFS data for Eu_{2}O_{3} was used, which indicates one Eu site coordinated by six oxygen atoms. FT-EXAFS spectra of Eu/TiO were curve-fit by assuming that the contribution from the first shell determined the structural parameters, including coordination numbers (N), bond distance (r), and Debye-Waller factors (σ), as summarized in Table 2. The peak at 2.0 Å in Fig. 8 can be attributed to the Eu-O bond. Although the bond distances were almost constant at 2.4 Å, the coordination numbers have slightly different values over the pH range from 2 to 12, and the coordination number tended to increase with decreasing pH. This tendency agrees with the previously discussed number of inner-sphere water molecules of Eu^{3+} estimated from the luminescence lifetime of Eu^{3+} in H_{2}O or D_{2}O. However, the change in coordination number obtained by EXAFS is not as large as the change of inner-sphere water molecules of Eu^{3+} estimated from the luminescence lifetime. The number of inner-sphere water molecules estimated from the luminescence lifetime shows the number of water molecules directly coordinated to interlayer Eu^{3+}, while the coordination number obtained from EXAFS shows the number of total oxygen atoms including the oxygen atoms of water molecules directly coordinated to interlayer Eu^{3+} and free water molecules around interlayer Eu^{3+}. Therefore, the result of EXAFS may indicate that the amount of water molecules in the interlayer is nearly constant in the pH range from 2 to 12. We suggest that a fine hydration state change of Eu^{3+}, without a change in the total water amount, brings out a change in emission as pH varies.

We propose the following mechanism for Eu^{3+} emission in Eu/TiO. The obtained results are summarized as follows.
Water molecule effects:
1) Intercalated water molecules in Eu/TiO promote energy transfer from the TiO_{2-δ} nanosheet host layer to Eu^{3+}, and result in a higher emission.

**Figure 8.** Fourier transform of k^{3}-weighted Eu L_{III}-edge EXAFS spectra for Eu/TiO powder in 0.1 M NaCl solution. Circles: experimental data; solid line: fitting.

**Table 2.** Fitting results for Eu EXAFS for Eu/TiO at various pH.

<table>
<thead>
<tr>
<th>Sample</th>
<th>bond type</th>
<th>coordination numbers</th>
<th>bond length R (Å)</th>
<th>σ² (Å²)</th>
<th>R factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu/TiO in 0.01M HCl</td>
<td>Eu-O</td>
<td>7.5</td>
<td>2.42</td>
<td>0.087</td>
<td>8.34</td>
</tr>
<tr>
<td>Eu/TiO in 0.01M NaCl</td>
<td>Eu-O</td>
<td>7.1</td>
<td>2.42</td>
<td>0.087</td>
<td>5.86</td>
</tr>
<tr>
<td>Eu/TiO in 0.01M NaOH</td>
<td>Eu-O</td>
<td>6.7</td>
<td>2.43</td>
<td>0.087</td>
<td>11.14</td>
</tr>
</tbody>
</table>

k-range: 3-12 Å R-range: 1.320-2.486
2) However, the Eu\(^{3+}\) emission is decreased because of phonon quenching by inner-sphere water molecules surrounding Eu\(^{3+}\).

3) Ultimately, the emission intensity of Eu\(^{3+}\) increases with increasing amount of intercalated water, because effect 1) is stronger than effect 2).

pH dependence:

4) The number of inner-sphere water molecules surrounding Eu\(^{3+}\) decreases with increasing pH. As a result, effect 2) decreases with decreasing inner-sphere water molecules, leading to an increase in the emission intensity.

5) Low pH will bring about an increase in recombination between electrons and holes produced by bandgap excitation under UV illumination, leading to a decrease in the emission of Eu\(^{3+}\), and a decrease in the efficiency of energy transfer from the TiO\(_{2-d}\) nanosheet host layer to Eu\(^{3+}\) at low pH. As a result, the emission intensity of Eu\(^{3+}\) decreases. In addition, the number of inner-sphere water molecules surrounding Eu\(^{3+}\) increase with decreasing pH. As a result, effect 2) increases with increasing inner-sphere water molecules, leading to a decrease in the emission intensity.

4. Conclusions

Preparation of layered oxides intercalated with Eu\(^{3+}\) ions was successful with self-assembly deposition method based on the electrostatic interaction between negative charged oxide nanosheets and Eu\(^{3+}\) ions. XRD and TGA data revealed that water was also co-intercalated and coordinated interlayer Eu\(^{3+}\) ions. Eu\(^{3+}\) intercalated layered oxide prepared from TiO\(_{2-d}\) nanosheets (Eu/TiO) showed strong red emission of Eu\(^{3+}\). There is an obvious energy transfer between the host TiO\(_{2-d}\) nanosheets and the intercalated Eu\(^{3+}\). The presence of interlayer water molecules was found to be inevitable for the emission with high intensity. Removal of interlayer water molecules by heating or dehydrating resulted in less contribution of the host layer to the emission. Consequently, it should be noted that the interlayer water molecules strongly promote the photoluminescence of the interlayer lanthanide cation by the energy transfer. In addition, the Eu\(^{3+}\) emission intensity of Eu/TiO in 0.01 M NaOH aqueous solution (high pH) was stronger than that in 0.01 M HCl aqueous solution (low pH). A mechanism for this emission change was proposed, and involved two phenomena. One is a recombination-based change in the efficiency of energy transfer from the TiO\(_{2-d}\) nanosheet to Eu\(^{3+}\). Photoproduced electrons in TiO\(_{2-d}\) nanosheets more readily recombine with photoproduced holes at low pH than at high pH. The other phenomenon is a fine hydration state change of Eu\(^{3+}\) without a change in the total water amount. At high pH, the number of inner-sphere water molecules of Eu\(^{3+}\) is smaller than that at low pH. This small number of inner water molecules may lead to the high emission intensity.

Acknowledgments

This research was partially supported by the Ministry of Education, Culture, Sports, Science and Technology, Scientific Research of Priority Areas "Panoscopic Assembling and High Ordered Functions for Rare Earth Materials" and a Grant-in-Aid for Young Scientific Research (B) (No. 19750173).

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