Photoluminescence Property of Titanate Layered Oxide Intercalated with Tb^{3+} Ions by Electrostatic Self-assembly Deposition Method

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Titanate layered oxide intercalated with Tb^{3+} ions was prepared by electrostatic self-assembly deposition method using the exfoliated $H_2Ti_4O_9$ (Ti_4O_9 nanosheet). The naked Tb^{3+} green emission through energy transfer from Ti_4O_9 nanosheet was observed. The efficiency of the energy transfer decreased with decrease in the layer distance.

Several types of titanate layered oxides and TiO_2 nanoparticles doped with rare earth ions have attracted attention as luminescence materials.[1–12] Some researchers reported that TiO_2 was an excellent host for Eu^{3+} ions, and this material could yield efficient red luminescence through energy transfer from the host to the Eu^{3+} ions,[6–12] while green luminescence of Tb^{3+} ions through the energy transfer was very weak. A mechanism for the energy-transfer process has been proposed that the excited energy in the host matrix undergoes relaxation to the defect levels and that the energy is transferred to the rare earth ions.[10] Since the excited states of Tb^{3+} is relatively high, it does not show any energy transfer at all.[10] Thus, defect levels of host TiO_2 matrix higher than the excited states of Tb^{3+} are at least necessary to obtain the Tb^{3+} emission through the energy transfer.

Recently, titanate nanosheets have attracted attention as host materials because of its high crystallinity. We can easily synthesize titanate layered oxides intercalated with rare earth ions with electrostatic self-assembly deposition (ESD) method. The synthesis of the layered oxides with ESD method occurs as a result of combination of negatively charged titanate nanosheets and rare earth cations according to the electrostatic principles.[11,12] It is reported that the strong red luminescence through energy transfer from $Ti_{1.81}\square_{0.19}O_4(Ti_{1.81}O_4)$ nanosheet (□: vacancy) to Eu^{3+} was obtained in the layered oxide intercalated with Eu^{3+}, while green (Tb^{3+}) luminescence through energy transfer was very weak for this type of layered oxide.[11,12] In this work, we researched the Tb^{3+} luminescence property through energy transfer from alternative Ti_4O_9 nanosheet prepared by exfoliation of $H_2Ti_4O_9$ to Tb^{3+}. As a result, the naked green luminescence through energy transfer was obtained, and the luminescence intensity decreased with decreasing layer distance.

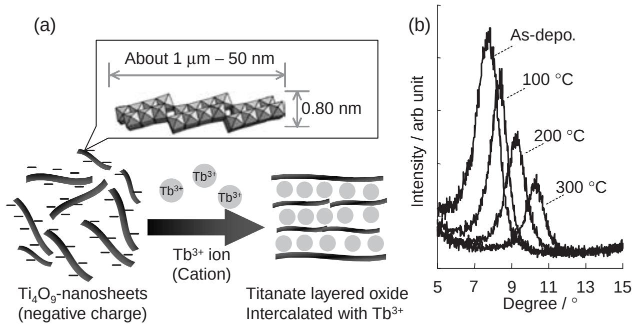

Figure 1. Schematic illustration of ESD method (a), and XRD patterns of the intercalated titanate layered oxides treated at various temperatures (b).

$K_2Ti_4O_9$ (KTO) was used as a starting material, which was synthesized by conventional solid-state method.[13] Ti_4O_9 nanosheet was prepared by the protonation and exfoliation of the KTO.[13] The nanosheet has a thickness in the order of nanometer with length and width in the order of micrometer. Intercalation compound of titanate layered oxide with Tb^{3+} cation was prepared from the solutions of Ti_4O_9 nanosheets and the acetate salt of Tb^{3+} (Figure 1a). ESD method was simply done by adding 10 mL of colloidal solution of nanosheets into an aqueous solution containing Tb^{3+} ions under controlled pH. The pH of the colloidal solution was carefully adjusted to 7.5–8.0 with 0.1 M HCl solution. Mixing two solutions resulted in an immediate precipitation, which consists of the titanate layered oxide intercalated with Tb^{3+} ions. Films were prepared by applying the precipitate on a Pt substrate, allowed to dry at room temperature, and subsequently heat-treated at various temperatures for 2 h. The titanate layered oxide intercalated with Tb^{3+} is described as Tb/Ti_4O_9. The crystal structure was 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 spectrophotometer (ICP, Seiko Instruments, SPS7800). UV–vis absorption spectra of the deposited oxides were measured by a UV–vis spectrometer (Jasco V-550). Excitation and emission spectra were analyzed by a Jasco FP-6500 Spectrofluorometer with a source of 150-W Xe lamp.

Figure 1b shows the XRD patterns of the Tb/Ti_4O_9 treated at various temperatures. The diffraction peaks reflect the corresponding the basal spacing (layer distance) of the layered oxides. The layer distance decreased with increasing treatment temperature. From the results of TG/DTA, FTIR, and XPS data, the main weight loss by heat treatment was found to be as a result of the loss of the interlayer water. Treatment of the sample in low humidity resulted in the decrease of the layer distance, while treatment in high humidity resulted in the increase of layer distance. Consequently, the decrease in the layer distance is assumed to be caused by the removal of interlayer water. Treating Tb/Ti_4O_9 at 300 °C, the interlayer water was almost removed and the interlayer distance was about 1 Å, which corresponded to the diameter of Tb^{3+} ion.

The composition of Tb/Ti_4O_9 was $Tb_{0.50}Ti_{4.00}O_9$, which was obtained by ICP analysis. The negative charge of the Ti_4O_9 nanosheets may be neutralized only if 0.66 mol of Tb^{3+} exists in

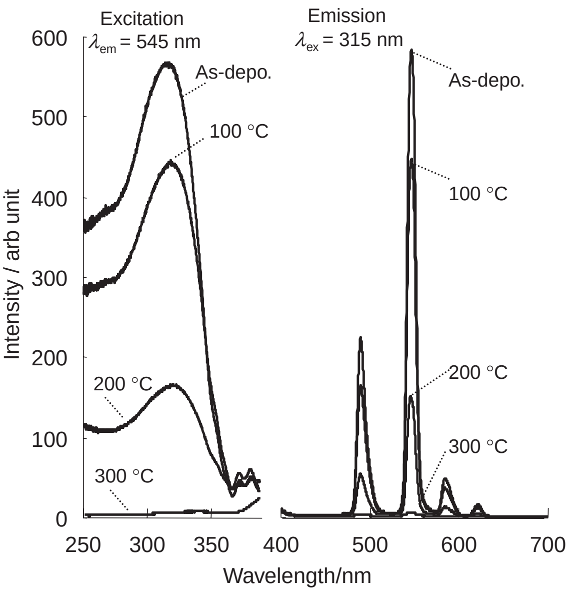

Figure 2. Room-temperature emission and excitation spectra of Tb/Ti_4O_9 treated at various temperatures.

the interlayer of 1 mol of layered oxide according to the chemical composition of the original layered compound. The estimated composition from the experimental data is in harmony with those based on the given neutrality theory. Small deviations in the value from the original composition may come from proton cointercalation. According to these results, we confirmed that the titanate layered oxides intercalated with Tb^{3+} ions were obtained with ESD methods.

Figure 2 shows the room-temperature emission and excitation spectra of Tb/Ti_4O_9 treated at various temperatures. The emission peaks from 480 to 650 nm were associated with the $^5D_4$–^7F_J ($J = 3$–6) transition. In the excitation spectra, the broad peak at 250–350 nm and several peaks between 350 and 380 nm were observed. The latter was 4f intratransition of Tb^{3+} ion. The broad excitation spectra (250–350 nm) corresponded to the UV–vis absorption spectra of Tb/Ti_4O_9 and the intensity of excitation band (250–350 nm) of terbium acetate solution enhanced on the Ti_4O_9-nanosheet surface (see Supporting Information).[14] These results indicate that the broad excitation peak is assigned to the energy transfer from Ti_4O_9 nanosheet to Tb^{3+}. The Tb^{3+} emission assigned to the energy transfer from Ti_4O_9 nanosheets was about 100 times as strong as that from $Ti_{1.81}O_4$ nanosheet (see Supporting Information).[14] The strong Tb^{3+} emission through energy transfer means that the defect levels of host Ti_4O_9-nanosheet matrix are higher than the excited states of Tb^{3+} or that there is little defect in the host Ti_4O_9-nanosheet matrix.

The emission intensity through the energy transfer decreased with increasing treatment temperature. For the Tb/Ti_4O_9 films treated at various humidity, the Tb^{3+} emission for the sample treated at 5% humidity was weaker than that for the sample before treatment, while that for 100% humidity was the strongest. Figure 3 shows Tb^{3+} emission intensity assigned to energy transfer as a function of layer distance for various samples. The layer distances were controlled by humidity (5–100%) and/or heat treatment (RT–300 °C) in terms of the amount of water in the interlayer. It was found that the emission intensities decreased with decreasing layer distance.

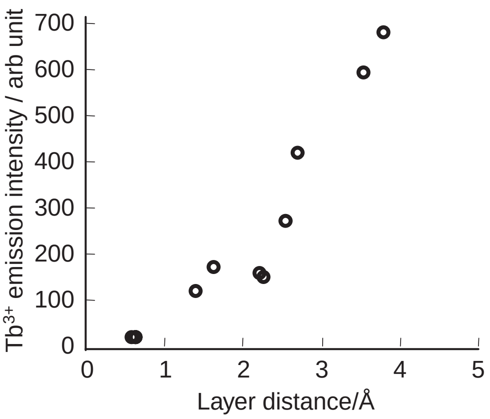

Figure 3. Tb^{3+} emission ($\lambda_{ex} = 315$ nm, $\lambda_{em} = 545$ nm) intensity assigned to energy transfer as a function of layer distance for various samples. The layer distances were controlled by humidity (5–100%) and/or heat treatment (RT–300 °C).

In conclusion, we synthesized the titanate layered oxide intercalated with Tb^{3+} with ESD method using Ti_4O_9 nanosheets. The Ti_4O_9 nanosheet was an excellent host for Tb^{3+} ions and this material could yield efficient green luminescence through energy transfer from the host to the Tb^{3+} ions. The energy transfer was strongly depended on the interlayer distance.

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14 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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