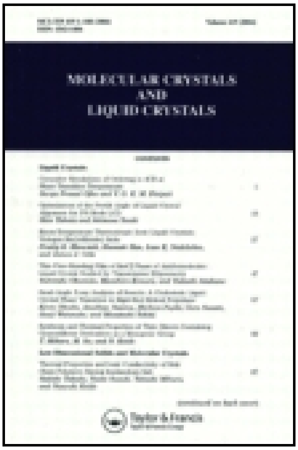

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Synthesis and Photoluminescence Properties of Niobate Layered Oxides Intercalated with Rare Earth Ions by Electrostatic Self-Assembly Methods

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The niobate layered oxides intercalated with Tb^{3+} *or* Eu^{3+} *ions were prepared by the electrostatic self-assembly deposition method. The* Tb^{3+} *ions in the interlayer exhibited green luminescence by energy transfer from the host* NbO_6 *layer to the guest* Tb^{3+} *ions, which was based on the niobate nanosheet band gap excitation. The* Tb^{3+} *emission intensity decreased with decreasing interlayer water molecules, indicating that the presence of interlayer water molecules is inevitable for the* Tb^{3+} *emission assigned to the energy transfer. On the other hand, the emission intensity of* Eu^{3+} *in the interlayer was weaker than that of* Tb^{3+}*.*

Keywords: electrostatic self-assembly deposition; energy transfer; layered oxide; nanosheet

INTRODUCTION

Inorganic nanosheets prepared by the exfoliation of the layered oxides have attracted much attention as a nano-building block to assemble nanostructure because the nanosheets have a thickness in the order of nanometres with a length and width in the order of

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micrometres [1–11]. The nanosheets are prepared by the exfoliation of $Cs_xTi_{2-x/4}\square_{R/4}O_4$ ($\square$:vacancy) [1,2], $KTiNbO_5$ [3] and $K_4Nb_6O_{17}$ [4]. By building up the nanosheets, new layered oxides that cannot be prepared with conventional solid-state methods can be reassembled at room temperature. As a reassembling method, electrostatic self-assembly deposition (ESD) techniques are reported [7]. The driving force of the assembling method is electrostatic interaction between cationic species and nanosheet with negative charge. Various kinds of layered oxides can be easily prepared under controlled pH in a solution by the ESD method. In our previous study, we found some interesting photoluminescence properties of titanate layered oxides intercalated with rare earth ions prepared by the ESD method using the exfoliated $Cs_{0.76}Ti_{1.81}\square_{0.19}O_4$ sheets ($Ti_{1.81}O_4$-nanosheets) [11]. The Eu^{3+} in the interlayer of $Ti_{1.81}O_4$-nanosheets exhibited red luminescence at room temperature by energy transfer from the nanosheets to Eu^{3+} ions, while Tb^{3+} in the interlayer exhibited no luminescence [11]. The energy transfer of Eu^{3+} emission was based on the nanosheet band gap excitation. The Eu^{3+} emission increased with increasing the amount of interlayer water molecules, in contrast to the general knowledge of the diminishing effect of the presence of water on emission in similar cases. The nanospace in the interlayer of nanosheets is expected to create a specific environment for the energy transfer. Utilizing and controlling this specific environment, we will develop new luminescence materials. However, there are a few reports on the photoluminescence property for the layered oxide composed of nanosheets.

In this article, we report the photoluminescence property of the niobate layered oxide intercalated with Tb^{3+} or Eu^{3+} prepared by ESD method. The Tb^{3+} emission decreased with decreasing interlayer water molecules, indicating that the presence of interlayer water molecules is inevitable for the Tb^{3+} emission assigned to the energy transfer. On the other hand, the Eu^{3+} emission increased with decreasing interlayer water molecules.

EXPERIMENTAL

Synthesis

$K_4Nb_6O_{17}$ was prepared by conventional solid-state methods [4]. Protonation of the $K_4Nb_6O_{17}$ carried out in 1 M HCl solution resulted in $H_4Nb_6O_{17}$. The proton exchanged powder was exfoliated in tetrabutylammonium (TBA) solution for 72 h. The amount of TBA in the solution was 8-fold higher than that of powder in molar ratio. The subsequent centrifugation of the solution under 3000 rpm for 30 min yielded colloidal suspension of niobate nanosheets. The intercalation of rare earth cations into the interlayer of layered oxides was carried out using the ESD method, which was simply done by adding 10 ml of colloidal solution of niobate nanosheets into an aqueous rare earth solution under controlled pH. The pH of the colloidal solution was carefully adjusted to 7.5–8 with 0.1 M HCl solution. Acetate salts of lanthanide cations (Wako Chemicals) were used without any further treatment. Mixing two solutions resulted in an immediate precipitation, which consists of a single phase niobate layered oxides intercalated with rare earth cations. Intercalation with ESD method occurs as a result of combination of negatively charged niobate nanosheets and rare earth cation according to the electrostatic principles. Films were prepared by applying the precipitate on a glass substrate and allowed to dry at room temperature. The prepared layered oxide is denoted as RE/NbO (RE: rare earth ion) for convenience in this article.

MEASUREMENTS

The crystal structure and orientation of the films were analyzed from X-ray diffraction patterns (using CuKα 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 an UV-vis spectrometer (Jasco V-550). Thermogravimetric differential thermal analysis curves were obtained by Seiko TG/DTA. Excitation and emission spectra were analyzed by Jasco FP-6500 Spectrofluorometer with a source of 150 W Xe lamp.

RESULTS AND DISCUSSION

Figure 1 shows the structural model of $K_4Nb_6O_{17}$, which is composed of NbO_6 host layers and K^+ guest ions. The protonation of $K_4Nb_6O_{17}$ in acid solution resulted in $H_4Nb_6O_{17}$. The host NbO_6 layers are exfoliated by the treatment with TBA solution. Figure 2 shows a typical AFM image of the exfoliated NbO_6 host layer (niobate nanosheet). The lateral size was about several hundreds nanometer, and the thickness was about 1 nm. Almost all nanosheets existed as a mono-nanosheet in the solution.

Intercalation of rare earth ions into the niobate nanosheet layers was successfully obtained by the ESD method. The ESD method needs pH adjustment in order to prevent the possible formation of lanthanide hydroxide at high-pH regions and $H_4Nb_6O_{17}$ layered oxide at

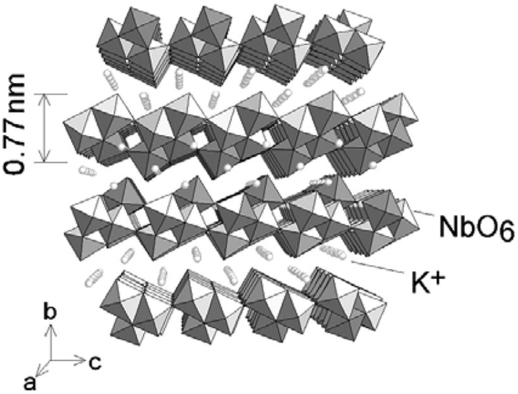

FIGURE 1 The structural model of $K_4Nb_6O_{17}$.

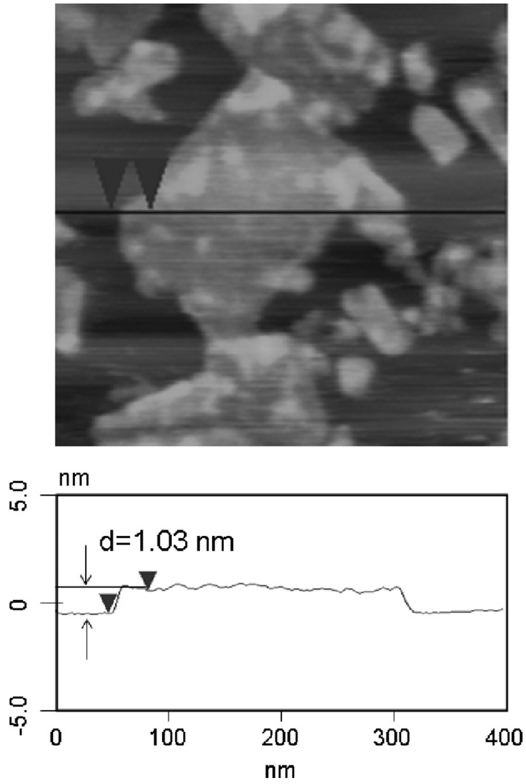

FIGURE 2 AFM image of niobate nanosheets.

low-pH regions, because the initial values of the NbO_6 nanosheet and lanthanide cation solutions fall generally into quite acidic and alkali regions, respectively. The pH values are in a reasonable range so as not to result in any hydroxide formation, when the pH of the exfoliation solution is adjusted to around 7.5. After mixing both solutions, the final pH stood stable at about 6.5–5.5, which is equally acceptable for both solutions so as not to yield any lanthanide hydroxides and $H_4Nb_6O_{17}$ layered oxide. Therefore, all intercalation reactions succeeded and this was also supported by ICP and XRD data.

Figure 3 shows the TGA and DTA curves of Tb/NbO prepared by ESD. The main weight loss appeared to be a result of removal of the intercalated water. Since the intercalated layered oxide does not have any TBA molecules according to FTIR and XPS data, the weight loss can be assigned to the loss of water only. All samples gave rise to a broad DTA peaks in the weight loss range. The peak covers overlapped endothermic evaporation peaks and exothermic peaks ascribable to reordering in the crystal structure. This is a typical behavior of this type of layered oxides [7,12]. Compositions of the layered oxides were estimated on the basis of ICP and TGA data. The compositions of Tb/NbO and Eu/NbO were $Tb_{1.39}Nb_6O_{17} \cdot 10.8H_2O$ and $Eu_{1.36}Nb_6O_{17} \cdot 11.9H_2O$, respectively. The water content was calculated from the thermal analysis data and indicates that the intercalated lanthanide ions exist as an aqua ion and are coordinated with 7–9 water molecules under ambient conditions. Calculation was done

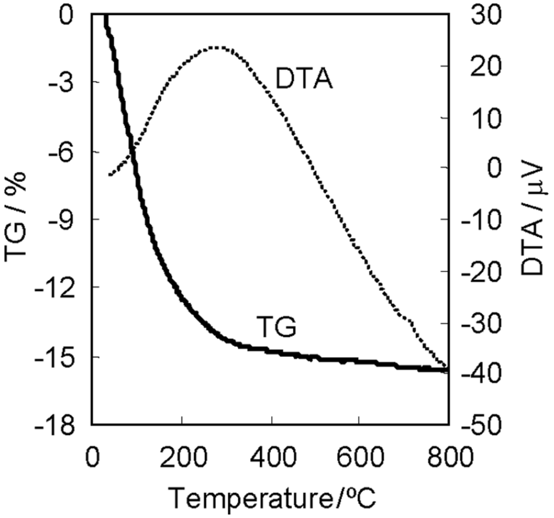

FIGURE 3 TG and DTA curves of Tb/NbO.

under the assumption that a significant portion of the intercalated water molecules surrounds lanthanide cations in the interlayer, because lanthanides have a high tendency of hydration in an aqua environment. The negative charge of the niobate nanosheets may be neutralized only if 1.33 mol of trivalent cations exists in the interlayer of 1 mol of layered oxide according to the chemical composition of the original layered compound. The estimated compositions from the experimental ICP data are in harmony with those based on the given neutrality theory. Small deviations in these values from the original composition may come from the excess amount of lanthanide adsorbed on the nanosheet surfaces and/or hydronium co-intercalation.

Figure 4 shows the XRD patterns of Tb/NbO treated at various temperatures. The diffraction peaks reflects the basal spacing of RE/NbO. The heat treatment results in the shift of the peak 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. The layer distances of as-deposited and 300°C-treated samples were 5.0 and 0.8 Å, respectively, The XRD patterns of Eu/NbO samples also showed the same manner with that of Tb/NbO samples. As the temperature increases, the number of coordinated water molecules

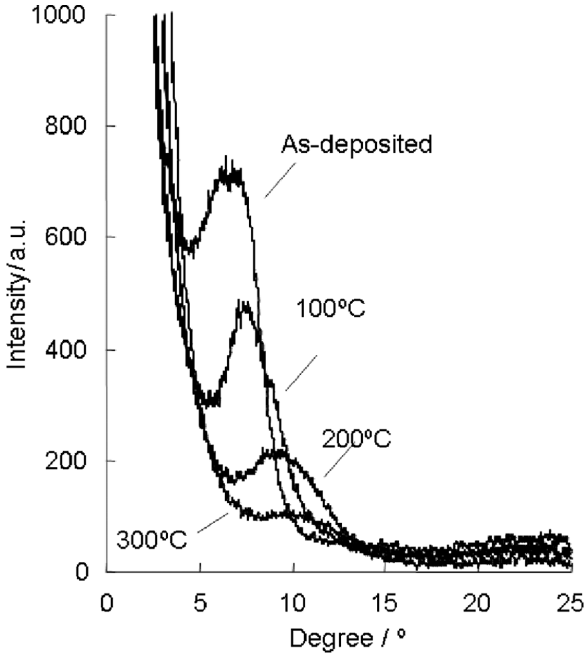

FIGURE 4 XRD patterns of Tb/NbO treated at various temperatures.

decreases, and finally, the layer distance represents a value close enough to accommodate a bare lanthanide cation. In addition, decreasing intensity and broadening of the diffraction peak point out the weakening in the crystallinity of the layered oxide.

UV-vis spectra of Tb/NbO are shown in Figure 5. A red shift on the absorption edge relative to the niobate nanosheet was observed, which can be assigned to the host layer-guest ion interaction and resultant reduction in the quantum size effect of niobate nanosheets. On the other hand, the slight shift on the absorption edge as a result of heat treatment may be described by a phenomenon related to the loss of interlayer water and consequent improvement in the interaction of the host layers with each other at shorter interlayer distances.

Figure 6 shows the room-temperature emission and excitation spectra of the Tb/NbO 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 emission peaks, the green $^5D_4$-$^7F_5$ emission at around 545 nm was the strongest. Many excitation peaks of Tb^{3+} ions exist in the range of 320–400 nm, which were associated with the 4f intra-transitions of Tb^{3+}. As the temperature increased, the broad peak intensities at around 250–350 nm decreased and the position of the top peak shifted to the higher wavelength side (red shift). The red shift on the top peak position at 250–350 nm in excitation spectra corresponded to that on the absorption edge in UV spectra, which indicates that the broad excitation peak at around 250–350 nm is assigned to the energy transfer from niobate nanosheets to the Tb^{3+}. The intensity of the energy transfer band decreased with increasing temperature. The heat treatment results in the decrease in the interlayer distance as shown in Figure 4. The

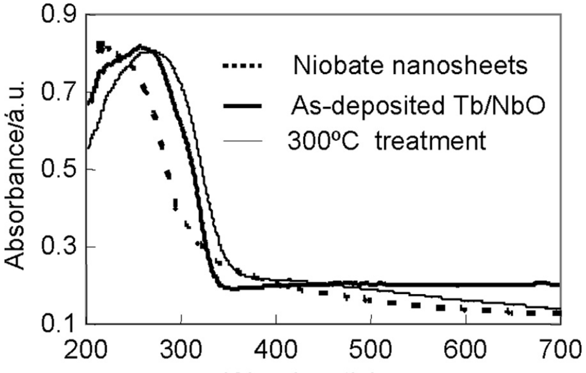

FIGURE 5 UV-vis spectra of Tb/NbO systems.

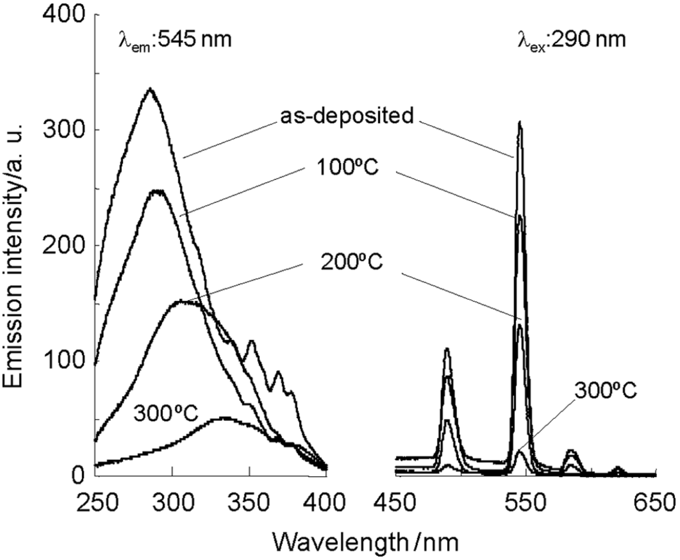

FIGURE 6 The room-temperature emission and excitation spectra of the Tb/NbO treated at various temperatures.

decrease in the interlayer distance resulted from the loss of the interlayer water by heat treatment. This means that the energy transfer from niobate nanosheet to the Tb^{3+} is promoted by the interlayer water. In our previous study, we reported that the emission of Eu^{3+} intercalated titanate nanosheet based on the energy transfer decreased with decreasing the interlayer water [13]. However, the detailed mechanism of the change in the energy transfer by heat treatment is complicated because reordering of the interlayer structure such as the change in the symmetry of guest Tb^{3+} ions may occur with decreasing interlayer water. The quantum efficiency of Tb^{3+} in as-prepared Tb/NbO achieved in solution was about 0.1% relatively to quinine sulfate.

Figure 7 shows the room-temperature emission and excitation spectra of the Eu/NbO treated at various temperatures. The most intense emission peaks were observed at around 614 nm, which were assigned to the $^5D_0$-$^7F_2$ electric dipole transition. The second intense peaks were observed at around 592 nm, which were assigned to the $^5D_0$-$^7F_1$ magnetic dipole transition. The excitation peaks at 320–400 nm were assigned to the 4f intra-transition of Eu^{3+}. In the same manner with Tb/NbO system, the broad excitation peaks at 250–300 nm was shifted to higher wavelength side by heat-treatment. The broad excitation

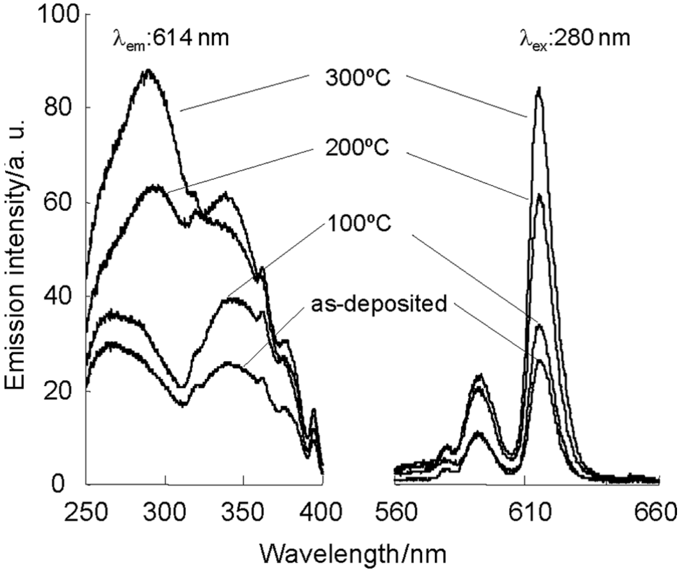

FIGURE 7 The room-temperature emission and excitation spectra of the Eu/NbO treated at various temperatures.

peak at around 250–350 nm is expected to be assigned to the energy transfer band from niobate nanosheets to the Eu^{3+}. The intensity of the energy transfer band increased with increasing temperature. This may be explained as follows. When the interlayer distance decreased with increasing temperature, the distance between niobate nanosheets and Tb^{3+} ions decreased. And interlayer water that has a diminishing effect on emission was decreased by heat-treatment. As a result, the efficiency of the energy transfer increased by heat treatment. However, the emission intensity of Eu/NbO was weaker than that of Tb/NbO, and the quantum efficiency of Eu^{3+} in as-prepared Eu/NbO was 0.01% or less relatively to quinine sulfate.

The difference in quantum efficiency between Tb/NbO and Eu/NbO are related to the energy transfer from niobate nanosheets. The energy transfer in Tb/NbO was larger than that in Eu/NbO. In the case of titanate nanosheets, the energy transfer from titanate nanosheet to Eu^{3+} was larger than that to Tb^{3+} [10]. 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 the energy is transferred to the rare earth ions [10]. In the case of Tb/NbO system, it is considered that interlayer water assist the energy transfer from the defect levels to rare earth ions. Perhaps, the vibration of interlayer water presumably adjust the energy gap between defect levels of nanosheet and the excitation levels of the rare earth ion.

CONCLUSIONS

The layered niobate oxides intercalated with Tb^{3+} or Eu^{3+} were prepared by ESD method. The Tb^{3+} ions in the interlayer exhibited green luminescence by energy transfer from the host NbO_6 layer to the guest Tb^{3+} ions. The Tb^{3+} emission decreased with decreasing interlayer water molecules. This indicates that the presence of interlayer water molecules is inevitable for the Tb^{3+} emission assigned to the energy transfer. The energy transfer in Tb/NbO was larger than that in Eu/NbO. In the Eu/NbO system, the effect on the energy transfer assist by interlayer water was not observed. The Eu^{3+} emission in the interlayer increased with decreasing interlayer water molecules, which is due to the loss in interlayer water causing diminishing effect on emission.

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