Photochemical host–guest interaction in Tb^{3+} and Eu^{3+} ion-exchanged $K_{2-x}H_xTi_2O_5$ layered oxides

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Luminescence of Eu^{3+} and Tb^{3+} intercalated in $K_{2-x}H_xTi_2O_5$ layered oxides is observed by exciting the layered titanate host indicating that the energy transfer *via* electron–hole trapping from the layered host to the guest in the interlayers occurred.

Energy- and electron-transfer processes have been studied using various types of organic and inorganic host–guest materials. This phenomenon is especially important for rare-earth phosphors doped in inorganic bulk materials.[1] Ion-exchangeable layered oxides with structural regularity are one of the interesting host materials. Applications of the layered oxides to photochemistry, materials chemistry *etc.* have been extensively investigated.[2] The photochemical interaction in energy- and electron-transfer processes between oxide layers (hosts) and substances in interlayers (guests) is of particular interest from the viewpoint of the development of new host–guest systems. Recently, the host–guest interaction in the luminescent properties of $[Ru(bpy)_3]^{2+}$ intercalated in layered titanates and niobates has been reported.[3] Here, the photochemical host–guest interaction induced by the excitation of layered oxide hosts is revealed by the photoluminescence properties of $K_{2-x}H_xTi_2O_5$ layered oxides exchanged with rare-earth metal ions.

$K_2Ti_2O_5$ was synthesized by melting a mixture of TiO_2 (Kanto Chemicals, 99.0%) and K_2CO_3 (Kanto Chemicals) at 1270 K for 1 h in air using a platinum crucible.[4,5] H^+- and Ln^{3+}-exchanged derivatives were prepared in aqueous $LnCl_3$ (0.02 m, 40 ml) containing 1 g of $K_2Ti_2O_5$ powder. About 50% of K^+ in $K_2Ti_2O_5$ can easily be exchanged with H^+ even in distilled water.[5] Therefore, the H^+-exchange should partly take place during the ion-exchange reactions in aqueous $LnCl_3$ solutions; the trivalent rare-earth metal ion-exchanged derivatives are denoted $K_{2-x-3y}H_xLn_yTi_2O_5$. The compositions of the ion-exchanged derivatives were determined by EDX (Kevex, DeltaPlus). Photoluminescence was measured for powdered samples at room- and liquid-nitrogen-temperatures using a quartz cell and a fluorometer (Spex, Fluoromax™).

Fig. 1 shows the emission spectra of H^+-, Eu^{3+}- and Tb^{3+}-exchanged $K_{2-x}H_xTi_2O_5$ obtained by excitation at 320 nm at 77 K. The compositions of obtained materials were $K_{0.7}H_{1.3}Ti_2O_5$, $K_{0.60}H_{1.2}Eu_{0.04}Ti_2O_5$ and $K_{0.85}H_{1.0}Tb_{0.05}Ti_2O_5$, respectively. A broad emission band was observed at 520 nm for $K_{0.7}H_{1.3}Ti_2O_5$ although an emission band was observed at 420 nm by excitation at 270 nm for $K_2Ti_2O_5$.[6] Such a shift by H^+-exchange in emission spectra has also been observed for layered potassium niobates.[7] It is noteworthy that the emission comes from the host of two-dimensional titanate sheets. For $K_{0.60}H_{1.2}Eu_{0.04}Ti_2O_5$ and $K_{0.85}H_{1.0}Tb_{0.05}Ti_2O_5$, the host emission was partly quenched and emission of the rare-earth metal ions was observed (Eu^{3+}, $^5D_0 \rightarrow {}^7F_{1,2}$; Tb^{3+}, $^5D_4 \rightarrow {}^7F_{4,5,6}$). Moreover, the ratios of luminescence intensities of Eu^{3+} and Tb^{3+} to those of the hosts were increased by increasing the degree of ion exchange.

Fig. 2 shows the excitation spectra of the ion-exchanged derivatives at 77 K. A broad excitation band with an onset at 350 nm was observed for $K_{0.7}H_{1.3}Ti_2O_5$. For $K_{0.60}H_{1.2}Eu_{0.04}Ti_2O_5$ and $K_{0.85}H_{1.0}Tb_{0.05}Ti_2O_5$, broad excitation bands with onsets at 350 nm were observed in addition to the peaks due to direct excitation of the rare-earth metal ions (360, 376 and 393 nm for Eu^{3+}, 367 and 377 nm for Tb^{3+}). Especially for $K_{0.85}H_{1.0}Tb_{0.05}Ti_2O_5$, the intensity of the broad band was larger than that of the direct excitation of Tb^{3+}. These broad bands were similar to that for $K_{0.7}H_{1.3}Ti_2O_5$. Luminescence of $K_{0.7}H_{1.3}Ti_2O_5$ was not observed at 300 K because non-radiative transitions in titanate layers and/or electron transfer quenching by H^+ in interlayers occurred. At 300 K, only the peaks due to the direct excitation of Eu^{3+} and Tb^{3+} were observed for the $K_{0.60}H_{1.2}Eu_{0.04}Ti_2O_5$ and $K_{0.85}H_{1.0}Tb_{0.05}Ti_2O_5$ powder but broad bands were not obtained. Moreover, such a band was not obtained in the excitation spectrum of an aqueous Tb^{3+} solution. From these results, it was concluded that the broad band was due to the excitation of titanate layers. Accordingly, the

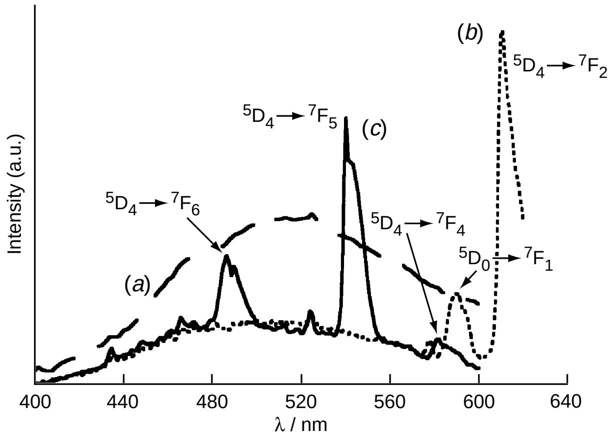

Fig. 1 Emission spectra of (*a*) $K_{0.7}H_{1.3}Ti_2O_5$, (*b*) $K_{0.60}H_{1.2}Eu_{0.04}Ti_2O_5$ and (*c*) $K_{0.85}H_{1.0}Tb_{0.05}Ti_2O_5$ at 77 K obtained by excitation at 320 nm

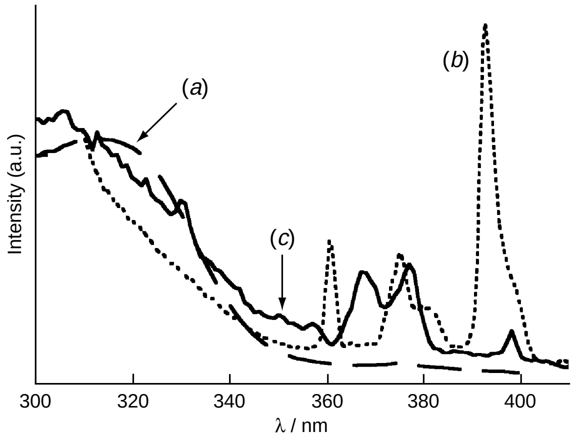

Fig. 2 Excitation spectra of (*a*) $K_{0.7}H_{1.3}Ti_2O_5$ (monitored at 520 nm), (*b*) $K_{0.60}H_{1.2}Eu_{0.04}Ti_2O_5$ (monitored at 591.5 nm) and (*c*) $K_{0.85}H_{1.0}Tb_{0.05}Ti_2O_5$ (monitored at 541.5 nm) at 77 K

emission spectra in Fig. 1 which had been obtained by excitation at 320 nm were due to the host excitation.

The absorption spectra of Pr^{3+}, Sm^{3+}, Eu^{3+}, Tb^{3+}, Dy^{3+} and Er^{3+} ions more or less overlap with the host emission spectra.[8] Therefore, the resonant energy transfer would have been possible energetically for all the rare-earth metal ion-exchanged derivatives. Unexpectedly, however, only Eu^{3+} and Tb^{3+} showed luminescence by the host excitation even though the amounts of rare-earth metal ions exchanged were similar in all samples ($K_{0.60}H_{1.2}Eu_{0.04}Ti_2O_5$, $K_{0.58}H_{1.4}Pr_{0.02}Ti_2O_5$, $K_{0.85}H_{1.0}Tb_{0.05}Ti_2O_5$, $K_{1.2}H_{0.68}Sm_{0.04}Ti_2O_5$, $K_{0.57}H_{1.4}Dy_{0.02}Ti_2O_5$ and $K_{0.64}H_{1.3}Er_{0.03}Ti_2O_5$). Only the host emission was observed for the $K_{0.58}H_{1.4}Pr_{0.02}Ti_2O_5$, $K_{1.2}H_{0.68}Sm_{0.04}Ti_2O_5$, $K_{0.57}H_{1.4}Dy_{0.02}Ti_2O_5$ and $K_{0.64}H_{1.3}Er_{0.03}Ti_2O_5$ powders indicating the lack of the energy transfer from the host layer to the guest ion. Eu^{3+} and Tb^{3+} can easily assume other oxidation numbers such as Eu^{2+} and Tb^{4+}. Therefore, the present result can be explained as follows; electrons and holes produced by host excitation in titanate layers can be trapped by Eu^{3+} and Tb^{3+} located in interlayers, respectively, and holes and electrons successively can recombine at their ions resulting in the luminescence, *i.e.* electrons and holes act as carriers of the excitation energy. Photocatalytic reactions proceed at interlayers of $K_{2-x}H_xTi_2O_5$[9] indicating that the electrons and holes can actually be transferred to substances in the interlayers. The energy levels of the conduction and valence bands of the titanate layers would satisfy the redox reactions of Eu^{3+} and Tb^{3+} judging from the band structures of various titanates.[10,11]

In conclusion, in the $K_{2-x-3y}H_xLn_yTi_2O_5$ layered oxide system, Eu^{3+} and Tb^{3+} in interlayers showed luminescence upon excitation of the titanate layers. This observation indicates energy-transfer processes *via* electron–hole trapping from layered titanate hosts to guests in interlayers. The present study demonstrates the energy transfer in two-dimensional systems by probing luminescence of guests of rare-earth metal ions. This will be of particular interest as the novel photochemical host–guest system in which the direct excitation of stable layered oxide hosts plays an important role.

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