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Photoluminescence of Layered Potassium Niobates ($K_4Nb_6O_{17}$ and KNb_3O_8) and Effects of Hydration and H^+-exchange on the Luminescence Properties

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KNb_3O_8 showed blue luminescence of 450 nm at 300 K. The emission spectra of $K_4Nb_6O_{17}$ and KNb_3O_8 at 77 K were red-shifted by H_2O intercalation and H^+-exchange, indicating that the photochemical properties of these hosts were changed with interlayer conditions.

Layered compounds are extensively used as hosts which serve interlayer as the two dimensional space for ion-exchange and intercalation. Photochemistry of photoresponsive compounds such as $Ru(byp)_3{}^{2+}$ intercalated in clay has also been studied.1-3) However, functions of hosts themselves have hardly been reported. It is important to study how the host property is changed with interlayer conditions if the host has some interesting properties. Some potassium niobates with layered structures show the high photocatalytic activity for water decomposition.4) Luminescence of niobates has been studied for a long time,5,6) especially by Blasse *et al.* It is one of evaluation points for phosphors if they show luminescence at room temperature. However, only a few ternary alkali or alkaline earth niobates show luminescence at room temperature. We report here the room temperature photoluminescence of KNb_3O_8 and novel effects of water intercalation and H^+-exchange on the photoluminescence of $K_4Nb_6O_{17}$ and KNb_3O_8 with layered structures.

Layered potassium niobates were prepared by melting mixtures of Nb_2O_5 (Wako Pure Chemical, 99.9%) and K_2CO_3 (Kanto Chemical) at 1443 K (1 h) for $K_4Nb_6O_{17}$ and 1473 K (10 h) for KNb_3O_8 in a platinum crucible.7) Excess K_2CO_3 (20-30 mol%) was added to compensate for the loss due to volatilization and to get good crystallinity. H^+-exchange was carried out at 300 K in 1 M HCl (30 h) and 2 M HNO_3 (70 h) for $K_4Nb_6O_{17}$ and KNb_3O_8, respectively. Powdered samples were used for luminescence measurements at room and liquid nitrogen temperatures (77 K) using a fluorometer (Spex, Fluoromax^{TM}, light source; 150 W Xe lamp, photomultiplier tube; R928P). Spectra were not corrected for excitation light intensity and sensitivity of the photomultiplier tube.

Excitation and emission spectra of KNb_3O_8 at 300 K are shown in Fig. 1. The broad luminescence at 450 nm was observed by excitation at 315 nm. Only a few ternary alkali or alkaline earth niobates are known to show luminescence at room temperature.5,6) Moreover, the excitation wavelength of KNb_3O_8 is longer and the Stokes shift (ca. 10000 cm^{-1}) is smaller compared with those of other niobates ($CaNb_2O_6$ etc.) which have already been reported to show luminescence at room temperature.5,6) It should be stressed from these points that KNb_3O_8 has arisen as one of interesting niobates for luminescent materials.

$K_4Nb_6O_{17}$ and KNb_3O_8 have layered structures8,9) and the potassium ions can be exchanged with other cations.10,11) At first, we investigated the effect of H^+-exchange on the photoluminescence of KNb_3O_8. In contrast with KNb_3O_8, H^+-exchanged KNb_3O_8 (H^+/KNb_3O_8) hardly showed photoluminescence at room temperature while it did at 77 K. This is one of the drastic effect by H^+-exchange. Measurements were carried out at 77 K for the examination of the effect of H^+-exchange on the spectra. As shown in Fig. 2, the emission spectrum of KNb_3O_8 was red-shifted (10 nm) by the H^+-exchange while the peak position of the excitation

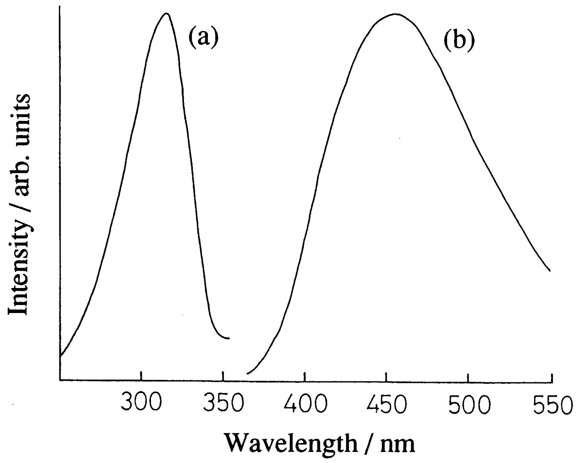

Fig. 1. Photoluminescence spectra of KNb_3O_8 at 300 K.
(a); excitation spectrum monitored at 450 nm,
(b); emission spectrum excited at 315 nm.

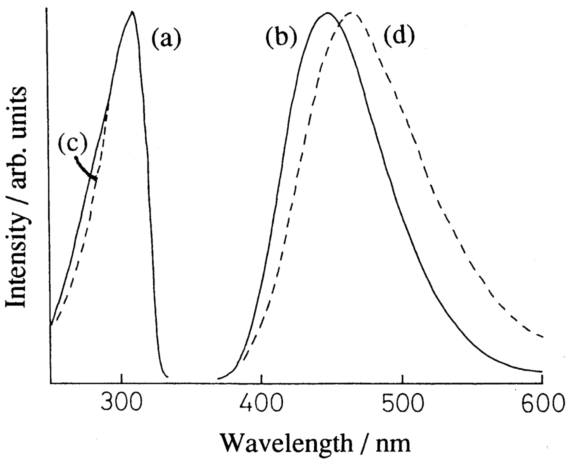

Fig. 2. Effects of H^+-exchange on photoluminescence of KNb_3O_8 at 77 K.
(a); KNb_3O_8: excitation spectrum,
(b); KNb_3O_8: emission spectrum,
(c); H^+/KNb_3O_8: excitation spectrum,
(d); H^+/KNb_3O_8: emission spectrum.

spectrum of H^+/KNb_3O_8 was almost the same as that of KNb_3O_8. The d value of the (010) plane which was determined by X-ray diffraction was shifted from 10.65 Å to 11.39 Å by the H^+-exchange, indicating clearly that the red-shift was due to the H^+-exchange.

Next, we studied the photoluminescence of $K_4Nb_6O_{17}$. On the $K_4Nb_6O_{17}$ compound, hydrated compounds ($K_4Nb_6O_{17}\cdot 3\ H_2O$ and $K_4Nb_6O_{17}\cdot 4.5\ H_2O$) are known to exist as well as unhydrated one.7) Therefore, the effect of hydration was also examined as well as that of H^+-exchange. Figure 3 shows the excitation and emission spectra at 77 K of $K_4Nb_6O_{17}$, $K_4Nb_6O_{17}\cdot 3H_2O$, and H^+-exchanged $K_4Nb_6O_{17}$ ($H^+/K_4Nb_6O_{17}$). Unhydrated $K_4Nb_6O_{17}$ showed bright blue luminescence at 77 K as had already been reported by Sanz-García *et al.*.12) The emission wavelength was red-shifted by hydration and H^+-exchange (5 and 20 nm, respectively). The excitation spectrum was also red-shifted by the hydration (5 nm). However, the peak position of the excitation spectrum of $H^+/K_4Nb_6O_{17}$ was almost the same as that of $K_4Nb_6O_{17}\cdot 3H_2O$.

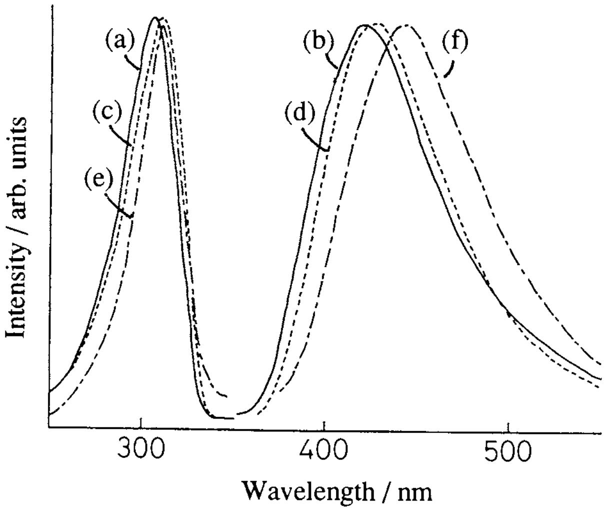

Fig. 3. Effects of hydration and H^+-exchange on photoluminescence of $K_4Nb_6O_{17}$ at 77 K.
(a); $K_4Nb_6O_{17}$: excitation spectrum,
(b); $K_4Nb_6O_{17}$: emission spectrum,
(c); $K_4Nb_6O_{17}\cdot 3H_2O$: excitation spectrum,
(d); $K_4Nb_6O_{17}\cdot 3H_2O$: emission spectrum,
(e); $H^+/K_4Nb_6O_{17}$: excitation spectrum,
(f); $H^+/K_4Nb_6O_{17}$: emission spectrum.

Blasse has suggested from a lot of their observations that the bond length between metal and oxygen is an important factor on the quenching temperature of luminescence.5) In general, ion-exchangeable layered oxide compounds have extremely short metal-oxygen bonds which stick out into the interlayer. The shortest bond lengths of Nb-O in $K_4Nb_6O_{17}$ and KNb_3O_8 are 1.70 Å and 1.736 Å, respectively.8,9) The Nb-O bonds with short distances can contribute to the luminescence at relatively high temperatures. Hydration and H^+-exchange probably affect the coordination state of the Nb-O bonds, resulting in the change in luminescence properties. The similar behavior was observed on $K_2Ti_2O_5$ with layered structure.13)

In conclusion, it was found that KNb_3O_8 showed blue luminescence at 300 K. The novel effects of water intercalation and H^+-exchange on photoluminescence properties of hosts (layers) were demonstrated for $K_4Nb_6O_{17}$ and KNb_3O_8 with layered structures. This observation will give us some ideas for controlling the host properties of layered compounds, resulting in the development of new functional materials.

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