Photoluminescence of layered perovskite oxides with triple-octahedra slabs containing titanium and niobium

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Study of the photochemical properties of layered compounds can be expected to lead us to the development of new photofunctional materials [1]. Various oxides with layered perovskite structures have been synthesized as layered compound groups [2–4]. Dion–Jacobson (KCa2Nb3O10, etc.) [2, 3] and Ruddlesden–Popper (K2La2Ti3O10, etc.) [4(b)] series are the representative layered perovskite oxides containing titanium and niobium. Recently, Gopalkrishnan et al. have synthesized bridging compounds of Dion–Jacobson and Ruddlesden–Popper phases (K2/5La2Ti3/5–,–xNb, O10) [4(c)]. They consist of three-octahedral thick perovskite slabs. It has been reported that some layered perovskite oxides which consist of titanium and niobium oxides work as photofunctional materials such as photocatalysts [5] and phosphors [6]. Moreover, they seem to be interesting as hosts of lanthanoid phosphors since many layered perovskite oxides contain lanthanum ions [7–9]. In these systems, the energy transfer process from hosts (layered oxides) to guests (lanthanoid ions) is important. Therefore, it is important to study the luminescent properties of native layered oxides to obtain basic data on their photophysical and photochemical properties. This communication reports the luminescent properties of a series of layered perovskite oxides with three-octahedral thick perovskite slabs (K2/5La2Ti3/5–,–xNb, O10 (x = 0, 0.25, 0.5, 0.75, and 1) and KM2Nb2O10 (M = Ca and Sr)).

Starting materials used were as follows; K2CO3 (Kanto Chemical; 99.5%), CaCO3 (Kanto Chemical; 99.5%), SrCO3 (Wako Pure Chemical; 95%), TiO2 (Kojyundo Chemical; 99.9%), Nb2O5 (Wako Pure Chemical; 99.9%), and La2O3 (Wako Pure Chemical; 99.99%). K2/5La2Ti3/5–,–xNb, O10 (x = 0, 0.25, 0.5, 0.75, and 1) and KM2Nb2O10 (M = Ca and Sr) were synthesized by calcining mixtures of starting materials in air using a platinum crucible according to the literature [2, 3, 4(c)]. Excess K2CO3 (20 mol %) was added. The calcination temperature and time for the synthesis of these compounds were 1273 K and 40 h for K2La2Ti3O10 and K1/5La2Ti2.75Nb0.25O10, 1323 K and 40 h for K1.5La2Ti2.5Nb0.5O10 and K1.25 La2Ti2.25Nb0.75O10, and 1423 K and 48 h for KLa2 Ti2.5NbO10 and KM2Nb2O10. Powdered samples were used for luminescence measurements at liquid nitrogen temperatures (77 K) using a spectrofluorometer (Spex, FluoromaxTM, light source; 150 W Xe lamp, photomultiplier tube; R928P).

K2La2Ti3O10 shows broad emission around 470 nm by excitation at 315 nm as shown in Fig. 1, as already reported in a previous paper [9]. The excitation spectrum has an onset at 330 nm.

Fig. 2 shows the luminescent properties of K1.75La2Ti2.75Nb0.25O10 which has been reported to be isostructural with K2La2Ti3O10 possessing the structure of the Ruddlesden–Popper phase [4(c)]. The emission spectrum with a maximum around 470 nm was obtained by excitation at 315 nm. Moreover, a shoulder around 520 nm is also observed. The excitation spectrum monitored at 465 nm has an onset at 330 nm, as observed in K2La2Ti3O10. The emission spectrum with a max-

![Figure 1](http://example.com/figure1.png)

**Figure 1.** PL of K2La2Ti3O10 at 77 K: (a) excitation spectrum monitored at 466 nm; (b) emission spectrum excited at 320 nm.

![Figure 2](http://example.com/figure2.png)

**Figure 2.** PL of K1.75La2Ti2.75Nb0.25O10 at 77 K: (a) excitation spectrum monitored at 540 nm; (b) excitation spectrum monitored at 465 nm; (c) emission spectrum excited at 315 nm; (d) emission spectrum excited at 350 nm.
imum around 540 nm was obtained by excitation at 350 nm. The excitation spectrum monitored at the wavelength of 540 nm has an additional peak around 360 nm. In contrast, $K_1.5La_2Ti_2.5Nb_0.5O_{10}$ and $K_1.25La_2Ti_2.25Nb_0.75O_{10}$ hardly showed luminescence.

Fig. 3 shows the luminescent properties of $KLa_2Ti_2NbO_{10}$ whose structure is similar to $KCa_2Nb_3O_{10}$ with the Dion–Jacobson phase. An emission spectrum with a maximum around 530 nm was obtained by excitation at 315 nm. In this case, a shoulder around 480 nm is observed. The shoulder is negligible in the emission spectrum obtained with excitation at 350 nm. Moreover, the shoulder around 360 nm is observed in the excitation spectrum monitored at 540 nm, as also observed in Fig. 2. The shoulder around 350 nm in the excitation spectrum obtained by monitoring at 490 nm is smaller than that obtained by monitoring at 540 nm.

It is clear from Figs 2 and 3 that $K_{2-x}La_2Ti_3Nb_xO_{10}$ ($x = 0.25$, and 1) has two luminescent centres at least. The emission around 480 nm and 540 nm corresponds to excitation at 315 nm and 350 nm, respectively. The former is the same as the luminescence centre of $K_2La_2Ti_3O_{10}$ observed in Fig. 1 indicating that it is due to lanthanum-titanate units. The latter is probably the luminescence from niobate units because the luminescence intensity at around 540 nm by excitation at 350 nm is increased as the ratio of niobium to titanium is increased.

In the case of $KSr_2Nb_3O_{10}$, the emission spectrum with a maximum at around 580 nm was obtained by excitation at 350 nm as shown in Fig. 4. The excitation spectrum has an onset at 390 nm. The luminescence intensity of $KSr_2Nb_3O_{10}$ is considerably higher than that of $KCa_2Nb_3O_{10}$. It is noteworthy that the photocatalytic activity of $KSr_2Nb_3O_{10}$ has been reported to be higher than that of $KCa_2Nb_3O_{10}$ [5] corresponding to the photoluminescence efficiency. The luminescence wavelength of $KSr_2Nb_3O_{10}$ which does not include titanium is longer than that of $KLa_2Ti_2NbO_{10}$, although $KSr_2Nb_3O_{10}$ is isomorphous with $KLa_2Ti_2NbO_{10}$. The emission and excitation bands are similar to that of a CsLaNb$_2$O$_7$ layered perovskite oxide [6] suggesting that the emission centre is the perovskite layer consisting of NbO$_6$ units, however, large differences between the double- and triple-octahedra thick perovskite slabs were not observed.

Blasse et al. have reported the relationship between the luminescent property and the metal–oxygen bond length [10]. In general, ion-exchangeable layered oxides have the extremely short metal–oxygen bonds which stick out into interlayers interacting with alkali cations because of large distortion by two-dimensional structures. For example, the shortest bond lengths of $K_2La_2Ti_3O_{10}$ and CsCa$_2Nb_3O_{10}$ and 0.1719 and 0.1743 nm, respectively [2, 11]. Therefore, the short metal–oxygen bonds could contribute to the luminescent properties of the perovskite layers as observed in other titanates and niobates. Energetically isolated titanate and niobate units have excitation bands with wavelengths shorter than around 300 nm and large Stokes shifts while semiconducting titanates such as SrTiO$_3$ have those with wavelengths between about 300 and 400 nm [10, 12, 13]. These facts suggest that the excitation energy in the layered perovskite oxides are delocalized, more or less, judging from the wavelengths of excitation and emission spectra.

In conclusion, $K_{2-x}La_2Ti_3Nb_xO_{10}$ ($x = 0$, 0.25, and 1) and $KSr_2Nb_3O_{10}$ with layered perovskite structures showed photoluminescence at 77 K, probably due to the charge transfer in two-dimensional titanate and niobate slabs. The emission spectra shifted to longer wavelength as the ratio of niobium to titanate increased independently of crystal phases.

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References