

Ultraviolet Luminescence of $\text{Rb}_4\text{Ta}_6\text{O}_{17}$ with a Layered Structure

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$\text{Rb}_4\text{Ta}_6\text{O}_{17}$ with a layered structure showed ultraviolet emission around 340 nm by photoexcitation at 270 nm. The ultraviolet emission was observed even at room temperature. The luminescent properties of $\text{Rb}_4\text{Ta}_6\text{O}_{17}$ were compared with those of $\text{K}_4\text{Nb}_6\text{O}_{17}$ with the similar layered structure and other tantalates. The Stokes shift was smaller than that of other tantalate phosphors. The excitation energy in $\text{Rb}_4\text{Ta}_6\text{O}_{17}$ was delocalized more or less.

Luminescent properties of oxides consisting of metal ions with d^0 configuration such as Ti^{4+} , Nb^{5+} , Ta^{5+} , V^{5+} , Mo^{6+} , and W^{6+} have been studied for a long time.¹⁻³ However, the number of reports on the luminescent properties of tantalates is much less than that of the other d^0 oxides. Tantalates which have been studied so far as phosphors possess bulk structures, and do not have any secondary structures such as regular layers or pores. On the other hand, microporous materials have unique properties due to their structures. For example, $\text{K}_3\text{Ta}_3\text{Si}_2\text{O}_{13}$ ⁴ and $\text{Rb}_4\text{Ta}_6\text{O}_{17}$ ⁵ show photocatalytic activities for water splitting into H_2 and O_2 in a stoichiometric ratio. Therefore, investigating the photophysical and photochemical properties of these microporous materials will be of importance in order to develop new photofunctional materials. One of the authors has reported that $\text{K}_4\text{Nb}_6\text{O}_{17}$ with the similar layered structure as $\text{Rb}_4\text{Ta}_6\text{O}_{17}$ shows blue photoluminescence at 77 K.^{6,7} The comparison in the luminescent properties between $\text{K}_4\text{Nb}_6\text{O}_{17}$ and $\text{Rb}_4\text{Ta}_6\text{O}_{17}$ is of interest from the view point of the effect of energy structures based on Ta and Nb. In the present paper, ultraviolet luminescent properties of $\text{Rb}_4\text{Ta}_6\text{O}_{17}$ with a layered structure are reported.

$\text{Rb}_4\text{Ta}_6\text{O}_{17}$ was synthesized by a solid state reaction. A mixture ($\text{Rb}:\text{Ta}=2.2:3$) of Rb_2CO_3 (Wako Pure Chemical, purity >97%) and Ta_2O_5 (Rare metallic, purity = 99.99%) was calcined at 1470 K for 40 h in air using a platinum crucible. The product was slowly cooled to 1020 K with the rate of 15 K/h and to room temperature naturally in the furnace. The product was confirmed by X-ray diffraction (Rigaku; RINT-1400). A diffuse reflection spectrum was obtained by using a UV-VIS-NIR spectrometer (JASCO; Ubest-570) and was converted from reflection to absorbance by the Kubelka-Munk method. Photoluminescence was measured *in vacuo* using a fluorometer (Spex; Fluoromax) and a cryostat (Janis).

Figure 1 shows diffuse reflection, excitation, and emission spectra of $\text{Rb}_4\text{Ta}_6\text{O}_{17}$. The energy gap was estimated to be 4.4 eV from the onset (280 nm) of the diffuse reflection spectrum. The ultraviolet emission around 340 nm was observed by the band gap excitation. The Stokes shift was 8500 cm^{-1} . The excitation spectrum agreed to the diffuse reflection spectrum.

Figure 2 shows the dependence of the photoluminescence intensity on temperature. Although the luminescence intensity was decreased with increasing the temperature, the ultraviolet emission was observed even at room temperature.

Figure 3 shows a glow curve. The spectrum was obtained by monitoring the thermoluminescence observed by increasing

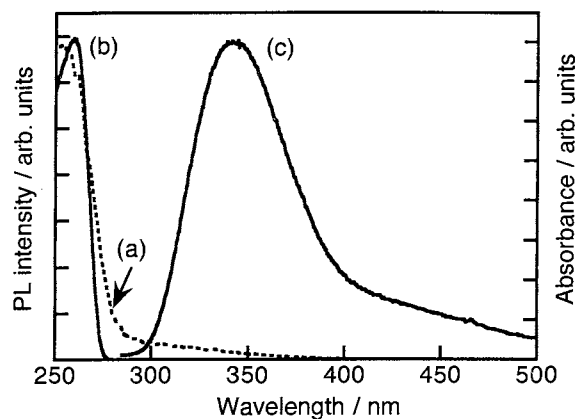


Figure 1. Diffuse reflection, excitation, and emission spectra of $\text{Rb}_4\text{Ta}_6\text{O}_{17}$. (a); DRS at 300 K, (b); excitation, and (c); emission spectra at 77 K.

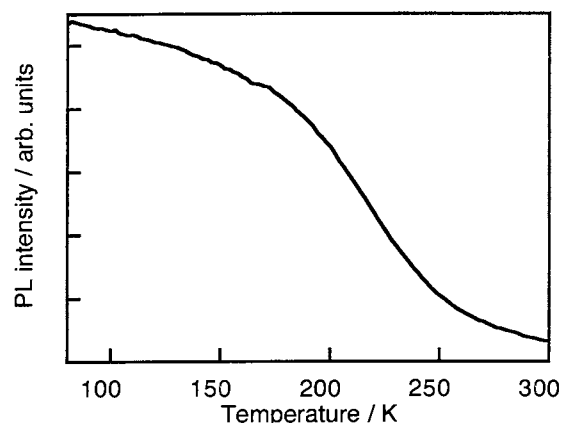


Figure 2. Dependence of photoluminescence intensity of $\text{Rb}_4\text{Ta}_6\text{O}_{17}$ on temperature.

temperature after photoexcitation at 77 K. The peak at 120 K suggests the existence of energy trap sites. The energy traps would be defects such as oxygen vacancies.

Figure 4 shows a Raman spectrum. The intense band was observed at 870 cm^{-1} . This band was assigned to be a double bond-like Ta-O bond which protrudes into the interlayer judging from the similarity to the band of $\text{K}_4\text{Nb}_6\text{O}_{17}$.

Photoluminescent properties of $\text{Rb}_4\text{Ta}_6\text{O}_{17}$, $\text{K}_4\text{Nb}_6\text{O}_{17}$, and other tantalates are summarized in Table 1. At first, the luminescent properties of $\text{Rb}_4\text{Ta}_6\text{O}_{17}$ with those of iso-structural $\text{K}_4\text{Nb}_6\text{O}_{17}$ is compared. The excitation and emission spectra of $\text{Rb}_4\text{Ta}_6\text{O}_{17}$ were observed at shorter wavelengths than those of $\text{K}_4\text{Nb}_6\text{O}_{17}$. The difference in the excitation energy is due to whether the material consists of Ta or Nb because the crystal structures does not differ to each other. The conduction band of

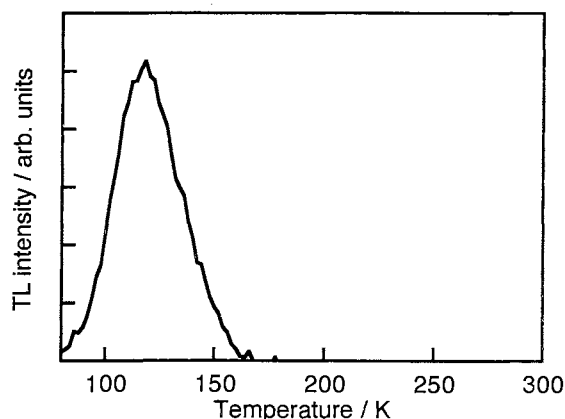


Figure 3. Glow curve of $\text{Rb}_4\text{Ta}_6\text{O}_{17}$.

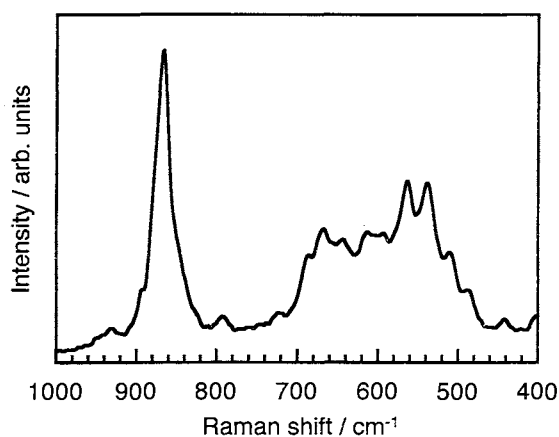


Figure 4. Raman spectrum of $\text{Rb}_4\text{Ta}_6\text{O}_{17}$.

$\text{Rb}_4\text{Ta}_6\text{O}_{17}$ consists of 5d of Ta while that of $\text{K}_4\text{Nb}_6\text{O}_{17}$ does of 4d of Nb, and the level of the former is higher than that of the latter. The luminescence of $\text{Rb}_4\text{Ta}_6\text{O}_{17}$ was observed at room temperature while that of $\text{K}_4\text{Nb}_6\text{O}_{17}$ was not. It indicates that the quenching temperature of $\text{Rb}_4\text{Ta}_6\text{O}_{17}$ is higher than that of $\text{K}_4\text{Nb}_6\text{O}_{17}$, suggesting that the probability of the nonradiation transition of $\text{Rb}_4\text{Ta}_6\text{O}_{17}$ is less than that of $\text{K}_4\text{Nb}_6\text{O}_{17}$.

Next, the luminescent properties of $\text{Rb}_4\text{Ta}_6\text{O}_{17}$ is compared with those of other tantalates. In general, the more the excitation energy is delocalized the smaller the excitation energy becomes.⁸⁻¹⁰ KTaO_3 is a semiconductor with an ideal perovskite structure. Therefore, the excitation energy is delocalized^{8,9} and therefore, that the excitation spectrum is in the position of the longest wavelength among those of other tantalates in Table 1. In contrast, the excitation energies of LiTaO_3 and $\text{Ba}_3\text{NaTaO}_6$ are localized in the TaO_6 octahedra, because the bond angle of O-Ta-O in LiTaO_3 is far from 180° and because the TaO_6 in $\text{Ba}_3\text{NaTaO}_6$ is isolated.⁸⁻¹⁰ Therefore, the excitation energies are larger than that of KTaO_3 . The excitation spectrum of $\text{Ba}_5\text{Ta}_4\text{O}_{15}$ is in the position between those of KTaO_3 and LiTaO_3 because the bond angle of O-Ta-O

Table 1. Comparison of luminescent properties among $\text{Rb}_4\text{Ta}_6\text{O}_{17}$, $\text{K}_4\text{Nb}_6\text{O}_{17}$, and some tantalates

Material	Excitation max. / nm	Emission max. / nm	Stokes shift / cm^{-1}	Ref.
$\text{Rb}_4\text{Ta}_6\text{O}_{17}$	265	340	8500	---
$\text{K}_4\text{Nb}_6\text{O}_{17}$	310	420	8400	7
KTaO_3	330	490	10200	8
LiTaO_3	235	340	14000	8
$\text{Ba}_3\text{NaTaO}_6$	245	325	10000	10
$\text{Ba}_5\text{Ta}_4\text{O}_{15}$	265	455	15500	9

in $\text{Ba}_5\text{Ta}_4\text{O}_{15}$ is close to 180° and therefore the excitation energy is delocalized more or less.⁹ The excitation energy of $\text{Rb}_4\text{Ta}_6\text{O}_{17}$ is similar to that of $\text{Ba}_5\text{Ta}_4\text{O}_{15}$ indicating that the excitation energy of $\text{Rb}_4\text{Ta}_6\text{O}_{17}$ is also delocalized. However, the emission spectrum of $\text{Rb}_4\text{Ta}_6\text{O}_{17}$ was observed considerably shorter wavelength than that of $\text{Ba}_5\text{Ta}_4\text{O}_{15}$.

Stokes shifts of $\text{Rb}_4\text{Ta}_6\text{O}_{17}$ and $\text{K}_4\text{Nb}_6\text{O}_{17}$ are smaller than those of other tantalates with bulk structures as shown in Table 1. This is probably due to the layered structure being independent of Ta and Nb. $\text{Rb}_4\text{Ta}_6\text{O}_{17}$ and $\text{K}_4\text{Ta}_6\text{O}_{17}$ have short metal-oxygen bonds formed by the zigzag structure of the layers. The bonds order and exist in high density in the layers. The characteristic bonds affect the energy state of the tantalate and niobate layers. The small Stokes shift means less loss of the excitation energy. It will be advantageous to use such a materials for photochemical systems such as photocatalysts.

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