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Energy structure and photocatalytic activity for water splitting of $Sr_2(Ta_{1-X}Nb_X)_2O_7$ solid solution

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Abstract

Photophysical and photocatalytic properties of $Sr_2(Ta_{1-X}Nb_X)_2O_7$ with layered perovskite structure were studied to explore the possibility of energy structure control by making a solid solution. The band gap of $Sr_2(Ta_{1-X}Nb_X)_2O_7$ was decreased as the ratio of niobium to tantalum was increased. The $Sr_2(Ta_{1-X}Nb_X)_2O_7$ solid solution photocatalysts loaded with NiO co-catalysts decomposed water into H_2 and O_2 in a stoichiometric ratio. A $NiO/Sr_2Ta_2O_7$ photocatalyst showed the highest activity. The photocatalytic activity was drastically decreased by substitution of a small amount of niobium ($X = 0.05$) for tantalum. However, a $Sr_2(Ta_{0.75}Nb_{0.25})_2O_7$ photocatalyst showed a relatively high activity among the solid solutions of $Sr_2(Ta_{1-X}Nb_X)_2O_7$ ($0 < X < 1$). The activities of $Sr_2(Ta_{1-X}Nb_X)_2O_7$ solid solution photocatalysts depended on the conduction band level and the efficiency of non-radiative recombination between photogenerated electron–hole pairs. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Photocatalyst; Solid solution; Energy structure; Water splitting; Tantalete; Niobate

1. Introduction

Photocatalytic water splitting has been extensively studied from a viewpoint of the photon energy conversion. It has been reported that some oxides show reasonable activities for water splitting into H_2 and O_2 in a stoichiometric ratio under UV irradiation [1–11]. However, an efficient photocatalyst for overall water splitting under visible light irradiation has never been reported. The band structure control is important to develop active photocatalysts with visible light response. Preparation of solid solution is one of the ways to control the band structure. Sayama et al. [4] have reported absorption spectra and photocatalytic activities of layered $A_4Ta_XNb_{6-X}O_{17}$ ($A = K, Rb$) solid solutions for water splitting under UV irradiation. However, the successive shift in the absorption spectra was not observed in the $A_4Ta_XNb_{6-X}O_{17}$ solid solution. On the other hand, the successive changes in absorption and photoluminescence spectra, and conduction band levels of In_2O_3–Ga_2O_3 solid solutions have been reported [12]. The photocatalytic activities were also changed according to the change in these properties.

A layered perovskite compound, $Sr_2M_2O_7$ ($M = Nb$ and Ta), has been studied as a ferroelectric material. The ferroelectric property of $Sr_2Ta_2O_7$ is different from that of $Sr_2Nb_2O_7$ [13] because the structural distortion of perovskite sheets is different from each other as shown in Fig. 1. $Sr_2Nb_2O_7$ shows a ferroelectric property at room temperature (Curie temperature: $T_c = 1615\,K$) and the spontaneous polarization axis is parallel to the *c*-axis [14]. It is due to the distortion of the NbO_6 octahedra and the perovskite framework. In contrast, the $Sr_2Ta_2O_7$ is paraelectric at room temperature ($T_c = 166\,K$) [15]. In their solid solutions, $Sr_2(Ta_{1-X}Nb_X)_2O_7$, the Curie temperature and the dielectric constant varied with the composition [13].

It has also been reported that $Sr_2M_2O_7$ ($M = Nb$ and Ta) are highly active photocatalysts for water splitting [7,9]. Inoue et al. have reported that the local structure in a ferroelectric crystal affects the activities of some titanate photocatalysts [10]. Therefore, the $Sr_2(Ta_{1-X}Nb_X)_2O_7$ solid solution is of interest as a photocatalyst material in order to examine the relationship between crystal structure and photocatalytic and photophysical properties.

In the present study, optical, photoluminescent, and photocatalytic properties of $Sr_2(Ta_{1-X}Nb_X)_2O_7$ solid solutions were investigated. The factors affecting photocatalytic activities of $Sr_2(Ta_{1-X}Nb_X)_2O_7$ solid solutions were discussed.

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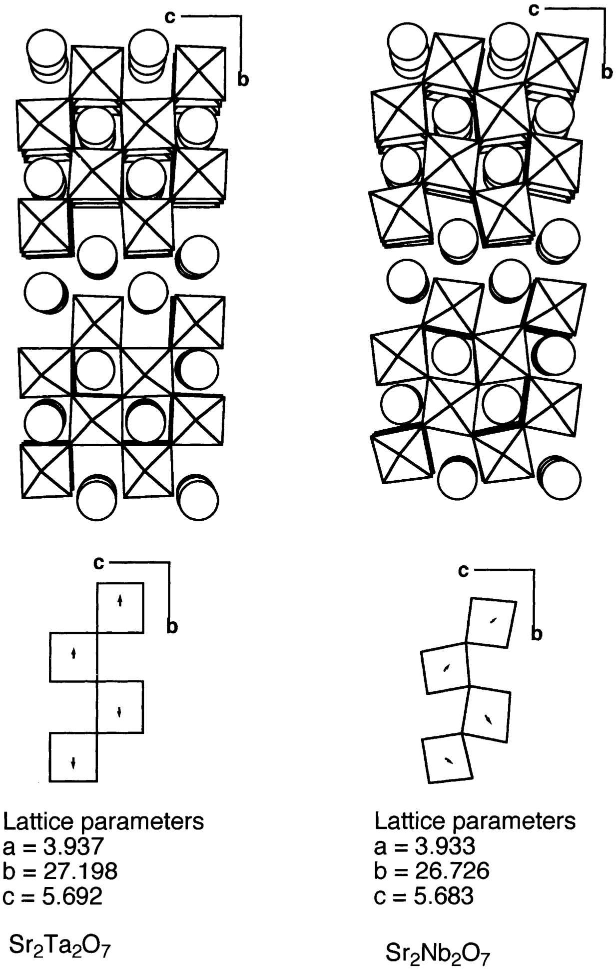

Fig. 1. Crystal structures of $Sr_2Ta_2O_7$ and $Sr_2Nb_2O_7$.

2. Experimental

$Sr_2(Ta_{1-X}Nb_X)_2O_7$ solid solutions were prepared by conventional solid state reactions. Starting materials of $SrCO_3$ (Kanto Chemical, 99.9%), Nb_2O_5 (Kanto Chemical, 99.95%) and Ta_2O_5 (rare metallic, 99.99%) were mixed in a stoichiometric ratio. The mixtures were calcined at 1450 K for 200 h in air using a platinum crucible. The obtained powder was confirmed by X-ray diffraction (XRD) (Rigaku, RINT-1400). NiO co-catalysts were loaded by an impregnation method from an aqueous $Ni(NO_3)_2$ solution. The photocatalysts loaded with the NiO co-catalyst were calcined at 640 K for 1 h in air. The pretreatment, hydrogen reduction (200 Torr) at 520 or 770 K for 2 h followed by oxygen oxidation (100 Torr) at 470 K for 1 h was carried out for the NiO-loaded photocatalysts, if necessary.

Photocatalytic reactions were carried out in a gas-closed circulation system. The photocatalyst powder (1 g) was dispersed in pure water (390 ml) by a magnetic stirrer in an inner irradiation cell made of quartz. The light source was a 400 W high-pressure mercury lamp (SEN, HL400EH-5). The amounts of H_2 and O_2 evolved were determined using a gas chromatograph (Shimadzu, GC-8A, TCD, Ar carrier).

Diffuse reflection spectra were obtained using a UV–Vis–NIR spectrometer (JASCO, Ubest V-570) and were converted from reflection to absorbance by the Kubelka–Munk method. Photoluminescence was measured in vacuo using a fluorometer (Spex, FluoroMax). Surface area was determined by a BET measurement apparatus (Coulter, SA3100).

3. Results

3.1. Characterization of $Sr_2(Ta_{1-X}Nb_X)_2O_7$ solid solutions

Fig. 2 shows the X-ray diffraction patterns of $Sr_2(Ta_{1-X}Nb_X)_2O_7$ solid solutions. All solid solutions showed almost the same XRD pattern. Some diffraction peaks such as (0 8 0) and (0 1 0 0) were shifted to higher angles as the ratio of niobium to tantalum in the solid solution was increased. The successive shift of the XRD pattern indicated that the crystals obtained were not mixtures of $Sr_2Nb_2O_7$ and $Sr_2Ta_2O_7$ phases, but $Sr_2(Ta_{1-X}Nb_X)_2O_7$ solid solutions. In contrast, several peaks were hardly shifted, for example (1 1 1) and (1 3 1). The *b*-axis length of $Sr_2Nb_2O_7$ is shorter than that of $Sr_2Ta_2O_7$, while the *a*- and *c*-axis lengths of $Sr_2Nb_2O_7$ are similar to those of $Sr_2Ta_2O_7$, resulting in diffraction peaks from planes of which interplanar spacing was affected by the *b*-axis length were shifted. A diffraction

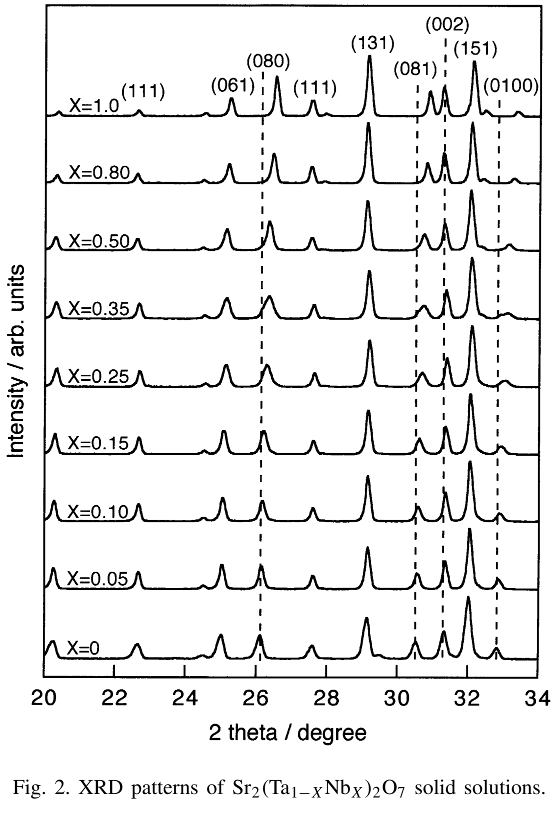

Fig. 2. XRD patterns of $Sr_2(Ta_{1-X}Nb_X)_2O_7$ solid solutions.

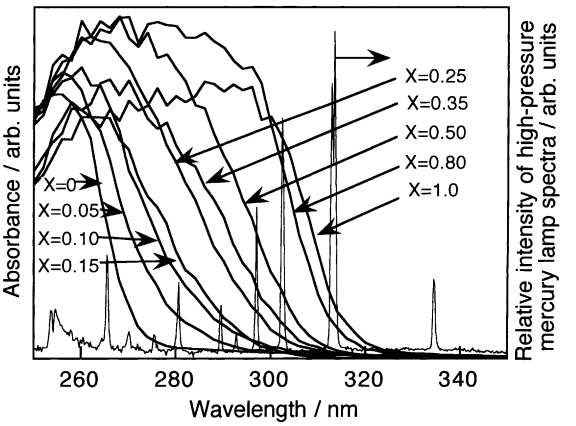

Fig. 3. Diffuse reflection spectra of $Sr_2(Ta_{1-X}Nb_X)_2O_7$ solid solutions and a spectrum of a high-pressure mercury lamp used.

peak of (0 0 2) was slightly shifted to higher angles and the degree of the shift was the largest for $Sr_2(Ta_{0.75}Nb_{0.25})_2O_7$.

Fig. 3 shows the diffuse reflection spectra of $Sr_2(Ta_{1-X}Nb_X)_2O_7$ solid solutions and the spectrum of a high-pressure mercury lamp used. $Sr_2Ta_2O_7$ had the shortest absorption edge. The absorption bands of solid solutions shifted to longer wavelengths as the ratio of niobium to tantalum in the solid solution increased. This shift also indicated that the crystals obtained were solid solutions. The band gaps of $Sr_2(Ta_{1-X}Nb_X)_2O_7$ solid solutions were estimated to be 3.9–4.7 eV from onsets of the absorption spectra. Thus, the band gap of the $Sr_2(Ta_{1-X}Nb_X)_2O_7$ solid solution was controlled by the change of a Ta/Nb ratio in the composition.

Photoluminescence of $Sr_2Nb_2O_7$ and $Sr_2Ta_2O_7$ at 77 K has been reported [16]. Photoluminescence spectra of $Sr_2(Ta_{1-X}Nb_X)_2O_7$ solid solutions excited by monochromatic light (260 nm) at 77 K are shown in Fig. 4. $Sr_2Ta_2O_7$ showed the most intensive luminescence. The luminescence intensity of the $Sr_2(Ta_{0.9}Nb_{0.1})_2O_7$ was remarkably decreased compared with that of $Sr_2Ta_2O_7$. However, in the region of $X \geq 0.25$ in $Sr_2(Ta_{1-X}Nb_X)_2O_7$, as the ratio of niobium to tantalum increased, the luminescence intensity of the solid solution increased. The luminescence intensity of $Sr_2(Ta_{0.5}Nb_{0.5})_2O_7$ was almost the same as that of $Sr_2Nb_2O_7$. Thus, it was revealed that the efficiency of the non-radiative transition in the $Sr_2Ta_2O_7$ crystal was least whereas it was significant for $Sr_2(Ta_{1-X}Nb_X)_2O_7$ solid solutions consisting of a small amount of niobium ($X \approx 0.1$).

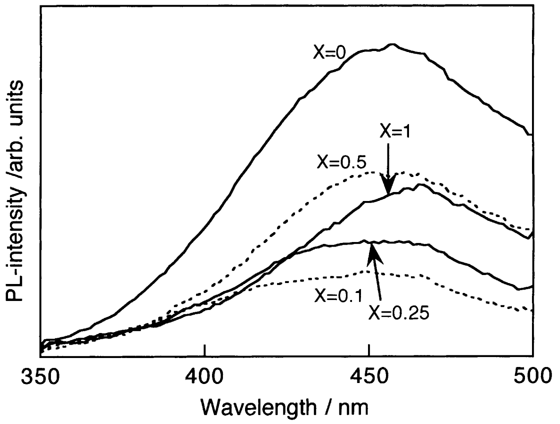

Fig. 4. Photoluminescence spectra of $Sr_2(Ta_{1-X}Nb_X)_2O_7$ solid solutions excited by monochromatic light (260 nm) at 77 K.

3.2. Photocatalytic water splitting over $Sr_2(Ta_{1-X}Nb_X)_2O_7$ solid solutions

The photocatalytic activities of $Sr_2(Ta_{1-X}Nb_X)_2O_7$ solid solutions loaded with NiO (0.15 wt.%) co-catalysts for water splitting are shown in Table 1. All $NiO/Sr_2(Ta_{1-X}Nb_X)_2O_7$ photocatalysts evolved H_2 and O_2 from pure water. For non-treated $NiO/Sr_2(Ta_{1-X}Nb_X)_2O_7$ photocatalysts, $NiO/Sr_2Ta_2O_7$ showed the highest activity, whereas $NiO/Sr_2Nb_2O_7$ showed the lowest activity. Activities of $NiO/Sr_2(Ta_{1-X}Nb_X)_2O_7$ consisting of small amounts of niobium were generally low. However, the activity of $NiO/Sr_2(Ta_{0.75}Nb_{0.25})_2O_7$ was relatively high among the solid solutions.

A photocatalytic activity for water splitting is increased by pretreatment, reduction followed by reoxidation, for NiO-loaded photocatalysts such as $NiO/SrTiO_3$ and $NiO/K_2La_2Ti_3O_{10}$ [10]. The activity of a pretreated $NiO/Sr_2Nb_2O_7$ photocatalyst was five times higher than that of the non-treated photocatalyst. In contrast, the pretreatment was not so effective for $NiO/Sr_2(Ta_{1-X}Nb_X)_2O_7$ ($X = 0.25$). These results indicated that the effect of the pretreatment depended on the composition. However, the order in photocatalytic activities of pretreated $NiO/Sr_2(Ta_{1-X}Nb_X)_2O_7$ photocatalysts was the same as that of non-treated photocatalysts.

Table 1
Photocatalytic water splitting over non-treated and pretreated NiO (0.15 wt.%)/$Sr_2(Ta_{1-X}Nb_X)_2O_7$ solid solutions (catalyst (1 g), pure water (390 ml), 400 W high-pressure mercury lamp, inner irradiation reaction cell made of quartz)

X	E_g (eV)[a]	Surface area (m^2/g)	Pretreatment[b]	Activity (μmol/h)	
				H_2	O_2
0	4.55	0.9	No	1000	500
			Yes	919	504
0.05	4.43	1.2	No	190	90
0.10	4.34	1.3	No	130	60
			Yes	149	62
0.15	4.27	1.0	No	200	96
0.25	4.13	1.2	No	240	110
			Yes	280	120
0.35	4.07	1.0	No	160	77
0.50	4.03	1.2	No	110	54
0.80	3.96	0.8	No	50	24
1.0	3.92	0.6	No	39	19
			Yes	217	97

[a] Estimated from onsets of the diffuse reflectance spectra.

[b] Reduction by H_2 (200 Torr) at 770 K for 2 h followed by oxidation by O_2 (100 Torr) at 470 K for 1 h.

4. Discussion

4.1. Factors affecting the photocatalytic activities

Conduction and valence band levels, the efficiency of non-radiative transition, and the number of absorbed photons are thought to be the main factors affecting the photocatalytic activity of the NiO/$Sr_2(Ta_{1-X}Nb_X)_2O_7$ solid solution.

The conduction and valence bands of a semiconductor photocatalyst have to possess appropriate potentials enough for redox potentials of H^+/H_2 and O_2/H_2O for water splitting, respectively. Valence bands of $Sr_2(Ta_{1-X}Nb_X)_2O_7$ solid solutions should have potentials enough for oxidation of water because the valence band levels formed with O 2p orbitals are estimated to be ca. 3 eV [17]. In semiconductor oxides consisting of the same group elements (Nb and Ta), the conduction band level becomes higher as the band gap is increased. These results indicate that the difference in the band gap between $Sr_2(Ta_{1-X}Nb_X)_2O_7$ solid solutions was attributed to that in the conduction band level. Therefore, the high conduction band level of $Sr_2Ta_2O_7$ with the largest band gap among $Sr_2(Ta_{1-X}Nb_X)_2O_7$ solid solutions is one of the main factors for its high activity. However, $Sr_2(Ta_{0.75}Nb_{0.25})_2O_7$ showed higher activity than $Sr_2(Ta_{1-X}Nb_X)_2O_7$ solid solutions ($0.05 \leq X \leq 0.15$) even if the former had a lower conduction band level due to a small band gap than the latter. The small shift of a diffraction peak (0 0 2) for $Sr_2(Ta_{0.75}Nb_{0.25})_2O_7$ might imply the effect of a framework change on the photocatalytic activity as shown in Fig. 2. The shifts of a diffraction peak (0 0 2) were probably due to the distortion of MO_6 octahedra. The distortion in $Sr_2(Ta_{1-X}Nb_X)_2O_7$ solid solution might lead to an effective charge separation. Moreover, the efficiency of non-radiative transition seems to affect the photocatalytic activity.

If non-radiative transition dominates in a photocatalyst, the number of electrons and holes to be involved in the reaction is decreased resulting in a decrease in the photocatalytic activity. The non-radiative transition also affects photoluminescence. Fig. 4 indicated that the photoluminescence intensity of $Sr_2(Ta_{0.9}Nb_{0.1})_2O_7$ was remarkably lower than those of $Sr_2Ta_2O_7$ and other solid solutions ($0.25 \leq X \leq 1$). This quenching of photoluminescence corresponded to the decrease in photocatalytic activities. In this region ($X \approx 0.1$), the framework of $Sr_2Ta_2O_7$ would be distorted around the niobium substituted. Such lattice distortion may act as a non-radiative transition center resulting in the low activity of the $Sr_2(Ta_{1-X}Nb_X)_2O_7$ solid solution ($0 < X < 0.1$). However, the non-radiative transition was suppressed as the ratio of niobium to tantalum in $Sr_2(Ta_{1-X}Nb_X)_2O_7$ solid solutions was increased ($X \geq 0.25$). It is considered that NbO_6 octahedra do not act as efficient non-radiative centers because of the relaxation of lattice distortion owing to the frameworks of $Sr_2(Ta_{1-X}Nb_X)_2O_7$ solid solutions which become similar to that of $Sr_2Nb_2O_7$.

The amount of photons absorbed by photocatalysts with larger band gaps is smaller than that absorbed by photocatalysts with smaller band gaps. This leads to different photocatalytic activities. As the ratio of niobium to tantalum in the $Sr_2(Ta_{1-X}Nb_X)_2O_7$ solid solution is increased, the amount of absorbed photon would become larger because of an increase in the absorbed line from the mercury lamp as shown in Fig. 3. $Sr_2(Ta_{0.75}Nb_{0.25})_2O_7$ was able to absorb the 297 nm line, while $Sr_2(Ta_{0.85}Nb_{0.15})_2O_7$ was not so. The relatively high activity of the $Sr_2(Ta_{0.75}Nb_{0.25})_2O_7$ may be due to the amount of absorbed photons. However, the activities of $Sr_2(Ta_{1-X}Nb_X)_2O_7$ ($0.35 \leq X \leq 1$) were smaller than those of $Sr_2(Ta_{0.75}Nb_{0.25})_2O_7$ even if the amount of photons absorbed by $Sr_2(Ta_{1-X}Nb_X)_2O_7$ ($0.35 \leq X \leq 1$) was larger than that of the $Sr_2(Ta_{0.75}Nb_{0.25})_2O_7$. Moreover, the non-radiative transition was well suppressed in this region ($0.35 \leq X \leq 1$). Therefore, the reason for the high activity of $Sr_2(Ta_{0.75}Nb_{0.25})_2O_7$ was mainly due to the suppression of non-radiative transition as mentioned above when the activity was compared with that of $Sr_2(Ta_{1-X}Nb_X)_2O_7$ ($0 < X < 0.25$). In contrast, in the region of $0.25 \leq X \leq 1$ in the solid solution, the conduction band level mainly affects the photocatalytic activities. $Sr_2(Ta_{0.75}Nb_{0.25})_2O_7$ had the highest conduction band in that region. On the other hand, the NiO/$Sr_2Ta_2O_7$ showed the highest activity in spite of the small amount of absorbed photons.

The surface area may also be a factor affecting the photocatalytic activity. However, the relatively high activity of NiO/$Sr_2(Ta_{0.75}Nb_{0.25})_2O_7$ among the solid solution was not due to the surface area because surface areas of the solid solution ($0.05 < X < 0.5$) were almost the same as each other as shown in Table 1.

Thus the factors affecting the photocatalytic activities of NiO/$Sr_2(Ta_{1-X}Nb_X)_2O_7$ are the conduction band level and the efficiency of non-radiative transition rather than the amount of absorbed photons and surface area.

4.2. Pretreatment effects

In the case of a NiO-loaded photocatalyst, the migration of electrons photogenerated in the conduction band of the photocatalyst to the conduction band of the NiO co-catalyst for H_2 evolution is necessary for obtaining a high photocatalytic activity for water splitting. In the NiO/$Sr_2Nb_2O_7$ photocatalyst, the electron migration to the conduction band of NiO does not easily occur because of the small potential gap between the conduction band level of $Sr_2Nb_2O_7$ (estimated to be −0.98 eV vs NHE [17]) and that of NiO (−0.96 eV vs NHE [18]), resulting in the low activity of the non-treated NiO/$Sr_2Nb_2O_7$ photocatalyst. In contrast, the photocatalytic activity of the pretreated NiO/$Sr_2Nb_2O_7$ was five times higher than that of the non-treated one. In this case, the electron migration to the conduction band of NiO should easily occur through the Ni metal junction formed by pretreatment as previously reported for a NiO/$SrTiO_3$ photocatalyst [10]. The pretreatment would be effective for

NiO-loaded photocatalysts whose conduction band levels are close or lower than that of NiO. On the other hand, the remarkable effect of the pretreatment was not observed for the NiO/$Sr_2(Ta_{1-X}Nb_X)_2O_7$ ($0 \leq X \leq 0.25$). It is considered that the electron migration to NiO easily occurred in these photocatalysts even without pretreatment because of large potential gaps between the conduction band levels of these photocatalysts and that of NiO. Band gaps of these photocatalysts were larger than 4.0 eV. In addition to it, the authors have reported that effects of NiO co-catalysts were also observed in the $NaTaO_3$ (BG: 4.0 eV) [5] and $SrTa_2O_6$ (BG: 4.4 eV) [6] photocatalysts even without pretreatment. Therefore, the threshold band gaps for necessity of pretreatment is estimated to be about 4.0 eV (the conduction band is ca. −1.0 V) for NiO-loaded semiconductor oxide photocatalysts consisting of d^0 metal ions.

5. Conclusion

The conduction band level of the $Sr_2(Ta_{1-X}Nb_X)_2O_7$ solid solution with layered perovskite structure was controlled by changing the ratio of niobium to tantalum. Photoluminescence measurements revealed that the efficiency of non-radiative transition in the $Sr_2(Ta_{1-X}Nb_X)_2O_7$ depended on the composition. All NiO/$Sr_2(Ta_{1-X}Nb_X)_2O_7$ photocatalysts showed activities for water splitting into H_2 and O_2. It is suggested that the conduction band level and the efficiency of non-radiative transition predominantly affected the photocatalytic activities. The NiO/$Sr_2Ta_2O_7$ photocatalyst with the highest band gap and the least efficiency of non-radiative transition showed the highest activity among NiO/$Sr_2(Ta_{1-X}Nb_X)_2O_7$ photocatalysts. $Sr_2(Ta_{0.75}Nb_{0.25})_2O_7$ also showed a high activity among $Sr_2(Ta_{1-X}Nb_X)_2O_7$ solid solutions ($0 < X < 1$).

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