Preparation and Characterization of $LnTaO_4$ (Ln = La, Nd, Sm, Dy, Er and Tm)

Atsushi Fujita[1, a], Hiroaki Matsushita[2,b] and Akinori Katsui[1,c]

[1]Dept. of Materials Chemistry, [2]Dept. of Information and Communication Technology, School of High-Technology for Human Welfare, Tokai University, 317 Nishino, Numazu, Shizuoka 410-0318, Japan
[a]5AFMM004@wing.ncc.u-tokai.ac.jp, [b]Matusita@wing.ncc.u-tokai.ac.jp, [c]ak102677@wing.ncc.u-tokai.ac.jp

Abstract

Lanthanide tantalite $LnTaO_4$ (Ln= La, Nd, Sm, Dy, Er and Tm) was synthesized by a solid state reaction between mixed powders of Ln_2O_3 and Ta_2O_5. The single-phase $LnTaO_4$ was prepared by sintering at temperatures of 1423-1673 K in air. The SEM observation showed that the particles were provided with the growth steps and the depeloped facets. The photocatalytic activity for water splitting of $LnTaO_4$ prepared was measured under UV light irradiation. The activity obtained was higher than that previously reported. These results suggested the crystallinity of $LnTaO_4$ photocatalysts correlates closely with the efficiency of water splitting.

Keywords : $LnTaO_4$, single phase, particle quality, photocatalytic activity, water spliting

1. Introduction

Photocatalytic water splitting is an important theme from the point of view of H_2 production for a fuel-cell. Many oxides and sulfides for appling to photocatalysts under UV or visible light irradiation have been investigated. Recently, oxides that include tantalum such as $ATaO_3$ (A= Li, Na and K) [1,2], $Sr_2Ta_2O_7$ [3] have been reported to exhibit high photocatalytic activities for water splitting under UV light irradiation. Especially, NiO-loaded $NaTaO_3$ doped with lanthanum has high apparent quantum yield of about 50% at 270 nm [4].

Lanthanide tantalite $LnTaO_4$ is one of tantaletes. Machida et al [5] studied on photocatalytic activity of $LnTaO_4$ (Ln=La,Ce,Pr,Nd and Sm) in connection to the effect of Ln 4f levels on the electronic structure, and concluded that the fact that the highest photocatalytic activity was attained by $LaTaO_4$ is due to the highest La 4f level position from the conduction band edge. Kudo et al suggested that a nonstoichiometry between metallic ions and a doping into tantaletes photocatalysts remarkably improve the activity of water splitting [2, 4].

The purpose of this study is to prepare single-phase $LnTaO_4$ (Ln= La, Nd, Sm, Dy, Er and Tm) with high-quality particles, and to clarify the effects of the crystallinity on the photocatalytic properties.

2. Experimental

$LnTaO_4$ (Ln= La, Nd, Sm, Dy, Er and Tm) was synthesized by sintering powder mixtures of oxides in alumina crucibles at 1423-1673 K for 10 h in air. La_2O_3 and Nd_2O_3 were prebaked at 1173 K for 10 h. The powders of $LnTaO_4$ prepared were pressed to the plates of 25 mm in diameter and 1 mm in thickness at 500 kgf/cm^2 and moreover heated at respective sintering temperatures at 2 h in air.

Samples prepared were identified by Scanning Electron Microscopy (SEM), UV/VIS/NIR diffuse reflectance spectroscopy (DRS) and X-ray diffractometry (XRD) with Cu-kα radiation.

The photocatalytic reactions were carried out in a gas-closed circulation system. The photocatalyst powder (0.5 g) was dispered in distilled water (350 ml) by a magnetic stirrer in an inner irradiation quartz reaction cell. The light source was a 450 W high pressure mercury lamp. The amounts of H_2 and O_2 evolved were determined by gas chromatography.

3. Results and Discussion

The critical sintering temperatures of $LnTaO_4$ for respective single phase were as follows; La TaO_4 and $SmTaO_4$ at 1523 K, $NdTaO_4$ at 1423 K, $DyTaO_4$ twice at1523 K, $ErTaO_4$ at 1673 K, $TmTaO_4$ twice at 1673 K. At below those temperatures unreacted Ln_2O_3 and Ta_2O_5 remained.

DRS spectra for powders of $LnTaO_4$ (Ln= La, Nd, Sm, Dy, Er and Tm) were measured in wavelengths ranging from 240 to 800nm at room temperature. The energy bandgaps were evaluated to be 4.0 eV for $LaTaO_4$, 4.1 eV for $NdTaO_4$, 3.7 eV for $SmTaO_4$, 4.3 eV for $DyTaO_4$, 3.7 eV for $ErTaO_4$ and 3.5 eV for $TmTaO_4$. It can be seen that the photoabsorption in $LnTaO_4$ is strong in the UV region.

The microstructure of $LnTaO_4$ (Ln= La, Nd, Sm, Dy, Er and Tm) powders was observed by SEM. Fig.1 shows the

SEM photographs for $LnTaO_4$ (Ln= La, Nd, Sm and Dy) sintered at 1673K. The parcticles are 1.0-2.0 μm in size.Their surfaces are smooth and have developed facets. Fig.2 shows the photograph for the enlarged $DyTaO_4$ particle. The particle has many growth steps with the widths of 70-140 nm. The same step structure was observed in other $LnTaO_4$ (Ln=La, Nd and Sm) particles. This high crystallinity is probably attributed to higher sintering temperature.

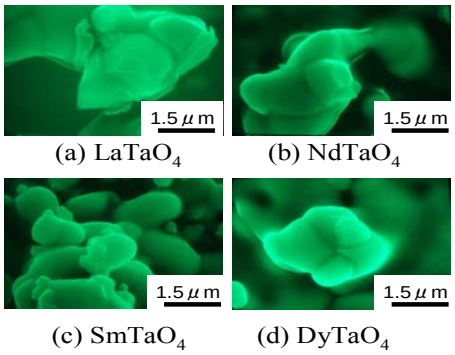

Fig. 1. SEM photographs of $LnTaO_4$ (Ln=La, Nd, Sm and Dy).

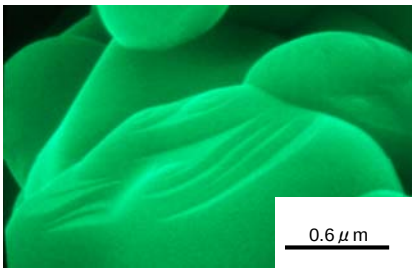

Fig. 2. SEM photograph of $DyTaO_4$.

Table 1 shows the photocatalytic activity of $LnTaO_4$ (Ln=La, Nd and Sm). $LaTaO_4$ exhibits the highest value in the efficiency of H_2 evolution. This is associated with so much an empty 4f band in the conduction band [5]. $LaTaO_4$ also exhibits the activity in O_2 evolution, and however the efficiency is extremely low.

Table 1 Photocatalytic Activity of $LnTaO_4$ for Water Splitting

$LnTaO_4$	μ mol/ h	
	H_2	O_2
$LaTaO_4$	12.6	0.04
$NdTaO_4$	8.78	0
$SmTaO_4$	10.16	0

The values shown in Table 1 were higher than those in [5]. This is probably due to that all of the $LnTaO_4$ samples in this work are a single phase being composed of the particles with high crystal quality. All of samples in [5] that were sintered at 1473K included a trace of Ta_2O_5 and therefore, it is considered that their crystallinity was not so much high.

4. Summary

Single-phase $LnTaO_4$ (Ln= La, Nd, Sm, Dy, Er and Tm) was synthesized by sintering powder mixtures of oxides, Ln_2O_3 (Ln=La, Nd, Sm, Dy, Er and Tm) and Ta_2O_5 at 1423-1673 K for 10 h in air. The particles exhibited high crystallinity with the growth steps and the developed facets. The photocatalytic activity for water splitting under UV light irradiation in $LnTaO_4$ prepared was higher than that previously reported. The highest efficiency in H_2 evolution was attained by $LaTaO_4$. This result suggested the crystallinity of photocatalysts correlates closely with the efficiency of water splitting.

5. Acknowledgements

The authors thank Prof. Akihiko Kudo and Mr.Toshiyasu Kurihara, Department of Applied Chemistry, Faculty of Science, Science University of Tokyo, for photocatalytic activity measurements of $LnTaO_4$.

6. References

1. T. Ishihara, H. Nishiguchi, K. Fukamachi and Y. Takita, *J.Phys.Chem.B* **103**(1999)1.
2. H. Kato and A. Kudo, *J.Phys.Chem.B* **105**(2001)4285.
3. A. Kudo, H. Kato and S. Nakagawa, *J.Phys.Chem.B* **104**(2000)571.
4. A. Kudo and H. Kato, *Chem.Phys.Lett.* **331**(2000)373.
5. M. Machida, S. Murakami, T. Kijima, S. Matsushima and M. Arai, *J.Phys.Chem.B* **105**(2001)3289.