



# Synthesis and photocatalytic properties of tetragonal tungsten bronze type oxynitrides



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## ABSTRACT

Synthesis of a series of oxynitride  $\text{Ba}_{3-x}\text{La}_x\text{Ta}_5\text{O}_{14-x}\text{N}_{1+x}$  ( $x=0-1.5$ ) with a tetragonal tungsten bronze (TTB) structure was examined using moist- $\text{NH}_3$  and 5%  $\text{NH}_3\text{-N}_2$  as nitriding atmosphere. The samples with  $x=0-1$  were successfully obtained as phase pure TTB oxynitride whereas the  $x=1.5$  samples gave a mixture of TTB oxynitride,  $\text{Ta}_3\text{N}_5$ , and  $\text{LaTaO}_4$ . Absorption of TTB oxynitrides in visible region was enhanced as increasing the content of nitrogen. TTB oxynitrides exhibited both of  $\text{H}_2$  and  $\text{O}_2$  evolution under visible light in the presence of methanol and silver ions, respectively, as sacrificial reagents. Nitrogen poor surface in the samples synthesized under moist- $\text{NH}_3$  atmosphere was modified by annealing treatment using 5%  $\text{NH}_3$ , resulting in improvement of photocatalytic activity for  $\text{H}_2$  evolution. Evaluation using monochromatic light revealed that the apparent quantum efficiency of  $\text{Ba}_2\text{LaTa}_5\text{O}_{13}\text{N}_2$  was higher than that of  $\text{Ba}_3\text{Ta}_5\text{O}_{14}\text{N}$ .

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## 1. Introduction

Water splitting photocatalysts have attracted much attention as a potential method for the solar hydrogen production [1–5]. Various kinds of research, such as development of new photocatalysts [6–23], cocatalysts [17,24–30], synthesis method [31–38], and modification [39–43], are conducted to make progress in photocatalytic water splitting. Crystal structure is an important factor to classify photocatalyst materials. Perovskite structure is known as a promising one for photocatalysts in both of oxide and oxynitride [1–3,10,12,13,21,41].  $\text{SrTiO}_3\text{:Al}$  and  $\text{NaTaO}_3\text{:La}$ , representative perovskite-type oxide photocatalysts, can split water with very high quantum efficiency [44,45]. These photocatalysts function under only ultraviolet excitation whereas many perovskite-type photocatalysts with response to visible light are also reported.  $\text{SrTiO}_3\text{:Rh}$  is a well known visible light responsive oxide photocatalyst for  $\text{H}_2$  evolution [32,39,43,46]. In the oxynitride system, many perovskite-type  $\text{ABO}_2\text{N}$ ,  $\text{ABON}_2$ , and solid solutions are reported as visible light responsive photocatalysts and photoanodes [1–3,12,13,17,21,31,34,36,40,41]. Especially, Domen and co-workers have recently achieved overall water splitting under visible light using  $\text{LaMg}_{1/3}\text{Ta}_{2/3}\text{O}_2\text{N}$  modified with a metal oxyhydroxide layer [41]. In perovskite structure,  $\text{MX}_6$  octa-

dra share corners with other octahedra to built characteristic framework. Tetragonal tungsten bronze (TTB) structure is common structure for materials with a general formula  $(\text{A}1)(\text{A}2)_2\text{B}_5\text{X}_{15}$  and is regarded as perovskite-related structure because it is also constituted of framework with corner-shared  $\text{MX}_6$  octahedra like as the perovskite structure (Fig. 1). Many TTB compounds, such as  $\text{K}_2\text{Ln}(\text{Nb,Ta})_5\text{O}_{15}$  ( $\text{Ln}$  = lanthanide),  $\text{KM}_2\text{Nb}_5\text{O}_{15}$ , and tetr- $\text{BaTa}_2\text{O}_6$ , can drive overall water splitting and/or  $\text{CO}_2$  reduction in water under ultraviolet irradiation [1–3,11,37]. Nitride and oxynitride are attractive material group for visible-light-driven photocatalysts because N 2p orbital form valence band at shallower position than O 2p orbital [47]. Most of oxynitride photocatalysts are of perovskite compounds especially for  $d^0$ -based oxynitrides whereas oxynitrides with other structures such as  $\text{TaON}$ ,  $\text{GaN:ZnO}$ ,  $\text{C}_3\text{N}_4$ ,  $\text{Y}_2\text{Ta}_2\text{O}_5\text{N}$  and  $\text{MgTa}_2\text{O}_{6-x}\text{N}_y$  are also reported [1–3,6,19]. Lerch et al. have recently succeeded in synthesis of a TTB oxynitride  $\text{Ba}_3\text{Ta}_5\text{O}_{14}\text{N}$  using a mixed gas of  $\text{NH}_3$  and  $\text{O}_2$  and revealed that  $\text{Ba}_3\text{Ta}_5\text{O}_{14}\text{N}$  modified with a cocatalyst is active for  $\text{H}_2$  evolution from an aqueous methanol solution under visible light [22]. Here we report synthesis of nitrogen content-controlled  $\text{Ba}_{3-x}\text{La}_x\text{Ta}_5\text{O}_{14-x}\text{N}_{1+x}$  using either moist- $\text{NH}_3$  or  $\text{NH}_3\text{-N}_2$  atmosphere. Effects of annealing treatment on properties of surfaces and photocatalytic activities are also discussed.

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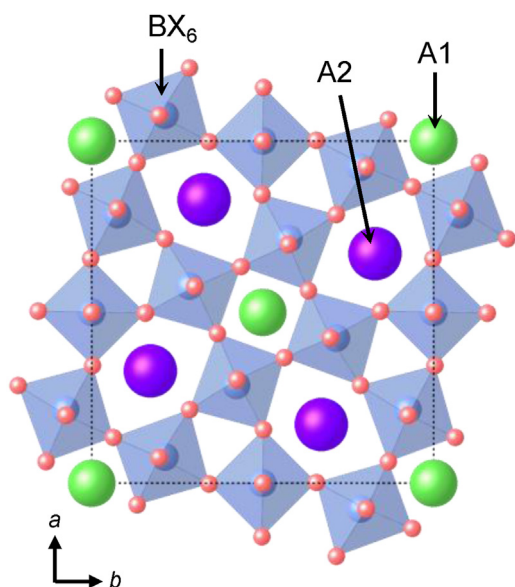


Fig. 1. General crystal structure of TTB compound (A1)(A2)<sub>2</sub>B<sub>x</sub>X<sub>15</sub>.

## 2. Experimental

### 2.1. Synthesis of Ba<sub>3-x</sub>La<sub>x</sub>Ta<sub>5</sub>O<sub>14-x</sub>N<sub>1+x</sub>

Powders of TTB-type oxynitrides Ba<sub>3-x</sub>La<sub>x</sub>Ta<sub>5</sub>O<sub>14-x</sub>N<sub>1+x</sub> were synthesized by nitridation of the corresponding amorphous oxide precursors. The precursors were obtained by a polymerizable complex method employing citric acid (CA, Wako Pure Chemical, 98%) and propylene glycol (PG, Kanto Chemical, 99.0%) as described elsewhere [21]. Barium carbonate (Kanto Chemical, 99.9%), lanthanum nitrate hexahydrate (Wako Pure Chemical, 99.9%), tantalum chloride (Furuuchi Chemical, 99.9%) were used as raw materials. PG, BaCO<sub>3</sub>, and La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O were added to a methanol solution dissolving TaCl<sub>5</sub>. The solution was heated at 353 K with stirring until being a transparent solution and was heated at 423 K to promote condensation and esterification between CA and PG. The obtained viscous resin matter was subjected to sequential heating at 523, 623, and 723 K using a mantle heater to decompose organic matter. After pyrolysis, the residue carbon species was removed completely by heating at 823 K for 2 h using a box furnace. The oxide precursors thus obtained were amorphous. Nitridation of the oxide precursors was performed at 1073–1273 K for 10 h in a stream of pure NH<sub>3</sub>, 5% NH<sub>3</sub>-N<sub>2</sub>, or moist-NH<sub>3</sub> with a flow rate of 100 mL min<sup>-1</sup> using a tubular furnace. The moist-NH<sub>3</sub> flow was achieved by bubbling NH<sub>3</sub> gas through a saturated aqueous ammonia solution at 298 K.

### 2.2. Characterization of Ba<sub>3-x</sub>La<sub>x</sub>Ta<sub>5</sub>O<sub>14-x</sub>N<sub>1+x</sub>

Crystal phases of samples were identified by powder X-ray diffraction technique with Cu Kα radiation (XRD; Bruker AXS, D2 Phaser). Diffuse reflectance spectra in ultraviolet-visible region (UV-vis) were taken by an absorption spectrometer (Shimadzu, UV-3100) using an integrating sphere. Contents of N were analyzed by a combustion analyzer (Horiba, EMGA-620W). The composition at surface was determined by X-ray photoelectron spectroscopy (XPS; Kratos, ESCA-3200). The samples were observed by a scanning electron microscope (SEM; Hitachi, SU1510). Specific surface areas of the samples were determined by the BET method from N<sub>2</sub> adsorption isotherms (Micromeritics, ASAP-2010).

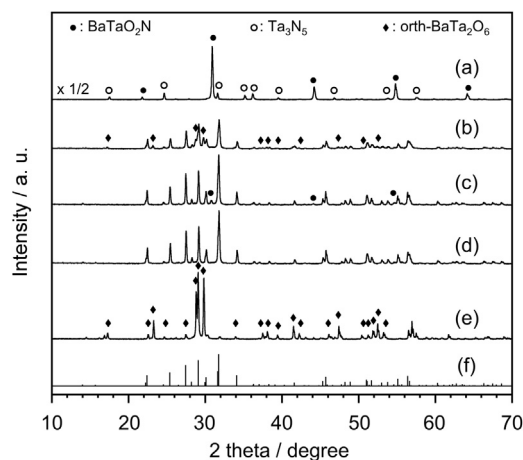


Fig. 2. XRD patterns of the samples obtained by nitridation of oxide precursors with Ba:Ta = (a–d) 3:5 and (e) 1:2 under various conditions; (a) 100% NH<sub>3</sub>, 1273 K, (b) 5% NH<sub>3</sub>, 1073 K, (c) 5% NH<sub>3</sub>, 1173 K, (d, e) moist-NH<sub>3</sub>, 1273 K. A simulated pattern of Ba<sub>3</sub>Ta<sub>5</sub>O<sub>14</sub>N is also presented as (f).

### 2.3. Evaluation of photocatalytic properties

Photocatalytic activities for H<sub>2</sub> and O<sub>2</sub> evolution in the presence of sacrificial reagents were measured using a gas-closed circulation system. The samples modified with 0.3 wt% of a Pt cocatalyst were used for H<sub>2</sub> evolution tests. Reactant solutions were 20 vol% methanol/water solution for H<sub>2</sub> evolution and 20 mM aqueous AgNO<sub>3</sub> solution with 0.1 g of La<sub>2</sub>O<sub>3</sub> powder as a pH buffer reagent for O<sub>2</sub> evolution. Photocatalyst (0.1 g) was dispersed in 150 mL of reactant solution in a reaction vessel with a top-window. Ten kPa of Ar was introduced into the system after deaeration. The suspended solution was irradiated with visible light (λ > 420 nm) using a 300 W Xe-arc lamp (Excelitas, Cermax PE300BF) with an optical cut-off filter. Monochromatic light from an illumination system (Asahi Spectra, MAX-303) was used for analysis of action spectra. Evolved gas was analyzed using an online gas chromatograph (Shimadzu, GC-14 B with MS-5A column, TCD detector, and Ar carrier). Apparent quantum efficiencies (η<sub>app</sub>) were determined by following equation,

$$\eta_{\text{app}}(\%) = (R_{\text{H}_2} \times 2) / \{I / ((1240/\lambda) \times 1.602 \times 10^{19} \times N_A)\} \times 100$$

where  $R_{\text{H}_2}$ ,  $I$ ,  $\lambda$  and  $N_A$  represent the rate of H<sub>2</sub> production in a unit of mol s<sup>-1</sup>, power of the monochromatic incident light in a unit of J s<sup>-1</sup> (W), wavelength of monochromatic light in a nm unit and the Avogadro constant, respectively.

## 3. Results and discussion

### 3.1. Synthesis condition of Ba<sub>3</sub>Ta<sub>5</sub>O<sub>14</sub>N

Nitridation of the oxide precursor with Ba:Ta = 3:5 was conducted under various conditions to find suitable nitriding condition for Ba<sub>3</sub>Ta<sub>5</sub>O<sub>14</sub>N (Fig. 2). The sample nitridized under pure NH<sub>3</sub> contained no TTB phases and was a mixture of perovskite-type BaTaO<sub>2</sub>N and Ta<sub>3</sub>N<sub>5</sub>. This result suggested that nitridation reaction proceeded too much for Ba<sub>3</sub>Ta<sub>5</sub>O<sub>14</sub>N under pure NH<sub>3</sub>. Then, nitridation using 5% NH<sub>3</sub>-N<sub>2</sub> was conducted to reduce the degree of nitridation. The TTB compound was formed as a major phase with small amount of BaTaO<sub>2</sub>N impurity in nitridation at 1173 K whereas a mixture of TTB compound and orth-BaTa<sub>2</sub>O<sub>6</sub> was obtained by nitridation at 1073 K. When nitridation was performed under a moist-NH<sub>3</sub> flow, single phase of TTB compound was obtained. The samples obtained by nitridation using 5% NH<sub>3</sub>-N<sub>2</sub> or moist-NH<sub>3</sub> were basically pale yellow although the sample nitridized at 1173 K

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