

Flux Growth and Photocatalytic Water Oxidation Activity of Ta-Substituted BaNbO₂N Crystals

Mirabbos Hojamberdiev¹, Hajime Wagata¹, Kunio Yubuta², Shuji Oishi¹, Kazunari Domen³, and Katsuya Teshima^{1,4,*}

¹Department of Environmental Science and Technology, Faculty of Engineering, Shinshu University, 4-17-1 Wakasato, Nagano 380-8553, Japan

²Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan

³Department of Chemical System Engineering, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

⁴Center for Energy and Environmental Science, Shinshu University, 4-17-1 Wakasato, Nagano 380-8553, Japan

(Oxy)nitrides are regarded as an emerging class of inorganic materials for photocatalytic water splitting due to their smaller band gap, suitable band structure, stability, and nontoxicity [1]. As BaTaO₂N can harvest visible light up to 660 nm and showed an IPCE value of 10% [2] and generated a current density of 25 mA cm⁻² [3] at 1.2 V_{RHE}, the effect of substitutional tantalum on photocatalytic water oxidation activity of BaNbO₂N crystals was investigated in this study. The BaNb_{1-x}Ta_x(O,N)₃ ($x = 0.00, 0.25, 0.50, 0.75,$ and 1.0) crystals were directly grown by an NH₃-assisted flux method at 900°C for 7 h × 2 times. The diffraction peaks of Ta-substituted BaNbO₂N crystals became slightly broader and their positions shifted to higher angle than that of BaNbO₂N crystals, indicating the overall lattice contraction. Compared with that of BaNbO₂N crystals with more-faceted morphology ($d_{50} = 0.38 \mu\text{m}$), an average size of Ta-substituted BaNbO₂N crystals exponentially decreased ($d_{50} = 0.31, 0.28, 0.24,$ and $0.17 \mu\text{m}$) and the crystals became less faceted with increased tantalum content. It is thought that the decrease in the tantalum content tends to minimize the surface Gibbs energy of those faces that became the most thermodynamically stable. The BaTaO₂N crystals showed an onset of light absorption at $\lambda \approx 660$ nm, whereas the decrement in the tantalum content shifted an absorption edge toward longer wavelength ($\lambda \approx 680$ nm). However, the intensity of background absorption monotonically increased with decreasing the tantalum content due to the presence of considerable amount of reduced niobium species and anion deficiency. The BaNb_{1-x}Ta_x(O,N)₃ ($x = 0.25, 0.50, 0.75,$ and 1.0) crystals loaded with CoO_x showed higher photocatalytic activity for O₂ evolution compared with CoO_x-loaded BaNbO₂N crystals due to the shift of valence band to more positive side and the lowered densities of mid-gap states associated with defects.

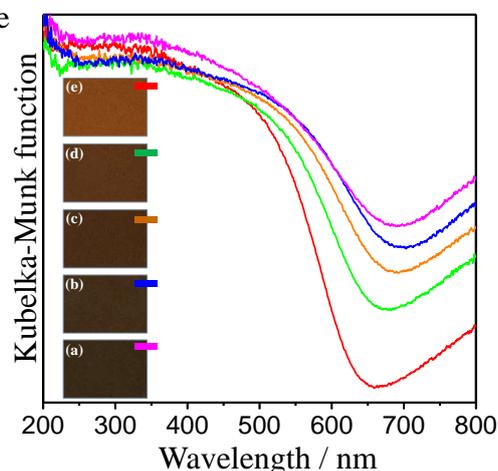


Figure 1. UV-Vis diffuse reflectance spectra of BaNbO₂N (a), BaNb_{0.75}Ta_{0.25}O₂N (b), BaNb_{0.50}Ta_{0.50}O₂N (c), BaNb_{0.25}Ta_{0.75}O₂N (d), and BaTaO₂N (e) crystals.

References

- [1] K. Maeda and K. Domen, "New non-oxide photocatalysts designed for overall water splitting under visible light," *J. Phys. Chem. C*, **2007**, *111*, 7851–7861.
- [2] M. Higashi, K. Domen, and R. Abe, "Fabrication of an efficient BaTaO₂N photoanode harvesting a wide range of visible light for water splitting," *J. Am. Chem. Soc.*, **2013**, *135*, 10238–10241.
- [3] K. Ueda, T. Minegishi, J. Clune, M. Nakabayashi, T. Hisatomi, H. Nishiyama, M. Katayama, N. Shibata, J. Kubota, T. Yamada, and K. Domen, "Photoelectrochemical oxidation of water using BaTaO₂N photoanodes prepared by particle transfer method," *J. Am. Chem. Soc.*, **2015**, *137*, 2227–2230.