

可視光応答型光触媒 TaON の結晶構造と電子密度
(東京工業大学) 八島正知・ 脇田崇弘 (東京大学) リーユンギ・堂免一成

【Introduction】 Overall water splitting using a photocatalyst is an attractive solution for the supply of clean and recyclable hydrogen energy, while certain photocatalysts decompose waste materials and hazardous compounds. In the present work, the crystal structure and electron density of an active TaON photocatalyst sample under visible-light excitation are investigated by neutron diffraction for confirmation of anion ordering, and synchrotron powder diffraction for high-precision analysis of the crystal structure and electron density. Density functional theory (DFT) is employed for theoretical calculations of the electron density distribution and partial density of states. The present work was published in *Chem. Mater.*; **2007**; *19*(3) pp 588 - 593.

【Experiments】 TaON samples were prepared by heating Ta₂O₅ powder under flowing NH₃ (20 mL min⁻¹) at 1123 K for 15 h. Neutron powder diffraction experiments were performed using the Kinken powder diffractometer in order to ensure high-efficiency and high-resolution measurements. The diffractometer, HERMES, is installed at the JRR-3M Japan Research Reactor of the Japan Atomic Energy Agency (JAEA) in Tokai, Japan and is operated by the Institute of Materials Research of Tohoku University. Incident neutrons with a fixed wavelength of 1.8150 Å were obtained by a vertically focusing (331) Ge monochromator and a 12'-∞-22' collimator. Synchrotron x-ray powder diffraction experiments were performed using the multiple-detector system installed at the BL-4B₂ beam line of the Photon Factory, High Energy Accelerator Research Organization (KEK), Japan. A monochromatized 1.20200 Å x-ray beam was utilized. Powder diffraction data from the sample at 298 K in air were collected in asymmetric flat-specimen reflection geometry with a fixed incident angle of 7.0°. Structural refinement with the neutron and synchrotron data was performed using the Rietveld analysis program RIETAN-2000. The MEM calculations were performed using the computer program PRIMA with a 64×64×64 pixel unit cell. The *ab initio* total energy program VASP (Vienna *Ab initio* Simulation Package) was employed for calculation of the valence electron-density distribution and partial density of states in TaON.

【Results and discussion】 All reflections in the neutron and synchrotron powder diffraction profiles were indexed as belonging to a monoclinic cell, indicating a single phase of baddeleyite-type TaON. The neutron and synchrotron data sets both indicate that the TaON material has a baddeleyite-type structure (space group, *P*2₁/*c*), with estimated unit cell parameters of $a = 4.94941(4)$ Å, $b = 5.01662(4)$ Å, $c = 5.16430(2)$ Å, $\alpha = 90^\circ$, $\beta = 99.6107(4)^\circ$, $\gamma = 90^\circ$, and $V = 126.426(2)$ Å³ (298 K). Occupational ordering of the anions occurs in alternate NTa₄ and OTa₃ layers normal to the [100] direction. The coordination numbers of Ta, N and O atoms are 7, 4 and 3, respectively. Bond valence sums for the oxygen and nitrogen atomic sites were calculated to be 2.1 and 3.2, respectively. Electron density analysis based on synchrotron diffraction data in combination with DFT calculations clearly showed covalent bonding between Ta and O atoms and between Ta and N atoms. Nuclear density map shows an atom near the stable position, while the MEM and DFT valence electron density maps clearly show covalent bonding between Ta and O atoms. The electron density distribution obtained using synchrotron data is consistent with the valence electron density distribution determined by DFT calculations. The results demonstrate two-dimensional networks of Ta–O and Ta–N covalent bonds arranged alternately along the [100] direction, corresponding to the occupational ordering of anions. The hybridization of anion 2p and Ta 5d orbitals attributable to the covalent bonds between Ta and O or N atoms results in enhanced dispersion of the valence band, raising the top of the valence band and realizing the visible-light response in TaON. The minimum electron density at the O–Ta bond decreases with increasing bond length, while the N–Ta bond does not exhibit such a systematic change. The high minimum electron density at the N–Ta(iv) bond suggests high covalency. Hybridization of the anion 2p and Ta 5d states around these bonds is expected to be responsible for the small band gap energy, allowing photocatalysis to occur at visible wavelengths of up to 530 nm. Here the atomic coordinates of the Ta(iv) is (0.70803, 0.95523, 0.78514).