Crystal Structure of Tantalum Oxynitride TaON, a Visible Light Responsive Photocatalyst

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Metal oxide photocatalysts have attracted extensive research for the purposes of solar energy conversion and environmental remediation. 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. Although a large number of photocatalysts have been proposed to date, most function only in the ultraviolet (wavelength $<$ 400 nm) region (e.g., TiO2) due to the inherently large band gap of metal oxides. Metal oxynitrides are candidates for visible-light responsive photocatalysts, and promising results have been reported for TaON, N-doped TiO2, and (Ga1-xZnx)(N1-xOx). TaON has been demonstrated to be responsive to excitation at wavelengths up to ca. 530 nm, with a suitable band gap (2.3 eV) position for overall water splitting. 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. This work was published in Masatomo Yashima, Yungi Lee and Kazunari Domen, " Crystal Structure and Electron Density of Tantalum Oxynitride TaON, a Visible Light Responsive Photocatalyst ", Chem. Mater., 19, [4] 588-593 (2007).

Neutron powder diffraction experiments were performed using the Kinken powder diffractometer in order to ensure high-efficiency and high-resolution measurements. The diffractometer, HERMES [2], 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 0.18150 nm were obtained by a vertically focusing (331) Ge monochromator. Diffraction data were collected at step intervals of 0.1 deg. over a 2 theta range of 8-150 deg. using 150 3He counters set at 1 ° intervals. Structural refinement was performed using the Rietveld analysis program RIETAN-2000 [3]. The peak shape was assumed to be a modified pseudo-Voigt function with asymmetry. The cut-off value was 7.00 $\times$ FWHM (full-width at half-maximum). The background of each profile was approximated by a 12-variable polynomial in (2theta)^n (n = 0...11). The parameters n were refined simultaneously with the unit cell, structural and profile parameters. The nuclear density of TaON was investigated by the maximum-entropy method (MEM) with MEM-based pattern fitting (MPF) [4]. The MEM calculations were performed using the computer program PRIMA [4] with a 64 $\times$ 64 $\times$ 64 pixel unit cell.

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. Rietveld analyses of the neutron and synchrotron diffraction data were thus performed assuming a baddeleyite-type structure. All the occupancy factors were therefore fixed at unity in the final

refinement. Isotropic harmonic atomic displacement parameters were used for all atoms. In a preliminary analysis, the atomic displacement parameters B for the three atoms were refined independently. However, as the refined atomic displacement parameter was negative, final refinement was conducted assuming B(Ta) = B(N) = B(O), where B(X) denotes the atomic displacement parameter of X atom. The calculated intensity obtained after final refinement was in good agreement with the observed data. The neutron and synchrotron data sets both indicate that the TaON material has a baddeleyite-type structure (space group, P21/c), with estimated unit cell parameters of a = 0.494941(4) nm, b = 0.501662(4) nm, c = 0.516430(2) nm, alpha = 90 °, beta = 99.6107(4) °, gamma = 90 °, and V = 0.126426(2) nm^3 (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. The NTa4 tetrahedron is linked with four corner-shared NTa4, four edge-shared NTa4, two corner-shared OTa3, and one edge-shared OTa3. The OTa3 triangle is linked with twelve corner-shared NTa4, one edge-shared NTa4, three corner-shared OTa3, and one edge-shared OTa3. These results indicate that the nitrogen atoms prefer to be four-coordinated in TaON, while oxygen atoms prefer to have three neighbors.

Figure 1 shows the refined crystal structure, MEM electron density distribution, MEM nuclear density distribution, and VASP valence electron density distribution on the b-c plane of the TaON photocatalyst over the range $1/4 < x < 3/4$. The nuclear density map shows an atom near the stable position, and the MEM and valence electron density maps clearly indicate covalent bonding between the Ta and N atoms. Again, the synchrotron-based electron density distribution (Fig. 1(b)) is in agreement with the DFT-based valence electron density distribution (Fig. 1(d)). These results suggest a two-dimensional network consisting of covalent bonds between Ta and N atoms, while the results of Ta-O layer indicate a two-dimensional network of covalent bonds between Ta and O atoms. The networks of Ta-N and Ta-O covalent bonds are arranged alternately along the c axis, corresponding to the ordering of NTa4 tetrahedra and OTa3 triangles.

References

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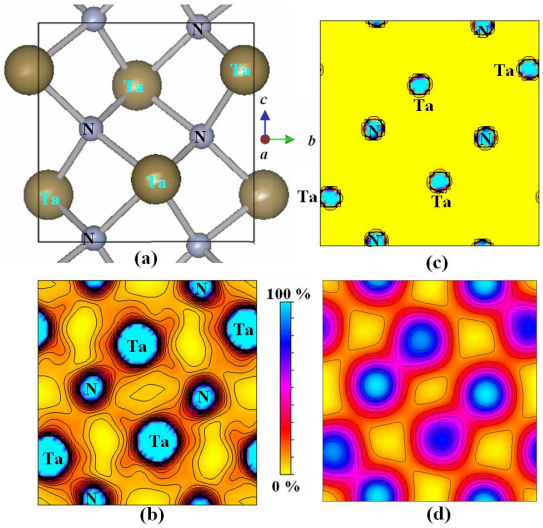

Fig. 1. (a) Refined crystal structure, (b) electron density, (c) nuclear density and (d) valence electron density distributions on the b-c plane of TaON over the range $1/4 < x < 3/4$.