Crystal Structure Refinement of visible-light driven photocatalyst

H. Ishikawa, T. Matsumoto, K. Uematsu, K. Toda, M. Sato
Niigata University

In recent years, photocatalytic materials that function under visible light have been studied extensively in an attempt to improve solar energy conversion and reduce the environmental impact of energy production. Overall water splitting using a heterogeneous photocatalyst is an attractive solution for the production of H2 as a clean and recyclable energy source. The overall water splitting reaction has already been well established in many wide gap oxide semiconductors in the early 1980s. These oxides absorb only the UV region photons. The response to visible light is, however, desired for photocatalytic water splitting from the view point of efficient solar energy conversion. In this study, we reported the crystal structure of yellow (Hf,Zr)V2O7 with V 3d electron.

The samples were prepared by a conventional solid state reaction. Starting materials were stoichiometric mixtures of HfO2, V2O5 and ZrO2 powders. The mixture was pressed into a pellet and heated in a platinum boat at 973 K for 4 h in air. The completion of the reaction and the phase purity of the samples were confirmed by powder X-ray diffraction methods. We performed neutron powder diffraction experiments on the Kinken powder diffractometer for high efficiency and high resolution measurements, HERMES with 0.18196 nm wavelength, of Institute for Materials Research(IMR), Tohoku University, installed at the JRR-3M reactor in Japan Atomic Energy Research Institute (JAERI), Tokai. The fine powder sample was sealed in a vanadium cylinder. Rietveld structure refinement was carried out with the program RIETAN2000.

Crystal structures of HfV2O7 were first reported by Turquat et al. They refined HfV2O7 on the basis of a cubic system with space group Pa-3 (a = 0.87530 nm) However, since these structures were deduced only from the electron and powder X-ray diffractions, the information on light elements, especially for oxygen atom, was quite poor. To investigate the substance Zr for Hf, the powder neutron diffraction data were collected from the single phase samples with x = 0.5.

The crystal structure of (Hf,Zr)V2O7 can be considered as related to the NaCl structure, with the (Hf,Zr)ZrO6 octahedron centered at the ideal Na site and the bridging oxygen of the V2O7 group at the ideal Na site and the bridging oxygen of the V2O7 group (O3V-O-VO3) at the Cl site. All of the diffraction peaks were well indexed on cubic system Pa-3(0.8742(1)nm). A good fitting profile were obtained with Rwp = 8.33 %.