Structure Analysis of Hydroxyapatite by High-Temperature Neutron Powder Diffraction

Naoyuki Kubo(A), Yukihiko Yonehara(A), Masatomo Yashima(B), Hirotaka Fujimori(C)
(A) Department of Materials Science and Engineering, Tokyo Institute of Technology, O-okayama 2-12-1, Meguro-ku, Tokyo, 152-8551, Japan; (B) Department of Chemistry and Materials Science, Tokyo Institute of Technology, O-okayama 2-12-1, Meguro-ku, Tokyo, 152-8551, Japan; (C) Graduate School of Science and Engineering, Yamaguchi Univ., Tokiwadai 2-16-1, Ube,Yamaguchi 755-8611, Japan

Hydroxyapatite (Ca10(PO4)6(OH)2) is one of the most interesting materials in current technologies due to its wide possible applications as biomaterials and electrical devices. Its physical and chemical properties relating to such uses strongly depend on the crystal structure. In particular the stability and mobility of OH ion in the structure of hydroxyapatite have been suggested to be closely related to the decomposition and protonic conductivity of hydroxyapatite. The OH lattice sites have been reported to be the conduction path of hydroxyapatite and to play an important role in the proton conduction. Thus, it is important to study the position of H atoms in the hydroxyapatite. Moreover, it is important to study the crystal structure at high temperatures where the fuel cell operates efficiently. However, information of hydrogen is difficult to be detected by the X-ray powder diffraction technique. Here, we report the structure analysis of hydroxyapatite, through a neutron powder diffraction study at high temperatures.

A stoichiometric hydroxyapatite sample with the atomic ratio of Ca/P=5/3 was prepared with a citric acid method. Neutron powder diffraction measurements were performed in air with a 150 detector system, HERMES, installed at the JRR-3M reactor in Japan Atomic Energy Agency, Tokai, Japan. Neutron with wavelength 1.84491 angstrom was obtained by the 331 reflection of a Ge monochromator. Diffraction data were collected in air at 673 K and 923 K. The experimental data were analyzed by Rietveld method. A computer program RIETAN-FP was utilized for the Rietveld analysis.

Rietveld analysis of hydroxyapatite at 673 K and 923 K was carried out assuming the P63/m space group. As shown in Figs. 1(a) and 1(b), the calculated intensities agreed well with the observed ones. At 673 K, the reliability factors and goodness of fit were Rwp = 4.26%, RI = 1.24%, RF = 0.57% and S = 3.79. Refined unit-cell parameters were a = 9.4794(3) angstrom, c = 6.91507(3) angstrom. At 923 K, the reliability factors and goodness of fit were Rwp = 3.26%, RI = 1.31%, RF = 0.65% and S = 2.89. Refined unit-cell parameters were a = 9.519(8) angstrom, c = 6.944(4) angstrom. These values are consistent with the literature. A part of this work was published in M. Yashima, Y. Yonehara and H. Fujimori, " Experimental Visualization of Chemical Bonding and Structural Disorder in Hydroxyapatite through Charge and Nuclear-Density Analysis ", J. Phys. Chem. C, 115, [50] 25077-25087 (2011).

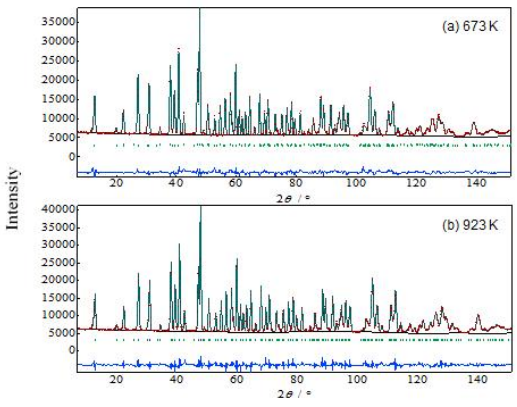

Fig. 1. Fig.1. Rietveld patterns of neutron powder diffraction data of hydroxyapatite measured at (a) 673 K and (b) 923 K.