BL-4B2/2010G144, 2011G640, 2013G216, 2013G053

Proton Diffusion Path and Electron Density of Hydroxyapatite

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1 Introduction

Calcium hydroxyapatite (HAp, $Ca_{10}(PO_4)_6(OH)_2$) is one of the most important bioceramics, the principal inorganic component of bone and teeth, catalysts and proton (H^+) conductor for energy conversions. Here, we report the visualization of the long-range proton diffusion pathway in HAp at 923 K and electron- and neutron scattering length-density density distributions of HAp [1-4].

2 Experiment

A stoichiometric (Ca/P=5/3) hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HAp) sample without impurity phases was prepared by a gel route. Neutron powder diffraction data of HAp were measured in air at 298 K, 673 K and 923 K (wavelength: 1.84491 and 1.84780 Å). High-angular-resolution synchrotron X-ray powder diffraction data were measured using the multiple-detector system at the BL-$4B_2$ beam line of the Photon Factory (wavelength: 1.197146(2) Å).

3 Results and Discussion

Synchrotron and neutron diffraction measurements showed that the present HAp is monoclinic ($P2_1/c$) at 298 K and hexagonal ($P6_3/m$) at 673 and 923 K (Fig. 1). The refined crystallographic parameters from the present neutron data at 923 K agree well with those from the present synchrotron data at the same temperature. The crystal structure of hexagonal HAp consists of (1) hydroxide anion (OH^-) in the hexagonal channel, (2) PO_4 tetrahedra and (3) Ca^{2+} cations. Figure 2 shows the electron-density distribution of HAp at 923 K. The hydrogen atom was confirmed to exist as a proton in the hexagonal axis (ex. 0, 0, 0.1993 at 923 K), because the electron-density distribution shows the charge transfer from hydrogen atom to oxygen one.

Using the refined structure and bond valence method, we have successfully visualized (1) one-dimensional proton diffusional pathways along the *c* axis in the hexagonal channel and (2) two-dimensional proton migration pathway network on the *ab* planes at z = 0 and 1/2. The proton diffusion and reorientation of hydroxide ions (OH^-) are a complex sinusoidal process in the hexagonal channel along the *c* axis, which is consistent with the anisotropic nuclear-density distribution of proton obtained by the neutron diffraction and maximum-entropy method.

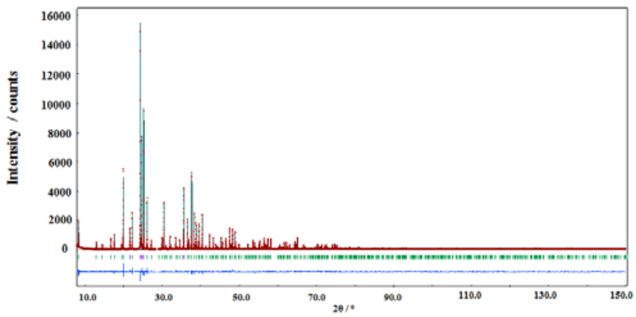

Fig. 1: Rietveld pattern of synchrotron X-ray powder diffraction data of HAp at 923 K.

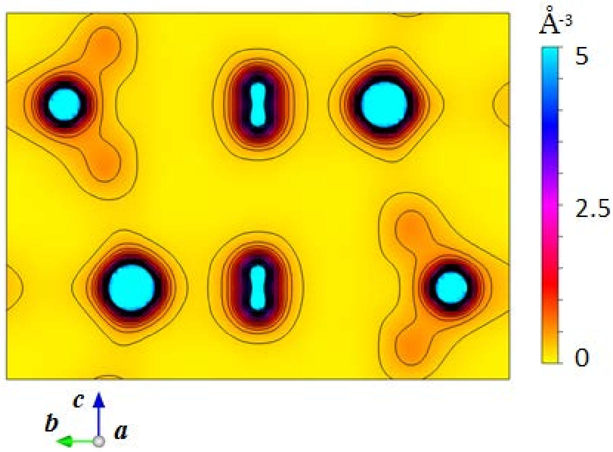

Fig. 2: Electron density distribution of HAp at 923 K. Covalent P-O and H-O bonds are seen.

References and achievements

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