Crystallography

4B2, 6C/2010G144

Crystal Structure and Electron Density Analysis of Monoclinic and Hexagonal Hydroxyapatites

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Introduction

Hydroxyapatite (HAp, $Ca_{10}(PO_4)_6(OH)_2$) is an important biocompatible material. This compound exhibits a reversible phase transition around 480 K between monoclinic (space group $P2_1/b$) and hexagonal (space group $P6_3/m$) phases. Chemical bonding is important to discuss the properties of HAp. Electron-density analysis is a powerful method to study the chemical bonding, but little experimental electron-density studies have been reported for HAp. The purpose of this work is to investigate the crystal structure and electron-density distribution of HAp through high-angular-resolution synchrotron powder diffraction data.

Experiment

A stoichiometric HAp sample with Ca/P=5/3 was prepared with a citric acid method. Synchrotron x-ray powder diffraction experiments of HAp were carried out at 298 and 923 K with a multi-detector system installed at the beam line BL-4B$_2$ of the Photon Factory, KEK, Japan. Crystal structure of HAp was refined by a Rietveld analysis program, RIETAN-FP. Experimental electron-density distribution was derived by maximum-entropy method (MEM) and MEM-based pattern fitting, and compared with valence electron density distribution through Density Functional Theory (DFT)-based calculations.

Result and Discussion

Rietveld analyses of synchrotron powder diffraction data of HAp indicated monoclinic and hexagonal symmetries at 298 and 923 K, respectively (Fig.1). Reliability factors and goodness of fit at 298 K were R_{wp} = 5.11 %, R_I = 3.13 %, R_F = 1.47 % and GOF = 1.69. Lattice parameters were a = 9.42070(8) Å, b = 6.88242(1) Å, c = 18.8455(2) Å. Reliability factors and goodness of fit at 923 K were R_{wp} = 7.17 %, R_I = 3.46 %, R_F = 2.50 % and GOF = 1.33. Lattice parameters were a = b = 9.51470(6) Å, c = 6.94364(3) Å.

MEM electron density map indicated that the P-O bond is covalent and that the Ca-O bond is more ionic, which is consistent with DFT valence electron density distribution. This is the first example of the experimental visualization of chemical bonding of HAp. In the monoclinic HAp the OH^- ions are fully ordered within c axis, while in hexagonal phase the OH^- ions are disordered and a mirror plane exists on the ab plane at z=1/4 and 3/4. Corresponding to the order-disorder nature of the monoclinic-hexagonal transition, the electron-density distributions around the OH^- ions of monoclinic and hexagonal HAp are asymmetric and symmetric, respectively.

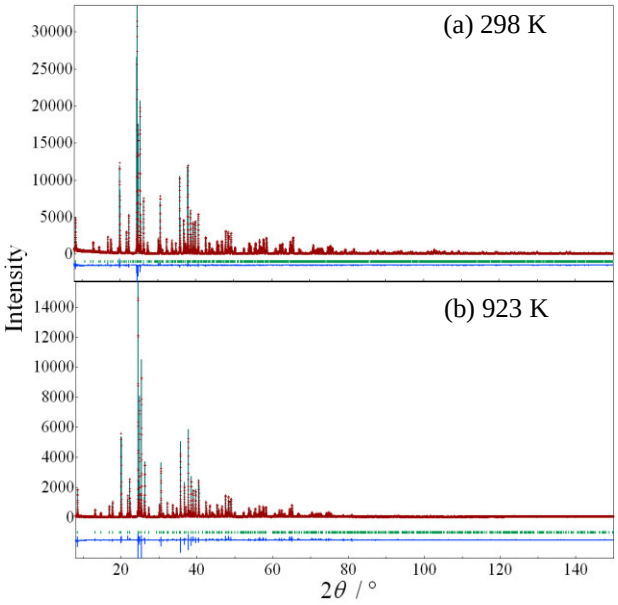

Fig.1 Rietveld patterns for synchrotron X-ray diffraction data of $Ca_{10}(PO_4)_6(OH)_2$ measured at (a) 298 K and (b) 923 K.