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Preparation and Structure Refinement of Monoclinic Hydroxyapatite

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Monoclinic hydroxyapatite was synthesized by a wet method followed by heating in air at 1473 K for 1 h. The product is carbonate-free and has a Ca/P ratio of 1.65, which is slightly lower than the theoretical value (1.67) of hydroxyapatite. The crystal structure was investigated by Rietveld refinement using X-ray powder diffraction data. The structure has monoclinic symmetry with the space group $P2_1/b$ (No. 14), $Z=4$, $Dx=3.14\ \mathrm{g\,cm^{-3}}$, and the lattice constants are $a=9.426(3)$ Å, $b=18.856(5)$ Å, $c=6.887(1)$ Å, and $\gamma=119.97(1)°$. The hydroxyl ions have an ordered arrangement along the hydroxyl columns. The hydroxyapatite prepared in the present study is 98% monoclinic.

***Key Words*: hydroxyapatite; monoclinic phase; wet method; Rietveld refinement; X-ray powder diffraction.**

INTRODUCTION

Recently, much attention has been paid to hydroxyapatite [$Ca_5(PO_4)_3OH$] because it is the main mineral component of bone and tooth and its ceramics are widely used as biomaterials. It is important to synthesize pure crystals and to clarify its crystal structure. The crystal structure of hydroxyapatite is known to be isostructural to that of fluorapatite [$Ca_5(PO_4)_3F$] which has hexagonal symmetry with the space group $P6_3/m$ (1, 2). The lattice constants of hexagonal hydroxyapatite are $a = 9.422$ Å and $c = 6.883$ Å (3). The hexagonal hydroxyapatite has mirror planes at $z = 1/4$ and 3/4 and the hydroxyl arrangement shows twofold disorder (2, 3).

The crystal system of the hydroxyapatite, synthesized by heating a chlorapatite [$Ca_5(PO_4)_3Cl$] single crystal in steam at 1473 K, has been reported to have monoclinic symmetry with the space group $P2_1/b$. The crystal has mimetic twinning (4). A model of hydroxyl ordering along the hydroxyl columns in the monoclinic hydroxyapatite was proposed based on structural refinement using X-ray single-crystal diffraction measurements (5). The single crystal was also twinned and was approximately 37% monoclinic. The lattice constants of the hydroxyapatite were $a = 9.4214(8)$ Å, $b = 2a$, $c = 6.8814(7)$ Å, and $\gamma = 120°$. The initial parameters that Elliott *et al.* employed for the structural refinement were taken from the structural parameters of hexagonal hydroxyapatite from Holly Springs (2). With respect to other monoclinic apatites, it has been reported that a synthetic chlorapatite (6) and a natural ternary apatite [$Ca_5(PO_4)_3$(F, OH, Cl)] (7) are in space group $P2_1/b$ based on single-crystal structural refinements, and carbonate–apatite [$Ca_{10}(PO_4)_6CO_3$] (8) is in space group Pb based on X-ray powder diffraction measurements.

In the previous studies, monoclinic hydroxyapatites were synthesized by both hydrothermal methods (9, 10) and dry methods (10–12). The hydroxyapatite synthesized by wet methods (13, 14) showed only a hexagonal structure, space group $P6_3/m$ (10). The monoclinic structure was obtained only for pure, stoichiometric samples (15).

This paper describes a method of preparation of pure and nearly stoichiometric monoclinic hydroxyapatite and the crystal structure as refined by the Rietveld method using X-ray powder diffraction data.

EXPERIMENTAL

Synthesis

Pure $CaCO_3$ powder was heated at 1323 K for 3 h, and the resultant CaO powder was hydrated with a third equivalent quantity of distilled water to produce $Ca(OH)_2$. One

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thousand milliliters of a 0.6 mol/liter H_3PO_4 solution was dropped slowly into 2000 ml of a vigorously stirred 0.5 mol/liter $Ca(OH)_2$ suspension at room temperature. The reaction mixture was aged for 3 days, and the final pH was 7.5. The resulting hydroxyapatite suspension was freeze-dried and heated in air at 1473 K for 1 h. The sample was cooled in a furnace to room temperature. The calcium and phosphorus contents were determined for the hydroxyapatite heated at 1473 K by inductively coupled plasma (ICP) emission spectrometry.

Infrared Spectroscopy

Infrared absorption spectra for freeze-dried hydroxyapatite and for the sample heated at 1473 K for 1 h were obtained at room temperature with a Hitachi I-2000 spectrometer in the range 4000 to 400 cm^{-1}. One milligram of sample was mixed with 200 mg of KBr powder ground to less than 37 μm.

X-ray Diffraction

X-ray powder diffraction measurements for the hydroxyapatite heated at 1473 K for 1 h were conducted at room temperature on a Rigaku RAD-rC diffractometer with graphite monochromatized Cu$K\alpha$ radiation at 50 kV and 140 mA. The intensity data were collected in 0.02° steps in the 2θ range 20° to 110°.

Structure Refinement

The crystal structure of hydroxyapatite was refined by the Rietveld method using the program RIETAN-94 (16). The initial peak shift, background, and profile-shape parameters were determined by refining the structure of Si powder (NBS-640b).

Initially, the Rietveld refinement was performed based on the hexagonal structure with the space group $P6_3/m$ (No. 176) using previously reported structural parameters (2). The structure was refined to $R_{wp} = 8.38$, $R_p = 6.06$, and $R_e = 6.34$. The refined atomic coordinates were similar within the estimated standard deviations to the reported values (2). Since there are weak reflections that are not matched to the calculated intensity, the synthetic hydroxyapatite should have lower symmetry. The refinement was then undertaken for the monoclinic structures with the space group $P2_1/b$ (No. 14). The monoclinic hydroxyapatite exhibits almost complete structural similarity to the hexagonal hydroxyapatite, and the monoclinic cell setting has the c axis as the unique axis. Figure 1 shows the projection of the refined monoclinic hydroxyapatite onto the (001). The origin of the monoclinic cell was shifted toward (0, $-1/2$, 0) against the hexagonal cell and the b-axis parameter was doubled. Therefore, the initial lattice constants were assumed to be $a = 9.4224$ Å, $b = 2a$, $c = 6.8825$ Å, and $\gamma = 120°$. The hexagonal coordinates were converted to monoclinic coordinates referring to the report for monoclinic chlorapatite (6) except for chlorine. The converted monoclinic coordinates were similar to those given by Elliott *et al.* (5) except for the oxygen atom of the hydroxyl group.

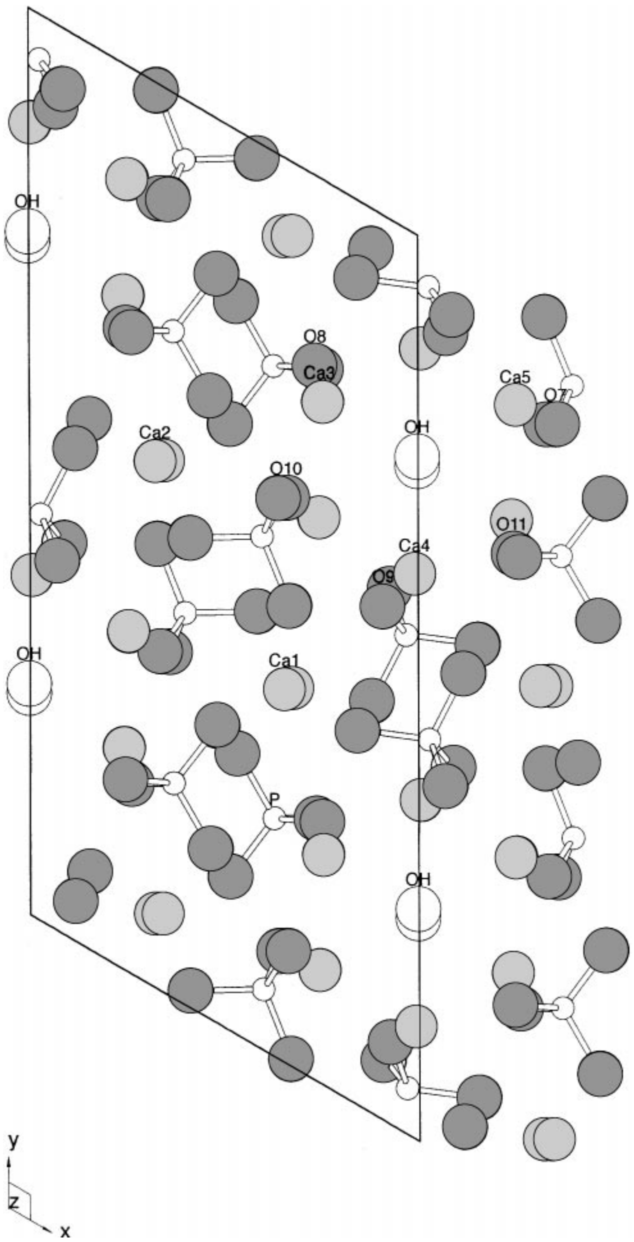

FIG. 1. Projection of refined monoclinic hydroxyapatite onto the (001) plane. Light gray circles indicates calcium; gray circles, oxygen; open circles, hydroxyl oxygen; small open circles, phosphorus.

Peak shift, background, scale, profile-shape, asymmetry, preferred-orientation, and lattice constants were refined incrementally. At this point, the structural parameters were refined, with individual thermal parameters and occupation factors of each atomic site kept constant. The initial individual thermal parameters were 1.0 Å^2. After several cycles of refinement, the individual thermal parameters were refined. The individual thermal parameters of phosphate oxygen were found to be nonpositive, and these were constrained to be equal. Nonlinear constraints were imposed on the P–O distances (1.55 ± 0.03 Å) and O–P–O angles ($109.47 \pm 3.00°$) in the phosphate tetrahedra. If these constraints were not imposed, P–O and O–O distances were calculated to be very short or long; 1.47 Å for P(1)–O(1) and 1.64 Å for P(3)–O(12). The occupation factors of all the atoms were assumed to be 1.0. In the final cycles, these parameters were refined together.

The percentage of monoclinic hydroxyapatite was calculated, assuming a two-phase mixture of the monoclinic and hexagonal structures. Using the refined hexagonal and monoclinic structural parameters, only scale parameters were refined.

RESULTS AND DISCUSSION

A single-phase sample of monoclinic hydroxyapatite was prepared with ease by the present method. As a result of ICP emission spectrometry, the chemical formula was calculated as follows: $Ca_{4.95}(PO_4)_{2.99}(OH)_{0.92}$. The hydroxyl content was calculated from the charge neutrality of calcium and phosphate ion contents. The Ca/P ratio was found to be 1.65. The ratio was slightly lower than the theoretical value (1.67) of hydroxyapatite. The purity of these synthetic hydroxyapatites was confirmed by infrared absorption spectroscopy. Figure 2 shows the infrared spectra of freeze-dried hydroxyapatite and of hydroxyapatite heated at 1473 K for 1 h. The hydroxyl stretching band and bending band were observed at 3574 and 630 cm^{-1}, respectively, for both samples. The broadending bands attributed to absorbed water were also observed each at about 3440 and 1630 cm^{-1}. The ν_3 bands of carbonate were observed at 1452 and 1422 cm^{-1} and the ν_2 band was at 874 cm^{-1}. The freeze-dried hydroxyapatite contains small amounts of carbonates. The positions of the carbonate bands were matched to those previously reported (17) for type B carbonate–hydroxyapatite (carbonate ions were substituted for phosphate ions). The crystal system of apatites in which the calcium ions were substituted for strontium or barium ions and hydroxyl ions for fluoride and carbonate ions was hexagonal (1, 11, 19, 20). Symmetry of the freeze-dried hydroxyapatite was not clarified because of low crystallinity. After the freeze-dried hydroxyapatite was heated at 1473 K for 1 h, the carbonate bands disappeared completely. The hydroxyl bands became very strong and sharp, and only the phosphate and hydroxyl bands were observed. There are no differences between the profiles of infrared spectra for the freeze-dried hydroxyapatite and the sample heated at 1473 K except for carbonate bands. The hydroxyapatite heated at 1473 K has no second phase including $Ca_3(PO_4)_2$ (18) and was found to be monoclinic with space group $P2_1/b$ as described below. The percentage of monoclinic structure is 98%. The previous wet method produced only hexagonal crystals. However, the hydroxyapatite synthesized by the present method is thermally stable and has monoclinic symmetry. The monoclinic hydroxyapatite in the present study is carbonate-free and slightly calcium-deficient.

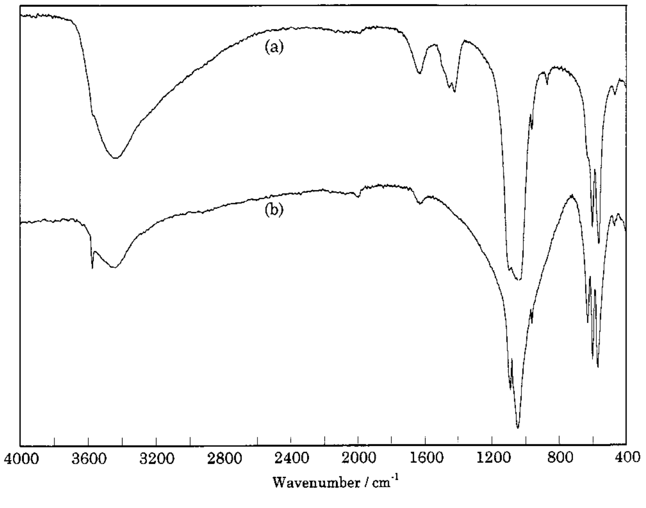

FIG. 2. Infrared absorption spectra of synthetic hydroxyapatite: (a) freeze-dried hydroxyapatite, (b) hydroxyapatite heated at 1473 K for 1 h.

The X-ray powder diffraction pattern of the heated hydroxyapatite was well fitted to the monoclinic model. Figure 3 shows the Rietveld refinement plots of the hydroxyapatite in the range 20° to 110° in 2θ. Table 1 summarizes the results of Rietveld refinement for the monoclinic hydroxyapatite. The lattice constants of the hydroxyapatite were found to be $a = 9.426(3)$ Å, $b = 18.856(5)$ Å, $c = 6.887(1)$ Å, and $\gamma = 119.97(1)°$. Figure 3 also shows the characteristic reflections of the monoclinic hydroxyapatite. These reflections are forbidden by the hexagonal symmetry. The Miller index and the relative intensity of the strongest intensity among these characteristic reflections are 212 and 1.3, respectively. The X-ray powder diffraction pattern based on monoclinic symmetry agreed with previous reports (5, 12).

Table 2 gives the atomic coordinates and individual thermal parameters of the monoclinic hydroxyapatite. The numbers of crystallographically independent sites of calcium and phosphate ions in the monoclinic hydroxyapatite are 5 and 3, respectively. Ca(1)*M* and Ca(2)*M* in the monoclinic structure are crystallographically equivalent to Ca(1)*H* in the hexagonal structure; Ca(3)*M*, Ca(4)*M*, and Ca(5)*M* are equivalent to Ca(2)*H*. The calcium triangles formed by Ca(3)*M*, Ca(4)*M*, and Ca(5)*M* correspond to

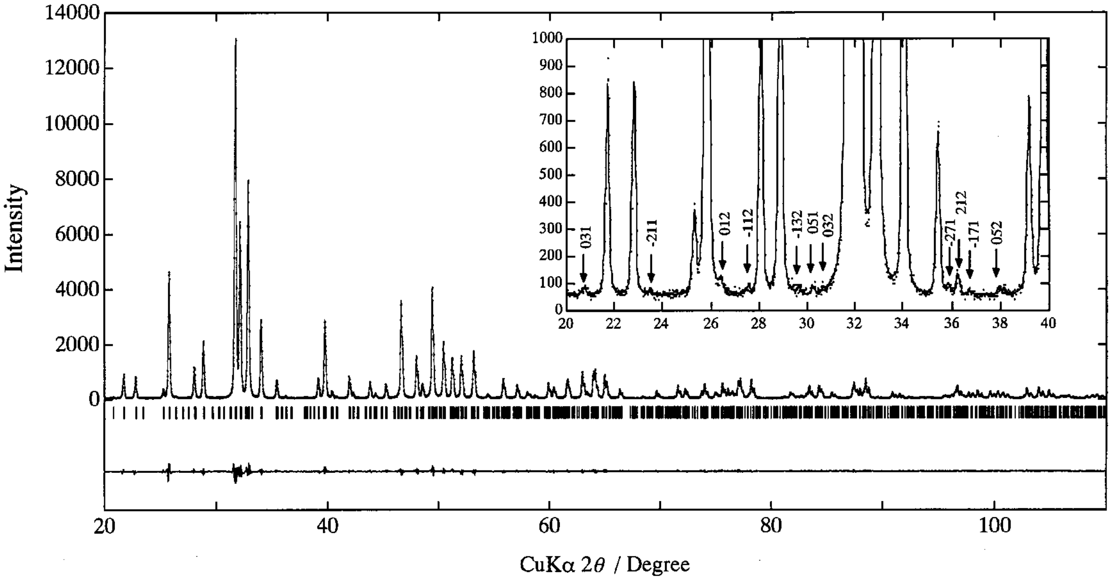

FIG. 3. Rietveld refinement plots of monoclinic hydroxyapatite. Dots show observed pattern, and the line represents calculated patterns. Arrows indicate characteristic reflections of monoclinic hydroxyapatite.

Ca(2)*H* triangles ($z = 1/4$, $3/4$). The mirror planes ($z = 1/4$, $3/4$) in hexagonal hydroxyapatite are absent; rather there are *b*-glide planes. In the previous study on monoclinic hydroxyapatite (5), enlargement of the oxygen triangles adjacent to the hydroxyl ions was described, but the interatomic distances were not discussed. The interatomic distances of calcium triangles calculated from the refined atomic parameters are shown in Table 3. The mean distance of Ca–Ca is similar to the value reported for the hexagonal hydroxyapatite (1, 2).

TABLE 1
Details of Rietveld Refinement for Monoclinic Hydroxyapatite

Compound	$Ca_{4.95}(PO_4)_{2.99}(OH)_{0.92}$
Space group	$P2_1/b$ (No. 14)
Z	4
Dx	3.14 g cm^{-3}
Cell parameters	$a = 9.426(3)$ Å
	$b = 18.856(5)$ Å
	$c = 6.887(1)$ Å
	$\gamma = 119.97(1)°$
Step scan increment (°2θ)	0.02
2θ range	20°–110°
No. of reflections ($CuK\alpha_{1,2}$)	2728
No. of structure parameters	73
No. of profile parameters	22
R_{wp}	7.58%
R_p	5.38%
R_e	6.09%

The greatest structural difference between monoclinic and hexagonal hydroxyapatite is the arrangement of the hydroxyl ions. This may affect the physical and chemical properties of hydroxyapatite. In monoclinic hydroxyapatite,

TABLE 2
Structural Parameters of Monoclinic Hydroxyapatite[a]

Atom	Site	x	y	z	B (Å^2)
$Ca^{2+}(1)$	4*e*	0.343(2)	0.5870(8)	0.0024(6)	0.6(2)
$Ca^{2+}(2)$	4*e*	0.324(2)	0.5819(8)	0.4997(6)	0.9(2)
$Ca^{2+}(3)$	4*e*	0.244(2)	0.245(1)	0.2458(1)	0.9(3)
$Ca^{2+}(4)$	4*e*	− 0.008(2)	0.6231(8)	0.754(1)	0.2(3)
$Ca^{2+}(5)$	4*e*	0.255(2)	0.3755(7)	0.745(1)	0.8(3)
P (1)	4*e*	0.401(2)	0.433(1)	0.248(1)	1.0(4)
P (2)	4*e*	0.629(2)	0.2629(9)	0.249(1)	0.7(3)
P (3)	4*e*	0.030(2)	0.4498(9)	0.746(1)	0.5(4)
$O^-(1)$	4*e*	0.330(3)	0.492(2)	0.240(2)	0.6(1)
$O^-(2)$	4*e*	0.484(3)	0.329(1)	0.739(2)	0.6
$O^-(3)$	4*e*	0.156(4)	0.586(2)	0.247(2)	0.6
$O^-(4)$	4*e*	0.587(2)	0.481(2)	0.265(3)	0.6
$O^-(5)$	4*e*	0.534(4)	0.311(2)	0.253(3)	0.6
$O^-(6)$	4*e*	0.119(4)	0.545(2)	0.769(3)	0.6
$O^-(7)$	4*e*	0.359(3)	0.380(1)	0.068(2)	0.6
$O^-(8)$	4*e*	0.738(3)	0.290(1)	0.059(2)	0.6
$O^-(9)$	4*e*	0.090(2)	0.433(1)	0.545(2)	0.6
$O^-(10)$	4*e*	0.338(2)	0.375(1)	0.422(3)	0.6
$O^-(11)$	4*e*	0.750(3)	0.289(1)	0.427(4)	0.6
$O^-(12)$	4*e*	0.073(2)	0.410(1)	0.912(4)	0.6
$O^-(H)$	4*e*	0.000(4)	0.245(2)	0.1924(9)	0.4(3)

[a] The thermal parameters of phosphate oxygen atoms are considered to be equal.

TABLE 3
Interatomic Distances (Å) in Monoclinic Hydroxyapatite

Ca(3)–Ca(4)[a]	3.99(3)
Ca(3)[b]–Ca(5)	4.12(2)
Ca(4)–Ca(5)[c]	4.07(2)
Mean distance	4.09
Ca(3)–O(H)	2.32(3)
Ca(4)[d]–O(H)	2.48(4)
Ca(5)[e]–O(H)	2.37(4)

[a–e] Symmetry codes: (a) $-x, 1-y, 1-z$; (b) $1+x, 1/2+y, 1/2-z$; (c) $1-x, 3/2-y, 1/2+z$; (d) $-x, 1/2-y, -1/2+z$; (e) $-x, 1/2-y, -1/2+z$.

the hydroxyls are aligned in an upper direction in some hydroxyl columns and a lower direction in the other hydroxyl columns due to the repulsion of calcium ions. These atomic arrangements and the bond lengths required that the hydroxyls be arranged in the order O–H, O–H, O–H in one hydroxyl column and H–O, H–O, H–O in another hydroxyl column, showing the ordered arrangement. This ordered arrangement of hydroxyls is similar to the model first proposed by Elliott *et al.* (5). In hexagonal hydroxyapatite, the positions of hydroxyl oxygen and hydrogen have been reported to be (0, 0, 0.2008) and (0, 0, 0.067) from a neutron diffraction study (2). This means that the hydroxyls are arranged in the order H–O, O–H, H–O, O–H, H–O, O–H along the c axis due to the mirror planes at $z = 1/4$ and $3/4$, and the occupancy factor of hydroxyl oxygen is 1/2. The arrangement of hydroxyl shows a two-fold disorder in hexagonal hydroxyapatite. The order or disorder in the hydroxyl arrangement may be a significant stabilizing factor for the monoclinic or hexagonal symmetry in synthetic hydroxyapatite.

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