



ACADEMIC  
PRESS

Available online at [www.sciencedirect.com](http://www.sciencedirect.com)

SCIENCE @ DIRECT®

Journal of Solid State Chemistry 175 (2003) 272–277

JOURNAL OF  
SOLID STATE  
CHEMISTRY

<http://elsevier.com/locate/jssc>

# Crystal structure analysis of $\beta$ -tricalcium phosphate $\text{Ca}_3(\text{PO}_4)_2$ by neutron powder diffraction

Masatomo Yashima,<sup>a,\*</sup> Atsushi Sakai,<sup>a</sup> Takashi Kamiyama,<sup>b</sup>  
and Akinori Hoshikawa<sup>b</sup>

<sup>a</sup>Department of Materials Science and Engineering, Interdisciplinary Graduate School of Science and Engineering,  
Tokyo Institute of Technology, Nagatsuta-cho 4259, Midori-ku, Yokohama 226-8502, Japan

<sup>b</sup>Neutron Science Laboratory, Institute of Materials Structure Science, High Energy Accelerator Research Organization, 1-1 Oho,  
Tsukuba, Ibaraki 305-0801, Japan

Received 11 January 2003; received in revised form 22 April 2003; accepted 8 May 2003

## Abstract

The crystal structure of sintered  $\beta$ -tricalcium phosphate,  $\text{Ca}_3(\text{PO}_4)_2$ , was refined using a high-resolution neutron powder diffraction data and the Rietveld method. This material was confirmed to have a rhombohedral structure (space group  $R\bar{3}c$ ,  $Z = 21$ ). Unit-cell parameters with higher precision ( $a = b = 10.4352(2) \text{ \AA}$ ,  $c = 37.4029(5) \text{ \AA}$ ,  $\alpha = \beta = 90^\circ$ , and  $\gamma = 120^\circ$  in the hexagonal setting) and positional parameters for oxygen with equal precision were obtained by the neutron powder diffraction technique, compared with the single-crystal X-ray diffraction data by Dickens et al. (J. Solid State Chem. 10 (1974) 232). The site Ca(4) with atomic coordinates [0.0, 0.0,  $-0.0851(6)$ ] was confirmed to be very different from the other four Ca sites: The position Ca(4) is three-fold coordinated with oxygen atoms, and has lower occupancy factor of 0.43(4), and a higher isotropic thermal parameter. On the contrary, each of the Ca(1), Ca(2), Ca(3), and Ca(5) is fully occupied by one Ca atom and these positions are coordinated with seven, eight, eight, and six oxygen atoms, respectively. The bond valence sums of Ca(4) and Ca(5) are lower (0.7) and higher (2.7), respectively, than the others (1.8–2.1).

© 2003 Elsevier Inc. All rights reserved.

**Keywords:** High-resolution neutron powder diffraction; Crystal structure; Biomaterials;  $\beta$ -tricalcium phosphate; Rietveld analysis; Bond length; Bond angles; Ionic radius; Bond valence sum

## 1. Introduction

Tricalcium phosphates (TCP,  $\text{Ca}_3(\text{PO}_4)_2$ ) are attractive materials for biologists, mineralogists, and inorganic and industrial chemists, since (1) they are some of the most important biomaterials [1–4] and (2) they have interesting optical properties [5]. TCP has three polymorphs of  $\beta$ ,  $\alpha$ , and  $\alpha'$ , depending on temperature [3]. As reported by Dickens et al. [6,7], the  $\beta$ -TCP crystallizes in the rhombohedral space group  $R\bar{3}c$  with unit-cell parameters  $a = 10.439(1)$ ,  $c = 37.375(6) \text{ \AA}$ .  $\beta$ -TCP has increasingly been used as a biocompatible material for bone replacement or for the coating of bone prostheses as well as apatites [4]. TCP can also be utilized as a precursor for the preparation of apatites [1,2]. The

solubility of  $\beta$ -TCP into water is about twice as high as that of hydroxyapatite [8].

In general,  $\beta$ -TCP is utilized in the form of powders and polycrystalline materials. However, there has been little work on the crystal structural analysis using polycrystalline materials in the literature. Only limited analyses have been done using conventional X-ray powder diffraction data to obtain the unit-cell parameters [9–11]. It is very difficult to obtain accurate crystal parameters by the conventional X-ray diffractometry, due to lower angular resolution. Here we investigate the crystal structure of  $\beta$ -TCP using high-resolution powder neutron diffraction data and the Rietveld method. To obtain the accurate positional parameters for oxygen atoms, we utilized the neutron diffractometry. Structural aspects of  $\beta$ -TCP are discussed using the crystal structure refined through neutron powder diffraction analysis.

\*Corresponding author. Fax: +81-45-924-5630.

E-mail address: [yashima@materia.titech.ac.jp](mailto:yashima@materia.titech.ac.jp) (M. Yashima).

## 2. Experimental procedure

### 2.1. Sample preparation

High-purity  $\beta$ -TCP was prepared by solid-state reactions from  $\text{CaHPO}_4$  and  $\text{CaCO}_3$ . Stoichiometric amounts of high-purity  $\text{CaHPO}_4$  (99.6% purity, Kyowa Chemical Industry Co. Ltd., Takamatsu, Japan) and  $\text{CaCO}_3$  (99.99% purity, Kojundo Chemical Lab. Co. Ltd., Sakado, Japan) powders were mixed for about 1.5 h in an agate mortar. The mixture was pressed into pellets under uniaxial pressure of 150 MPa. The pellets were sintered for 24 h at 1000°C to obtain a single phase of  $\beta$ -TCP. After firing, the sintered product was crushed and ground into powder for about 1 h for powder diffraction measurements. X-ray diffraction data were collected with a  $\text{CuK}\alpha$  X-ray diffractometer (Model Rint-2550V/PC, Rigaku Co., Tokyo, Japan). The formation of a single  $\beta$  phase was confirmed by the X-ray powder diffraction measurement.

### 2.2. TOF neutron powder diffraction measurement

A time-of-flight (TOF) neutron powder diffraction experiment was carried out at 24°C with a high-resolution and high-intensity diffractometer, *Sirius* [12], installed at the pulsed spallation neutron facility (KENS) in the High Energy Accelerator Research Organization (KEK), Tsukuba, Japan. The powdered sample was contained in a cylindrical vanadium cell: 9.2 mm in diameter and 20 mm in sample height. An array of 320 position-sensitive detectors (PSDs) installed in a backward bank with a  $2\theta$  range from 150° to 170° was used to collect the intensity data. Incident neutron spectra were monitored with a  $^3\text{He}$  counter. The difference in efficiency between the PSDs and the monitor counter was corrected using intensity data obtained in a separate measurement of incoherent scattering from vanadium. The unit-cell and structural parameters of  $\beta$ -TCP were refined by Rietveld analysis using a computer program *RIETAN-2001T* [13]. Neutron scattering lengths used in the Rietveld analyses were 4.700, 5.803, and 5.130 fm for Ca, O, and P atoms, respectively.

## 3. Data analysis, results and discussion

### 3.1. Rietveld refinement of neutron powder diffraction data for $\beta$ -TCP

Rietveld refinements of neutron powder diffraction data for  $\beta$ -TCP were done assuming the space group  $R3c$ . The unit-cell and structural parameters reported in the literature [6] were used for the initial values in the first preliminary refinement. In another preliminary

analysis, all the occupancy factors for five Ca sites were refined simultaneously, whereas all the isotropic thermal parameters at five Ca sites were assumed to have a same value:  $B(\text{Ca}(1)) = B(\text{Ca}(2)) = \dots = B(\text{Ca}(5))$ . In this analysis the refined occupancy factors were 0.96(1), 1.02(1), 0.92(1), 0.36(2), and 1.11(2) for Ca(1), Ca(2), Ca(3), Ca(4), and Ca(5) sites, respectively. Only the Ca(4) site had a significant deficiency of 0.64(2). There was a strong correlation between the occupancy and the isotropic thermal parameters. In the final refinement, the occupancy factors for Ca(1), Ca(2), Ca(3), and Ca(5) were fixed to be unity, whereas the isotropic thermal parameters for Ca(1) site  $B(\text{Ca}(1))$ ,  $B(\text{Ca}(2))$ ,  $B(\text{Ca}(3))$ , and  $B(\text{Ca}(4))$  were refined independently. The  $B(\text{Ca}(5))$  was assumed to be equaled to the  $B(\text{Ca}(3))$ , because the  $B(\text{Ca}(5))$  became a minus value in refining independently. All the thermal parameters were assumed to be isotropic, because the convergence in the refinements with anisotropic thermal parameters was difficult.

The result of the final refinement is shown in Tables 1 and 2. Table 3 shows selected bond lengths, coordination number (CN) of cations, bond valence sum (BVS) of cations [14], volume of polyhedron, quadratic elongation [15], and bond angle variance [15] calculated from the refined crystal parameters. Fig. 1 shows the Rietveld pattern of neutron powder diffraction data of  $\beta$ -TCP. The polycrystalline  $\beta$ -TCP material was confirmed to have a rhombohedral structure with unit-cell parameters  $a = b = 10.4352(2)$  Å,  $c = 37.4029(5)$  Å,  $\alpha = \beta = 90^\circ$ , and  $\gamma = 120^\circ$  in the hexagonal setting (space group  $R3c$ ,  $Z = 21$ ). The unit-cell parameters and atomic coordinates obtained in the final refinement of the neutron powder diffraction data agreed with those in the previous work through X-ray single-crystal work [6]. Only the difference between the present data and the literature data [6] was seen in the value of the fractional coordinate  $x$  for the O(7) site. For the present neutron powder data the value  $x(\text{O}(7)) = 0.0803$  gave much better fit of  $R_{\text{wp}} = 4.21\%$ , compared with the refinement  $R_{\text{wp}} = 8.45\%$  fixing the  $x(\text{O}(7))$  value to 0.1814 reported

Table 1

A part of refinement results of neutron-diffraction data for  $\beta$ - $\text{Ca}_3(\text{PO}_4)_2$ . Standard Rietveld agreement index [18] is used for the definition of the reliability factors

Space group	$R3c$
$Z$	21
Number of reflections used in the refinement	3449
Unit-cell parameters	
$a$	10.4352(2) Å
$c$	37.4029(5) Å
Reliability factors	
$R_{\text{wp}}$ 4.21%	$R_{\text{p}}$ 3.33%
$R_{\text{I}}$ 1.80%	$R_{\text{F}}$ 1.82%

Table 2  
Positional and isotropic thermal parameters of  $\beta$ -Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>

Atom	Site	Occupancy	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å <sup>2</sup> )
Ca(1)	18 <i>b</i>	1.0	−0.2741(6)	−0.1382(7)	0.1663(2)	0.38(9)
Ca(2)	18 <i>b</i>	1.0	−0.3812(6)	−0.1745(6)	−0.0332(2)	0.27(9)
Ca(3)	18 <i>b</i>	1.0	−0.2734(4)	−0.1486(5)	0.0611(2)	0.76(7)
Ca(4)	6 <i>a</i>	0.43(4)	0.0	0.0	−0.0851(6)	2.0(8)
Ca(5)	6 <i>a</i>	1.0	0.0	0.0	−0.2664(3)	0.76(7)
P(1)	6 <i>a</i>	1.0	0.0	0.0	0.0	0.41(13)
P(2)	18 <i>b</i>	1.0	−0.3128(4)	−0.1394(5)	−0.1315(2)	0.29(8)
P(3)	18 <i>b</i>	1.0	−0.3470(5)	−0.1536(5)	−0.2332(2)	0.14(8)
O(1)	18 <i>b</i>	1.0	−0.2744(6)	−0.0944(5)	−0.0917(2)	1.79(10)
O(2)	18 <i>b</i>	1.0	−0.2326(6)	−0.2167(6)	−0.1452(2)	1.66(12)
O(3)	18 <i>b</i>	1.0	−0.2702(5)	0.0088(5)	−0.1514(2)	0.77(9)
O(4)	18 <i>b</i>	1.0	−0.4779(5)	−0.2392(6)	−0.1373(2)	1.25(9)
O(5)	18 <i>b</i>	1.0	−0.4013(5)	−0.0488(5)	−0.2206(2)	0.44(8)
O(6)	18 <i>b</i>	1.0	−0.4262(6)	−0.3070(6)	−0.2150(2)	1.32(10)
O(7)	18 <i>b</i>	1.0	0.0803(5)	−0.1010(5)	−0.2229(2)	0.27(7)
O(8)	18 <i>b</i>	1.0	−0.3680(4)	−0.1742(5)	−0.2732(2)	0.84(8)
O(9)	18 <i>b</i>	1.0	0.0057(7)	−0.1376(5)	−0.0115(2)	1.36(8)
O(10)	6 <i>a</i>	1.0	0.0	0.0	0.0421(2)	1.06(14)

in the literature [6]. The estimated standard deviations for unit-cell parameters in this work were smaller than those in the literature [6,11]. It is worth noting that the positional parameters of oxygen obtained by the neutron powder diffraction technique have the estimated standard deviations of equal level with those reported in the X-ray single-crystal work [6]. Using the refined occupancy factors, the Ca/P and O/P molar ratios were estimated to be 1.490(6) and 4.000 in agreement with the values (1.50 and 4.000) calculated from the chemical formula Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>. The thermal parameter of Ca(3) was higher than those of Ca(1) and Ca(2). The isotropic thermal parameters of O(7) and O(5) were lower than those of the other oxygen atoms, while those of O(1) and O(2) were higher.

### 3.2. Crystal structural feature of $\beta$ -TCP

#### 3.2.1. Two columns in $\beta$ -TCP

Fig. 2 shows the crystal structure of  $\beta$ -TCP depicted using the refined crystal parameters (Tables 1 and 2). The crystal structure of  $\beta$ -TCP can be described by the two kinds of columns of A and B types, running along the *c*-axis [4,6]. The A column has the form of  $\cdots$ P(1)O<sub>4</sub> Ca(4)O<sub>3</sub> Ca(5)O<sub>6</sub> P(1)O<sub>4</sub> $\cdots$ , while the B column  $\cdots$ P(3)O<sub>4</sub> Ca(1)O<sub>7</sub> Ca(3)O<sub>8</sub> Ca(2)O<sub>8</sub> P(2)O<sub>4</sub> P(3)O<sub>4</sub> $\cdots$ . Each A column is surrounded by six B columns, while each B column by two A and four B columns (Fig. 2a). In the A column, all the *x* and *y* atomic coordinates of Ca(4), Ca(5), and P(1) have the value of zero, indicating that these atoms are located on the straight line of *x* = *y* = 0 as shown in Fig. 2b. On the contrary, in the B column the *x* and *y* atomic coordinates of Ca(1), Ca(2), Ca(3), P(2), and P(3) have

different values from each other, although the ideal values would be *x* =  $-\frac{1}{3}$  and *y* =  $-\frac{1}{6}$  (Fig. 2c). This indicates that the B column is distorted, compared with A column from the point of view of atomic positions. The B column has a dense structure compared with the A column. In the A column four Ca and two P atoms exist, while the B column has six Ca and four P atoms (Fig. 2). There are no sharing oxygen atoms among P(1)O<sub>4</sub>, Ca(4)O<sub>3</sub>, and Ca(5)O<sub>6</sub> groups in the A column. On the contrary, in the B column, there are some sharing atoms among the polyhedra. The Ca(2)O<sub>8</sub> and P(2)O<sub>4</sub> groups are linked by sharing corner. The Ca(1)O<sub>7</sub> and P(3)O<sub>4</sub> groups are also linked by sharing corner. The Ca(3)O<sub>8</sub> is linked with Ca(1)O<sub>7</sub> and Ca(2)O<sub>8</sub> groups by sharing edges.

#### 3.2.2. CaO<sub>*n*</sub> polyhedron in $\beta$ -TCP (*n*=3,6,7 and 8)

Calcium atoms are located at five crystallographic sites from Ca(1) to Ca(5) (Tables 2 and 3). Coordination polyhedron CaO<sub>*n*</sub> was investigated through the Ca–O bonds with lengths less than 2.8 Å. The CN for the Ca(1) site is 7: CN(Ca(1))=7, CN(Ca(2))=6 or 8, CN(Ca(3))=8, CN(Ca(4))=3, and CN(Ca(5))=6 (Table 3). It is worth noting that the Ca(4) is three-fold coordinated, suggesting weak bonding and the formation of deficiency. The Ca(4)O<sub>3</sub> polyhedron with very small volume (Table 3) has a planar shape as shown in Fig. 2. Each of the Ca(1), Ca(2), Ca(3), and Ca(5) sites is occupied by one Ca atom, while the Ca(4) site was confirmed to have a deficiency: the occupancy factor was estimated to be 0.43(4). This deficiency feature is consistent with results from single-crystal X-ray work [6]. The Ca(4) site has the higher isotropic thermal parameter of 2.0(8) Å<sup>2</sup> compared with other Ca

Table 3  
Selected bond lengths, CN, BVS, volume of polyhedron, quadratic elongation, and bond angle variance in  $\beta$ -Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>

<i>Ca environments</i>			
Ca(1) CN = 7 BVS = 2.0	O(6)	2.327(7) Å	
	O(5)	2.390(7) Å	
	O(8)	2.419(6) Å	
	O(4)	2.451(8) Å	
	O(9)	2.464(8) Å	
	O(4')	2.471(8) Å	
	O(3)	2.512(7) Å	
	Volume of Ca(1)O <sub>7</sub> polyhedron	20.46 Å <sup>3</sup>	
	Ca(2) CN = 6 or 8 BVS = 2.1	O(9)	2.357(8) Å
		O(3)	2.375(7) Å
O(1)		2.406(7) Å	
O(7)		2.422(8) Å	
O(7')		2.424(7) Å	
O(2)		2.419(7) Å	
O(5)		2.702(7) Å	
O(6)		2.744(8) Å	
Volume of Ca(2)O <sub>8</sub> polyhedron		26.08 Å <sup>3</sup>	
Ca(3) CN = 8 BVS = 1.8		O(3)	2.354(7) Å
	O(5)	2.393(6) Å	
	O(6)	2.547(7) Å	
	O(8)	2.568(7) Å	
	O(10)	2.573(4) Å	
	O(2)	2.599(7) Å	
	O(8')	2.622(7) Å	
	O(1)	2.689(6) Å	
	Volume of Ca(3)O <sub>8</sub> polyhedron	25.99 Å <sup>3</sup>	
	Ca(4) CN = 3 BVS = 0.65	O(1, 1', 1'')	2.531(6) Å
Volume of Ca(3)O <sub>3</sub> polyhedron		0.67 Å <sup>3</sup>	
Ca(5) CN = 6 BVS = 2.7	O(4, 4', 4'')	2.211(9) Å	
	O(7, 7', 7'')	2.312(9) Å	
	Volume of Ca(5)O <sub>6</sub> polyhedron	14.71 Å <sup>3</sup>	
<i>PO<sub>4</sub> group details</i>			
P(1) CN = 4 BVS = 4.9	O(9, 9', 9'')	1.528(4) Å	
	O(10)	1.574(9) Å	
	Volume of P(1)O <sub>4</sub> polyhedron	1.866 Å <sup>3</sup>	
	Quadratic elongation	1.0026	
	Bond angle variance BVS = 4.9	10.9° <sup>2</sup>	
P(2) CN = 4 BVS = 5.0	O(1)	1.554(7) Å	
	O(2)	1.512(6) Å	
	O(3)	1.567(7) Å	
	O(4)	1.518(5) Å	
	Volume of P(2)O <sub>4</sub> polyhedron	1.858 Å <sup>3</sup>	
	Quadratic elongation	1.0034	
Bond angle variance	12.9°		
P(3) CN = 4 BVS = 5.0	O(5)	1.536(6) Å	
	O(6)	1.545(6) Å	
	O(7)	1.550(5) Å	
	O(8)	1.510(6) Å	
	Volume of P(3)O <sub>4</sub> polyhedron	1.852 Å <sup>3</sup>	
	Quadratic elongation	1.0021	
Bond angle variance	7.6° <sup>2</sup>		

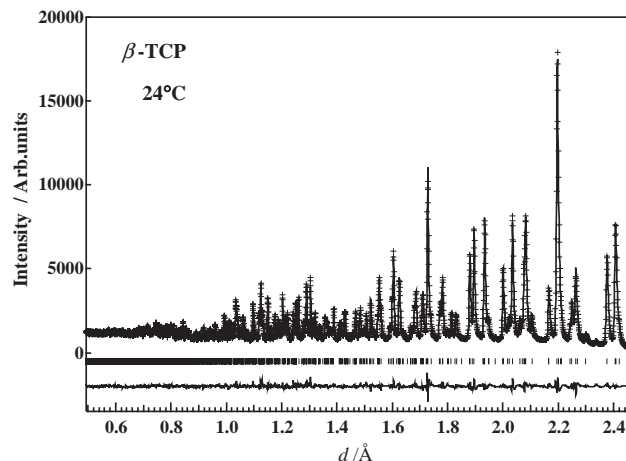


Fig. 1. Rietveld analysis pattern of neutron powder diffraction data measured by Sirius at 24°C. The solid lines are calculated intensities and crosses are observed intensities. The short vertical lines show the position of possible Bragg reflections. The difference between the observed and calculated intensities is plotted below the profile.

sites (Table 2), suggesting some disorder. The Ca(4) cation is also connected to three O(1) atoms with the highest thermal parameter of  $1.79 \text{ \AA}^2$ . BVSs [15] were calculated using the refined crystal data and the *VICS* computer program [16]. The BVS values were 2.0, 2.1, 1.8, 0.7, and 2.7 for Ca(1), Ca(2), Ca(3), Ca(4), and Ca(5) sites, respectively. A striking feature is the small BVS value for Ca(4) site 0.7, indicating that the Ca(4) is underbonded. This small value is consistent with the deficiency at this site. The BVS values for the Ca(1), Ca(2), and Ca(3) are nearly equal to 2 that is expected for Ca<sup>2+</sup> ion, while the Ca(5) site has a high BVS value of 2.7. This high value suggests overbonding in the Ca(5)O<sub>6</sub> polyhedron, corresponding to the short Ca(5)–O bond lengths (Table 3).

### 3.2.3. PO<sub>4</sub> polyhedron in $\beta$ -TCP

Phosphorus atoms are located at three crystallographic sites of P(1), P(2), and P(3) (Tables 2 and 3). Coordination polyhedron PO<sub>n</sub> was investigated through the P–O bonds with lengths less than 1.6 Å. All P atoms are four-fold coordinated with oxygen atoms:  $n = 4$ . The BVS values at P(1), P(2), and P(3) were 4.9, 5.0, and 5.0, respectively, indicating that the bonding in the PO<sub>4</sub> polyhedra behaves well. The quadratic elongations for the P(1)O<sub>4</sub>, P(2)O<sub>4</sub>, and P(3)O<sub>4</sub> are ranged from 1.0021 to 1.0034. The bond angle variances also have small values from 7.6° to 12.9°.

### 3.2.4. Bond lengths in $\beta$ -TCP

Average Ca–O bond distance was calculated for each Ca site and compared with the value expected from the ionic radius (Fig. 3). The ionic radii used were 1.00 Å for Ca with CN of 6:  $r(\text{Ca}[6]) = 1.00$ ,  $r(\text{Ca}[7]) = 1.06$ ,  $r(\text{Ca}[8]) = 1.12$ ,  $r(\text{Ca}[9]) = 1.18$ , and  $r(\text{O}[4]) = 1.38 \text{ \AA}$

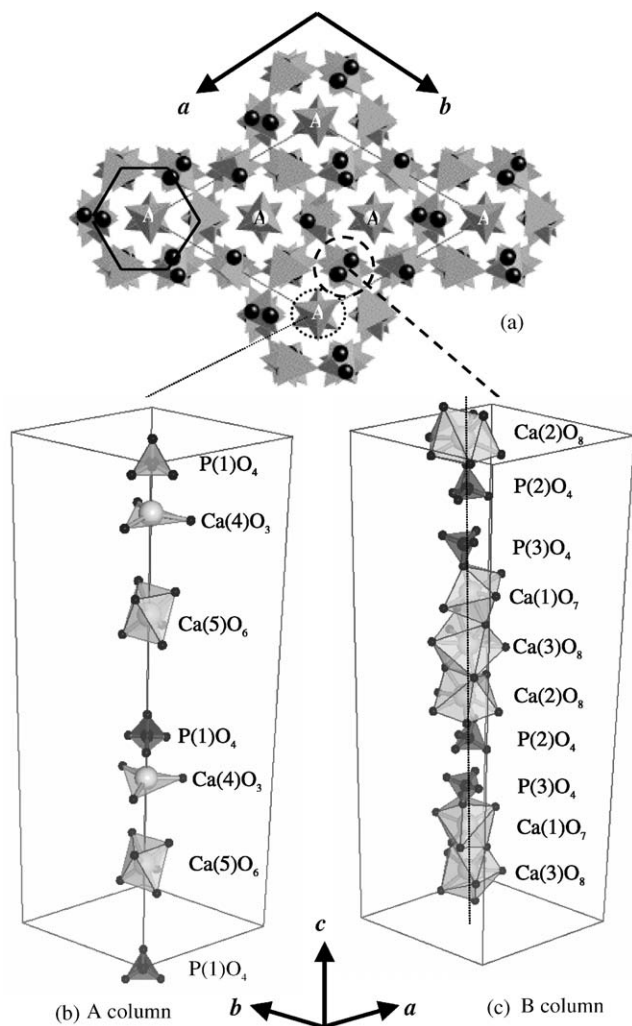


Fig. 2. (a) Projection of the crystal structure of  $\beta\text{-Ca}_3(\text{PO}_4)_2$  on the (001) plane, showing the A and B columns. 'A' denotes the A column, while no indication is given for B column. The rhombus in (a) denotes the hexagonal unit cell of  $\beta\text{-Ca}_3(\text{PO}_4)_2$ . (b) and (c) are the configurations of  $\text{CaO}_n$  and  $\text{PO}_4$  groups in the A and B columns, respectively, along the  $c$ -axis of the hexagonal cell ( $n = 3, 6, 7$ , and  $8$ ). (b) and (c) were made using a computer program *VICS* [16].

[17]. The expected Ca–O distance increased linearly with an increase of the CN of Ca. The average Ca–O distances at Ca(1), Ca(2), and Ca(3) sites that were obtained in the present structural analysis, agreed well with the expected values. The average Ca(5)–O distance calculated from the refined crystal structure was smaller than the expected value, corresponding to the high BVS value of 2.7. On the contrary, the observed average Ca(4)–O distance was much larger than the expected value as shown in Fig. 3, corresponding to the lower BVS value 0.7 for the Ca(4) site. The larger Ca(4)–O distance suggests weak bonding between oxygen and Ca(4) atoms accompanying with the low occupation rate 0.43 at the Ca(4) site. Thus, possible explanations of the larger isotropic thermal parameter and the deficiency at Ca(4) are the larger Ca(4)–O bond distances and the

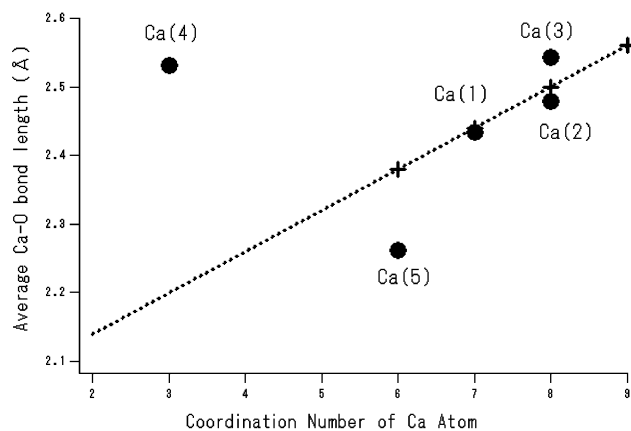


Fig. 3. Relationship between the CN and average Ca( $i$ )–O bond length in the  $\beta\text{-Ca}_3(\text{PO}_4)_2$  ( $i = 1, 2, 3, 4$ , and  $5$ ). The closed circles denote the average Ca( $i$ )–O distance obtained using the refined crystal parameters. The crosses are bond lengths estimated using ionic radii [17]. The linear dotted line is obtained by a fit to the Ca( $i$ )–O bond lengths expected by the ionic radii [17].

small CN value at Ca(4). These results indicate that the Ca(4) site is very different from other four Ca sites: The Ca(4) has lower occupancy factor of 0.43(4), a higher isotropic thermal parameter, a small BVS value, small CN and longer Ca–O distances.

### Acknowledgments

We acknowledge the Inamori foundation for the financial support and Kyowa Chemical Industry Co. for supplying the  $\text{CaHPO}_4$  powders. This work was done under the project no. 2002-B2-108 at the neutron science facility KENS, KEK, Japan.

### References

- [1] B.V. Rejda, J.G.J. Peelen, K. de Groot, *J. Bioeng.* 1 (1977) 93–97.
- [2] A. Bigi, L. Compostella, A.M. Fichera, E. Foresti, M. Gazzano, A. Ripamonti, N. Roveri, *J. Inorg. Biochem.* 34 (1988) 75–82.
- [3] R.W. Nurse, J.H. Welch, W. Gutt, *J. Chem. Soc.* 1959 (1959) 1077–1083.
- [4] J.C. Elliott, *Structure and Chemistry of the Apatites and Other Calcium Orthophosphates*, Elsevier, Amsterdam, The Netherlands, 1994.
- [5] J.F. Sarver, M.V. Hoffman, F.A. Hummel, *J. Electrochem. Soc.* 108 (1961) 1103–1110.
- [6] B. Dickens, L.W. Schroeder, W.E. Brown, *J. Solid State Chem.* 10 (1974) 232–248.
- [7] L.W. Schroeder, B. Dickens, W.E. Brown, *J. Solid State Chem.* 22 (1977) 253–262.
- [8] A. Makishima, H. Aoki, in: T. Yamaguchi, H. Yanagida (Eds.), *Bioceramics*, Giho-do Pub. Co., Tokyo, 1984, p. 28.
- [9] S. Nakamura, R. Otsuka, H. Aoki, M. Akao, N. Miura, T. Yamamoto, *Thermochim. Acta* 165 (1990) 57–72.
- [10] A. Bigi, G. Falini, E. Foresti, A. Ripamonti, M. Gazzano, N. Roveri, *Z. Kristallogr.* 211 (1996) 13–16.

- [11] N. Rangavittal, A.R. Landa-Canovas, J.M. Gonzalez-Calbet, M. Vallet-Regi, *J. Biomed. Mater. Res.* 51 (2000) 660–668.
- [12] S. Torii, T. Kamiyama, K. Mori, K. Oikawa, S. Itoh, M. Furusaka, S. Satoh, S. Ikeda, F. Izumi, H. Asano, *J. Phys. Chem. Solids* 60 (1999) 1583–1586.
- [13] T. Ohta, F. Izumi, K. Oikawa, T. Kamiyama, *Physica B (Amsterdam)* 234-236 (1997) 1093–1095.
- [14] I.D. Brown, D. Altermatt, *Acta Crystallogr. B* 41 (1985) 244–247.
- [15] K. Robinson, G.V. Gibbs, P.H. Ribbe, *Science* 172 (1971) 567–570.
- [16] F. Izumi, *J. Crystallogr. Soc. Jpn.* 44 (2002) 380–388.
- [17] R.D. Shannon, *Acta Crystallogr. A* 32 (1976) 751–767.
- [18] R.A. Young, E. Prince, R.A. Sparks, *J. Appl. Crystallogr.* 15 (1982) 357–359.