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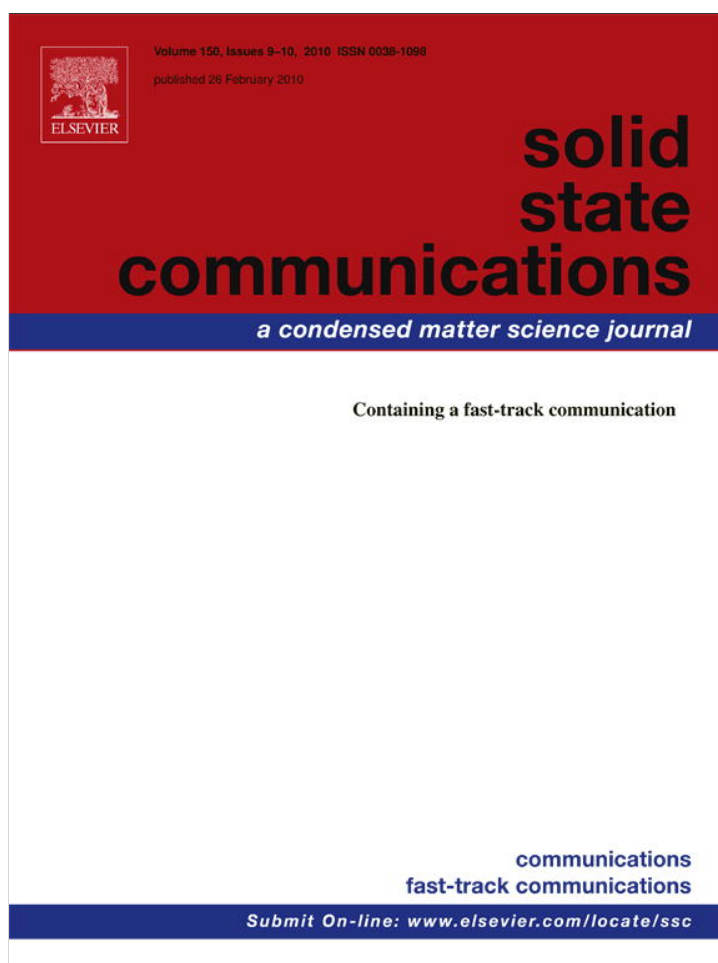


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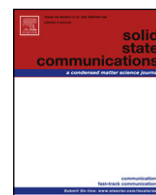
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X-ray diffraction study of β -Ca₃(PO₄)₂ at high pressure

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ABSTRACT

The β -tricalcium phosphate phase, β -Ca₃(PO₄)₂, has been studied at high pressures up to 15.4 GPa and room temperature in a diamond-anvil cell using angle-dispersive X-ray diffraction. No evidence of a phase transformation was observed in the present pressure range at 300 K. By fitting the pressure-volume data to a second-order Birch–Murnaghan equation of state, the bulk modulus, B_0 , was determined to be 79.5 ± 2.0 GPa.

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1. Introduction

Over the past 30 years, calcium phosphates have been in the limelight because of their biomedical applications and the absence of toxicity of their constituents. Many Ca–P materials have been widely used for bone reconstruction and replacement, bone defect-filling drug carriers, and coatings of metal prostheses [1–3]. Among them, β -tricalcium phosphate (β -TCP, Ca₃(PO₄)₂) and hydroxyapatite (HA, Ca₁₀(PO₄)₆(OH)₂) are the most important phosphates since they show an excellent biological compatibility and safety in living tissues [4–6]. Moreover, the β -TCP is found to be more advantageous than HA [7–9].

The physical properties of HA under high-pressure conditions have been investigated [10], however, there is little work on the properties and behaviors of the β -TCP under a high-pressure condition. The purpose of this study is to investigate the compressibility of a synthesized β -Ca₃(PO₄)₂ in a diamond-anvil cell to a high pressure combined with angle dispersive X-ray diffraction.

2. Experimental

High-purity β -TCP was prepared by solid-state reactions from CaHPO₄ and CaCO₃. Reagent-grade CaHPO₄ and CaCO₃ powders

were mixed in the proportion corresponding to the Ca₃(PO₄)₂ stoichiometry, and the mixture was ground sufficiently and pressed into pellets with a diameter of 5 mm under uniaxial pressure of 30 MPa. The pellets were sintered at 1300 K for 48 h to form a single phase. The sintered product was ground finely and characterized by a powder X-ray diffractometer. The X-ray pattern confirmed the formation of a single β -TCP phase.

The high-pressure X-ray diffraction experiments using a four-pin modified Merrill–Basset diamond-anvil cell with 500 μ m culets were carried out at Bayerisches Geoinstitut, Universität Bayreuth. The experimental method used in this study was similar to a previous study [11]. A Fe metal plate with an initial thickness of 250 μ m was used as a gasket. The central area of the plate was pre-indented to a thickness of about 45 μ m, and a hole of 250 μ m in diameter was drilled through it. The synthetic powdered β -TCP and a tiny ruby sphere (about 3 μ m in diameter) were loaded with the liquid He pressure medium into the hole in the gasket. The XRD patterns were recorded by a system consisting of a high-brilliance Rigaku rotating anode generator (Mo K α λ radiation, $\lambda = 0.7108$ Å) and a Bruker charge-coupled device (CCD) area detector. The collecting time of each pattern was 15 min. In order to obtain conventional one-dimensional diffraction spectra, all collected patterns were integrated using the Fit2D program [12]. The experimental pressure was monitored by the ruby fluorescence line [13], and the pressure error was estimated to be within 1 GPa.

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Table 1
Unit-cell parameters of β -TCP phase at various pressures.

P (GPa)	<i>a</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³)	(<i>c/c</i> ₀)/(<i>a/a</i> ₀)
0.0001	10.4318 (12)	37.323 (8)	3517.4 (8)	1.0000
1.9	10.3441 (12)	36.997 (9)	3428.3 (12)	0.9997
3.6	10.2768 (10)	36.758 (7)	3361.9 (8)	0.9997
5.7	10.2019 (9)	36.482 (7)	3288.3 (7)	0.9995
7.7	10.1314 (13)	36.242 (10)	3221.6 (10)	0.9998
9.4	10.0845 (11)	36.038 (8)	3173.9 (8)	0.9988
12.1	10.0136 (12)	35.835 (9)	3111.8 (10)	1.0002
13.6	9.9857 (12)	35.706 (9)	3083.4 (9)	0.9994
15.4	9.9535 (11)	35.524 (8)	3047.9 (8)	0.9975

Pressure values were determined by the ruby fluorescence method [13]. Number in parentheses represents the error of the lattice parameter. The data at 0.0001 GPa were obtained after decompression.

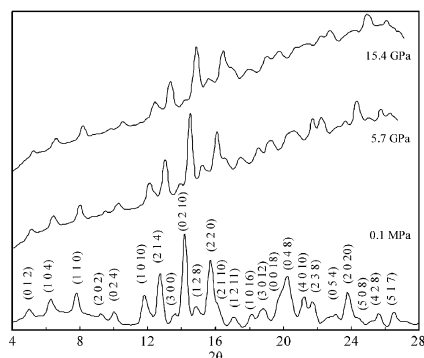


Fig. 1. Examples of X-ray diffraction patterns of β -Ca₃(PO₄)₂ at selected pressure and 300 K.

3. Results and discussion

Fig. 1 shows the representative powder X-ray diffraction patterns of β -TCP, crystallized in the rhombohedral structure with the space group *R3c* and *Z* = 21 [14,15]. The present X-ray diffraction data of the β -TCP phase at ambient pressure, collected after decompression, revealed its unit-cell dimensions of *a* = 10.4318(12) Å, *c* = 37.323(8) Å, and *V* = 3517.4(8) Å³, which are comparable to previous studies [14,15]. The high-pressure data were collected up to 15.4 GPa at room temperature (300 K). Although the peaks of β -TCP become slightly broader during increasing compression, they can be used to determine the sample volume with reliable uncertainty.

The effect of pressure on the unit-cell parameters and volume of the β -TCP phase is summarized in Table 1. And the evolution of unit-cell parameters (*a/a*₀) and (*c/c*₀) with pressure is plotted in Fig. 2. The unit-cell parameters of the β -TCP show a non-linear dependence on pressure over the pressure range. The (*c/c*₀)/(*a/a*₀) ratio of the β -TCP ranges from 0.9975 to 1.0002, essentially constant at 1, in the present pressure range, which indicates that the β -TCP is elastically isotropic (see Table 1 and Fig. 2).

The bulk modulus *B*₀ of β -TCP was derived by a least squares fitting of the data listed in Table 1 with a second-order Birch–Murnaghan equation of state [16]:

$$P = (3/2)B_0[(V/V_0)^{-7/3} - (V/V_0)^{-5/3}]$$

where *V* and *V*₀ denote the volumes at pressure *P* and ambient pressure, respectively. The results fit using v5.2 of the EosFit program [17], are *V*₀ = 3508.4(6.2) Å³, *B*₀ = 79.5(2.0) GPa, respectively. The unit-cell volume data of the β -TCP as a function of pressure and the compression curve calculated from these parameters are plotted in Fig. 3, compared with the compressible curve of HA calculated from previous study. In their study, Brunet et al. [10] fitted their experimental data of HA using a second-order Birch–Murnaghan equation of state. Therefore, it is possible to compare our data of β -TCP with the data of HA reported

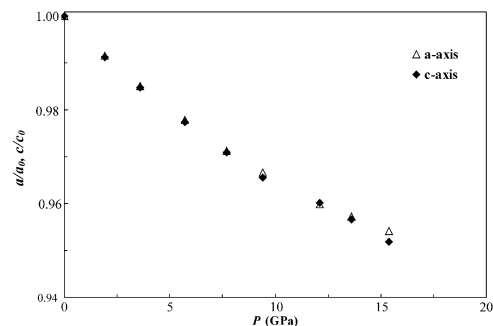


Fig. 2. Unit-cell parameters *a/a*₀ and *c/c*₀ of the β -Ca₃(PO₄)₂ at 300 K.

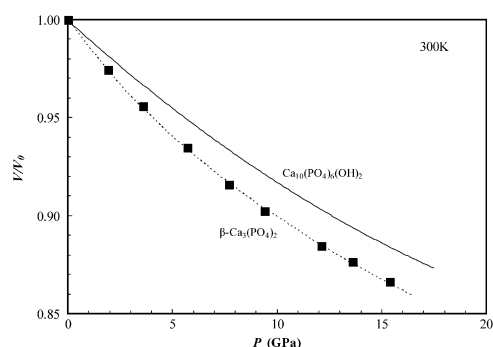


Fig. 3. Pressure–volume data for β -Ca₃(PO₄)₂ at 300 K. The dashed curve is the second-order Birch–Murnaghan equation fitting with *B*₀ = 79.5 GPa. The solid line represents the calculated *P*–*V* relationship of Ca₁₀(PO₄)₆(OH)₂ with *B*₀ = 97.5 GPa and *B*'₀ = 4 reported by Brunet et al. [10]. The error of pressure was estimated to be within 1 GPa in this study.

by Brunet et al. [10]. Obviously, the β -TCP is more compressible than HA, since the bulk modulus of β -TCP is substantially smaller (by about 20%) than that of HA (i.e. 97.5 GPa when *B*'₀ was fixed as 4) [10]. The differences in the elastic behavior of the β -TCP and HA can be attributed to the different compositions and structures since the β -Ca₃(PO₄)₂ has a rhombohedral structure belonging to the *R3c* space group [14], and in contrast, the Ca₁₀(PO₄)₆(OH)₂ is usually considered to be a hexagonal structure with space group *P6₃/m* [18].

4. Conclusions

The equation of state of synthetic β -Ca₃(PO₄)₂ was investigated by a diamond–anvil cell combined with X-ray diffraction up to a pressure of 15.4 GPa at 300 K. No phase transition was observed in the present study. Based on the experimental results, the bulk modulus of *B*₀ = 79.5(2.0) GPa was obtained using a second-order Birch–Murnaghan equation of state. The (*c/c*₀)/(*a/a*₀) ratio of the β -TCP is close to 1 in the present pressure range, implying an elastically isotropic behavior of the β -TCP.

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