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Equation of state of γ-tricalcium phosphate, γ-$Ca_3(PO_4)_2$, to lower mantle pressures

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ABSTRACT

The γ-tricalcium phosphate phase (γ-TCP), γ-$Ca_3(PO_4)_2$, is a high-pressure polymorph of tricalcium phosphate with a potential important implication as the reservoir of rare-earth elements and very large lithophile elements in the deep mantle. In situ synchrotron X-ray diffraction measurements of the γ-TCP phase have been carried out using a diamond-anvil cell to 40.29 GPa at room temperature, with a methanol-ethanol mixture as the pressure medium. The pressures in the measurements have been determined by using gold metal as the internal pressure calibrant. The third-order Birch-Murnaghan equation of state fitted to the experimentally defined unit-cell parameters suggests for the γ-TCP phase a density of $\rho_0 = 3.461(1)$ g/cm^3, an isothermal bulk modulus of $K_T = 100.2(13)$ GPa, and first pressure derivative of $K_T' = 5.48(16)$. When K_T' is fixed at 4, the derived K_T is 113.1(12) GPa.

Keywords: γ-$Ca_3(PO_4)_2$, equation of state, synchrotron X-ray diffraction, high pressure

INTRODUCTION

Apatite is well known as one of the common components of terrestrial and lunar rocks as well as of meteorites (Nash 1984), and contains very high levels of rare-earth elements (REEs) and very large lithophile elements (VLLEs). It breaks down to the γ-tricalcium phosphate phase [γ-TCP; γ-$Ca_3(PO_4)_2$], plus other phases, at pressures around 12 GPa (Murayama et al. 1986). The γ-TCP phase may be important in hosting the REEs and VLLEs in the deep Earth. Indeed, early experimental investigations suggested that the γ-TCP phase could be a potential important reservoir of REEs and VLLEs in the deep upper mantle (Murayama et al. 1986; Sugiyama and Tokonami 1987). The physical-chemical behaviors of the γ-TCP phase at high pressures are thus very important.

The γ-TCP phase is a high-pressure polymorph of tricalcium phosphate [TCP, $Ca_3(PO_4)_2$; Murayama et al. 1986]. Other polymorphs of TCP, including the α′-, α-, and β-phases (from high- to low-temperature stability), are stable at room pressure (Nurse et al. 1959; Welch and Gutt 1961; Fix et al. 1969). Previous study showed that the γ-TCP phase crystallizes in the rhombohedral system with a space group of $R\overline{3}m$ and unit-cell parameters of $a = 5.2487(6)$ Å and $c = 18.6735(36)$ Å (Sugiyama and Tokonami 1987). The γ-TCP phase has been found as a high-pressure phase in the Suizhou L6 chondrite and named as tuite (Xie et al. 2003). However, little is known about its thermodynamic and physical properties under high pressures.

In the present study, we investigated the pressure-volume equation of state (EoS) of a synthetic γ-$Ca_3(PO_4)_2$ at high pressures, using a diamond-anvil cell combined with synchrotron X-ray diffraction. In addition, we compared the density of the γ-TCP phase to those of apatites of different compositions, which break down to produce the γ-TCP phase at high pressures.

EXPERIMENTAL METHODS

The γ-TCP phase used in our synchrotron X-ray diffraction experiments was prepared by solid-state reaction from $CaHPO_4$ and $CaCO_3$. First, reagent-grade $CaHPO_4$ and $CaCO_3$ powders were mixed in a proportion corresponding to the $Ca_3(PO_4)_2$ stoichiometry. The mixture was ground for 2 h in an agate mortar and pressed into pellets with a diameter of 5 mm under a uniaxial pressure of 30 MPa. Second, the pellets were sintered in a conventional muffle furnace at 1300 K for 48 h to form a single phase of β-TCP. The sintered product was crushed and ground into powder and characterized by powder X-ray diffractometry. The XRD pattern confirmed a single β-TCP phase. Third, the β-TCP powder was used as the starting material to synthesize the γ-TCP phase. High-pressure and high-temperature synthesis was performed at 7 GPa and 1500 K for 24 h using a 5000-ton Kawai-type apparatus (USSA-5000) at the Institute for Study of the Earth's Interior, Okayama University. The synthesized product was characterized by a powder X-ray diffractometer and confirmed to be a pure γ-TCP phase. Finally, a mixture of γ-TCP plus about 10 wt% Au, the internal pressure marker, was prepared for later in situ X-ray diffraction measurements.

The high-pressure angle dispersive X-ray diffraction experiments using a symmetrical diamond-anvil cell were carried out at beamline X17C, National Synchrotron Light Source, Brookhaven

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National Laboratory. The experimental techniques used in this study were generally similar to those used in Liu et al. (2008). A T301 steel plate with an initial thickness of 250 μm was used as gasket. The central area of the plate was pre-indented to a thickness of about 30 μm, and a hole of 120 μm diameter was eroded electrically. The mixture of γ-TCP and Au, plus a couple of tiny ruby spheres, was loaded with the pressure medium (a 4:1 methanol-ethanol mixture) into the hole of the gasket. The ruby fluorescence method (Mao et al. 1978) was applied to guide the pressure increase. The incident synchrotron radiation beam was monochromatized to a wavelength of 0.4066 Å, and the beam size was collimated to ~25 × 20 μm^2. Two-dimensional images were recorded by using an online CCD detector. CeO_2 was used to calibrate the sample-detector distance. The X-ray diffraction patterns were collected for 10 to 30 min at each pressure, and later integrated as a function of 2θ using the Fit2d code software package (Hammersley 1996) to obtain conventional, one-dimensional diffraction profiles. The diffraction peak positions were determined using a peak-fitting program. The pressure was obtained, using the equation of state of Au proposed by Anderson et al. (1989), from the unit-cell volume determined using the 111, 200, and 220 diffraction lines of Au.

RESULTS AND DISCUSSION

The powder X-ray diffraction data of the γ-TCP phase at ambient pressure reveal that this phase has a rhombohedral structure ($R\bar{3}m$), with unit-cell dimensions of $a = 5.251(1)$ Å and $c = 18.692(2)$ Å. The observed and calculated X-ray diffraction patterns of the γ-TCP phase are shown in Table 1. The unit-cell volume and density of the γ-TCP phase at ambient pressure are 446.4(1) $Å^3$ and 3.461(1) g/cm^3, respectively. The unit-cell parameters and volume of the γ-TCP phase determined in this study are slightly larger than those values reported by Sugiyama and Tokonami (1987) (i.e., a = 5.2487 Å, c = 18.6735 Å, V = 445.5 $Å^3$).

The high-pressure X-ray diffraction data were collected to 40.29 GPa at ambient temperature. Figure 1 shows typical X-ray diffraction patterns obtained in this study. In addition to the diffraction peaks from the γ-TCP phase, there were diffraction peaks arising from the Au internal-pressure calibrant. The typical error in the pressure determinations was 0.20 GPa, based on the lattice parameters calculated using the diffraction lines of gold.

TABLE 1. Observed and calculated X-ray diffraction patterns of the γ-TCP phase at 0 GPa and 300 K

h k l	d_{obs} (Å)	d_{cal} (Å)	$d_{obs}/d_{cal^{-1}}$	I_{obs}
0 0 6	3.1126	3.1154	–0.0009	5
0 1 5	2.8871	2.8880	–0.0003	85
1 1 0	2.6251	2.6257	–0.0002	100
1 1 3	2.4191	2.4196	–0.0002	5
2 0 2	2.2096	2.2095	0.0000	23
0 0 9	2.0766	2.0769	–0.0001	15
1 1 6	2.0077	2.0077	0.0000	6
2 0 5	1.9421	1.9428	–0.0004	36
1 0 10	1.7283	1.7289	–0.0003	23
1 1 9	1.6289	1.6289	0.0000	2
1 2 5	1.5616	1.5618	–0.0001	14
3 0 0	1.5157	1.5160	–0.0002	14
2 0 11	1.3616	1.3612	0.0003	2
2 2 0	1.3131	1.3129	0.0002	14
2 1 10	1.2655	1.2653	0.0002	14

Note: Calculated *d* spacings are based on the rhombohedral unit-cell dimensions of a = 5.251 Å and c = 18.692 Å.

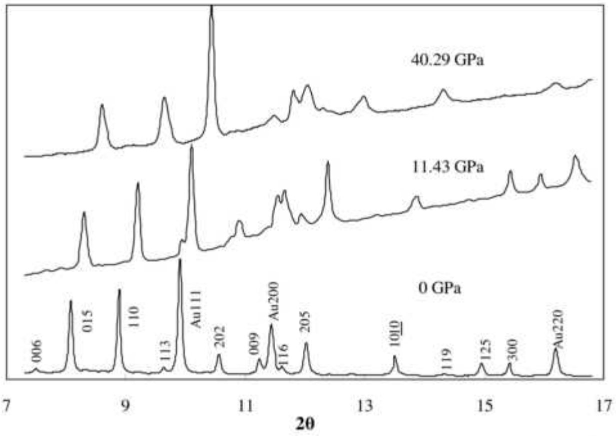

FIGURE 1. Representative X-ray diffraction patterns of γ-$Ca_3(PO_4)_2$ obtained in this study to 40.29 GPa at 300 K.

Although the peaks of gold and γ-TCP become broader with increasing compression (see Fig. 1) due to the development of non-hydrostatic conditions in the pressure medium, they can be used to determine the pressure and sample volume within reasonable uncertainties.

The effect of pressure on the unit-cell parameters and volumes of the γ-TCP phase is shown in Table 2, and the unit-cell parameters as functions of pressure are plotted in Figure 2. The divergence of the two unit-cell parameters shows that the a axis is more compressible than the c axis, and the ratio of c/a increases with increasing pressure (see Table 2), indicating an anisotropic elasticity for the γ-TCP phase. The pressure-volume data have been fitted to the third-order Birch-Murnaghan equation of state (Birch 1947) to determine the elastic parameters:

$$P = 3\,K_T f_E(1 + 2\,f_E)^{5/2}\,[1 + 3/2(K'_T - 4)\,f_E]$$

where P, K_T, and K'_T are pressure, isothermal bulk modulus, and the first pressure derivative of the isothermal bulk modulus, respectively. The term f_E, defined as $[(V_0/V)^{2/3} - 1]/2$, is the Eulerian

TABLE 2. Lattice parameters and volumes of the γ-TCP phase to 40.29 GPa

P (GPa)	*a* (Å)	*c* (Å)	*c/a*	Volume ($Å^3$)
0.0001	5.251(1)	18.692(2)	3.560(1)	446.4(1)
1.01(5)	5.229(1)	18.638(6)	3.564(1)	441.4(2)
2.12(7)	5.211(1)	18.588(5)	3.567(1)	437.2(2)
2.76(7)	5.199(1)	18.555(6)	3.569(1)	434.4(2)
3.87(5)	5.182(1)	18.517(4)	3.573(1)	430.7(1)
5.36(10)	5.163(1)	18.467(7)	3.577(2)	426.4(2)
8.10(10)	5.125(1)	18.375(6)	3.585(1)	418.1(2)
9.92(12)	5.103(1)	18.302(7)	3.587(2)	412.8(2)
11.43(9)	5.079(1)	18.244(7)	3.592(2)	407.6(2)
15.05(10)	5.041(1)	18.169(4)	3.604(1)	399.8(1)
16.88(19)	5.020(1)	18.111(3)	3.608(1)	395.3(1)
20.41(15)	4.987(1)	18.025(7)	3.614(2)	388.2(2)
24.06(15)	4.957(2)	17.957(9)	3.623(2)	382.3(2)
26.46(16)	4.932(2)	17.917(13)	3.633(3)	377.5(4)
28.26(19)	4.920(2)	17.888(11)	3.636(3)	375.1(3)
31.22(15)	4.896(1)	17.846(6)	3.645(1)	370.5(2)
33.71(17)	4.874(1)	17.804(7)	3.653(2)	366.4(2)
40.29(18)	4.832(2)	17.711(13)	3.665(3)	358.2(3)

Notes: Pressure was determined by the EoS of Au (Anderson et al. 1989). The number in the parentheses represents one standard deviation in the right-most digit. The measurement at 0.0001 GPa was obtained after decompression.

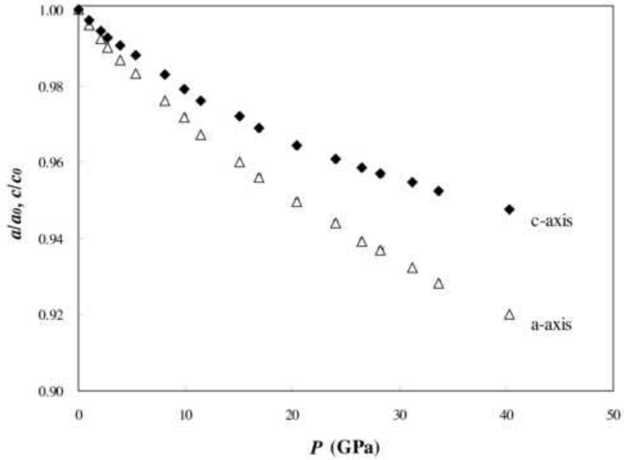

FIGURE 2. Unit-cell parameters *a* and *c* of γ-$Ca_3(PO_4)_2$ at 300 K. Note that the error bars are generally smaller than the symbols.

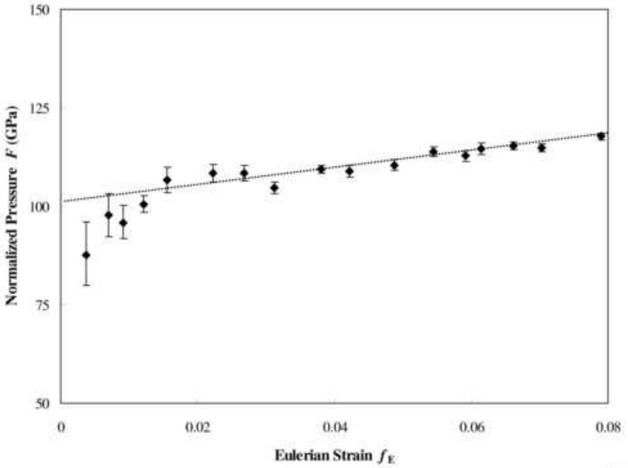

FIGURE 4. Eulerian strain-normalized pressure (f_E-F) plot of the γ-TCP phase. Dashed line represents the linear fit.

definition of finite strain. The zero-pressure volume and high-pressure volume are V_0 and V, respectively. The results from a least-squares fitting using the EosFit program (Angel 2001) are $V_0 = 446.3(1)$ Å^3, $K_T = 100.2(13)$ GPa, and $K'_T = 5.48(16)$, respectively. The unit-cell volume data as a function of pressure and the compression curve calculated from these fitted parameters are plotted in Figure 3. When the value of K'_T was set as 4, then $V_0 = 446.0(2)$ Å^3 and $K_T = 113.1(12)$ GPa were obtained.

To assess the quality of the Birch-Murnaghan EoS fit, the relationship between the Eulerian strain (f_E) and the normalized pressure $\{F = P/[3f_E\,(2f_E + 1)^{5/2}]\}$ was plotted in Figure 4. The f_E-F plot provides a visual indication of whether higher order terms, such as K'_T and K''_T, are significant in the equation of state. The positive slope of the f_E-F plot indicates that the first pressure derivative of the bulk modulus (K'_T) is higher than 4. Therefore, the value of the derived K'_T, 5.48(16), is consistent with the f_E-F plot analysis.

Since the γ-TCP phase is produced when apatite breaks down at ~12 GPa and 1300 °C (Murayama et al. 1986), it would be constructive to probe the difference in the physical-chemical properties between the γ-TCP phase and apatites. Figure 5 shows the pressure-density profiles of the γ-TCP phase and apatites of different compositions. As enough data on the elastic properties of these phases at high temperatures are not available, our calculation has been restricted to a temperature of 300 K (Table 3). It is obvious in Figure 5 that the density of the γ-TCP phase is about 10% higher than those of the apatites, implying that the γ-TCP phase is more stable at the pressure conditions of the deep mantle, in agreement with previous direct experimental observation (Murayama et al. 1986).

As mentioned earlier, apatite is an important repository for phosphorus, REEs, and VLLEs in the upper mantle (e.g., Pan and

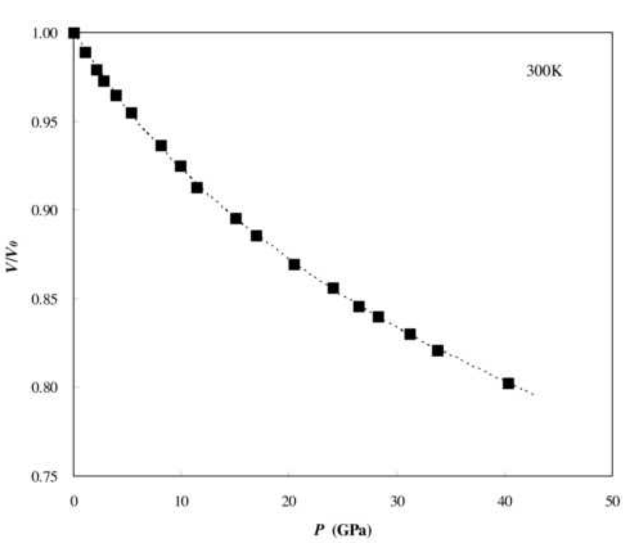

FIGURE 3. Pressure-volume data of γ-$Ca_3(PO_4)_2$ at 300 K. Dashed curve represents the third-order Birch-Murnaghan equation fitting with K_0 and K'_0 of 100.2 GPa and 5.48, respectively.

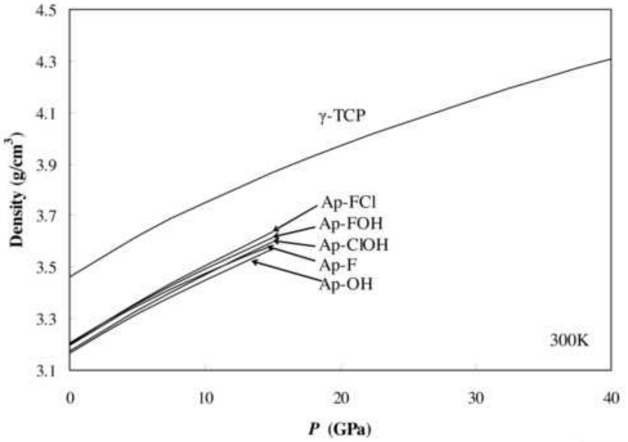

FIGURE 5. Comparison of the densities of the γ-TCP phase and apatites of different compositions at 300 K, with the γ-TCP phase shown as γ-TCP (this study), natural apatite $Ca_5(PO_4)_3F_{0.94}Cl_{0.06}$ as Ap-FCl (Matsukage et al. 2004), fluorapatite $Ca_5(PO_4)_3F_{0.975}OH_{0.025}$ as Ap-FOH (Brunet et al. 1999), chlorapatite $Ca_5(PO_4)_3Cl_{0.7}OH_{0.3}$ as Ap-ClOH (Brunet et al. 1999), fluorapatite $Ca_5(PO_4)_3F$ as Ap-F (Comodi et al. 2001), and hydroxyapatite $Ca_5(PO_4)_3OH$ as Ap-OH (Brunet et al. 1999).

TABLE 3. Parameters of the Birch-Murnaghan equations of state and densities of γ-$Ca_3(PO_4)_2$ and apatites

Composition	K_T (GPa)	K'_T	V_0 (Å^3)	ρ_0 (g/cm^3)	Reference
$Ca_3(PO_4)_2$	100.2	5.48	446.3	3.462	This study
$Ca_5(PO_4)_3OH$	97.5	4(fixed)	526.9	3.166	Brunet et al. (1999)
$Ca_5(PO_4)_3F_{0.975}(OH)_{0.025}$	97.9	4(fixed)	522.4	3.205	Brunet et al. (1999)
$Ca_5(PO_4)_3Cl_{0.7}(OH)_{0.3}$	93.1	4(fixed)	539.3	3.172	Brunet et al. (1999)
$Ca_5(PO_4)_3F$	93	5.8	524.2	3.195	Comodi et al. (2001)
$Ca_5(PO_4)_3F_{0.94}Cl_{0.06}$	91.5	4.0	524.2	3.201	Matsukage et al. (2004)

Notes: K_T, K'_T, and V_0 are the isothermal bulk modulus, the first derivative of the isothermal bulk modulus, and the zero-pressure volume at 300 K, respectively. ρ_0 is the density at 0 GPa and 300 K.

Fleet 1996), but eventually breaks down to produce the γ-TCP phase and other phases at about 12 GPa. Consequently the γ-TCP phase might be very important in hosting these elements under conditions at which apatites are not stable any more. The γ-TCP phase has, within its structure, two large cation sites with mean bond lengths of 2.739 and 2.588 Å, respectively (Sugiyama and Tokonami 1987). This unique arrangement gives the γ-TCP phase the capability to host cations larger than Ca. The structural properties of γ-TCP with high levels of REEs and VLLEs are currently under investigation.

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