

# The stability and equation of state for the cotunnite phase of TiO<sub>2</sub> up to 70 GPa

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**Abstract** The stability and equation of state for the cotunnite phase in TiO<sub>2</sub> were investigated up to a pressure of about 70 GPa by high-pressure in situ X-ray diffraction measurements using a laser-heated diamond anvil cell. The transition sequence under high pressure was rutile →  $\alpha$ -PbO<sub>2</sub> phase → baddeleyite phase → OI phase → cotunnite phase with increasing pressure. The cotunnite phase was the most stable phase at pressures from 40 GPa to at least 70 GPa. The equation of state parameters for the cotunnite phase were established on the platinum scale using the volume data at pressures of 37–68 GPa after laser annealing, in which the *St* value, an indicator of the magnitude of the uniaxial stress component in the samples, indicates that these measurements were performed under quasi-hydrostatic conditions. The third-order Birch-Murnaghan equation of state at  $K_0' = 4.25$  yields  $V_0 = 15.14(5)$  cm<sup>3</sup>/mol and  $K_0 = 294(9)$ , and the second-order Birch-Murnaghan equation of state yields  $V_0 = 15.11(5)$  cm<sup>3</sup>/mol and  $K_0 = 306(9)$ . Therefore, we conclude that the

bulk modulus for the cotunnite phase is not comparable to that of diamond.

**Keywords** TiO<sub>2</sub> · Cotunnite · Fluorite · Phase relation · Equation of state · High pressure

## Introduction

Titanium dioxide (TiO<sub>2</sub>) has many polymorphs, with anatase, brookite, and rutile being the most abundant in nature. The structures and stabilities of the high-pressure phases of TiO<sub>2</sub> are of great interest in the geosciences because of the accessible analog of metal dioxide in the rocky mantle and core of the Earth. Under high pressure, TiO<sub>2</sub> transforms into (in order of increasing pressure)  $\alpha$ -PbO<sub>2</sub>, baddeleyite, OI, and cotunnite phases (Olsen et al. 1999; Dubrovinskaia et al. 2001, 2002; Dubrovinsky et al. 2001; Ahuja and Dubrovinsky 2002a, b). Recently, Mattesini et al. (2004) reported the existence of a fluorite-like cubic phase together with the cotunnite phase at 48 GPa after heating at 1,900–2,100 K, and proposed that this cubic phase is the densest TiO<sub>2</sub> phase above 40 GPa based on the equations of states for both the cubic and cotunnite phases. They also suggested that the cubic phase, rather than the cotunnite phase, is the most stable phase above 40 GPa. Since several metal dioxides are known to transform into the cubic fluorite phase at high pressure, the existence of a fluorite phase has been postulated for TiO<sub>2</sub> (Lagarec and Desgreliers 1995; Haines et al. 1993). However, theoretical calculations predict that the cotunnite phase is more stable than the fluorite phase even above 40 GPa (Muscat et al. 2002), and the formation of the cotunnite phase has been reported at 64 GPa after heating at 1,800 K (Dubrovinsky et al. 2001; Dubrovinskaia et al. 2002; Ahuja and

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Dubrovinsky 2002a, b). Recent experimental and theoretical work also reported the formation of the cotunnite phase at 56–48 GPa and 1,800 K (Al-Khatatbeh et al. 2009). Therefore, the stability of the cotunnite phase in  $\text{TiO}_2$  still remains controversial.

It is also claimed that cotunnite-type  $\text{TiO}_2$  is the hardest known oxide as a very high isothermal bulk modulus and microhardness (Dubrovinsky et al. 2001; Dubrovinskaia et al. 2002; Ahuja and Dubrovinsky 2002a, b). The isothermal bulk modulus of the cotunnite phase was reported to be 431 GPa (Dubrovinsky et al. 2001; Dubrovinskaia et al. 2002; Ahuja and Dubrovinsky 2002a, b), and this value is close to that of diamond (444 GPa) (Sung and Sung 1996). However, the experiments in these studies were apparently conducted under non-hydrostatic conditions, because these experiments were performed without a pressure medium and the volume measurements were made by varying the pressure. This procedure produces large stress inhomogeneities in a sample. Moreover, these previous studies failed to mention the pressure scales that were used; this is a serious omission since pressure scales are crucial when discussing equations of state at very high pressures. No other experiments under hydrostatic conditions have been reported, and a recent theoretical study predicts the bulk modulus for the cotunnite phase to be in the range 221–362 GPa (Caravaca et al. 2009; Al-Khatatbeh et al. 2009). Therefore, it is still unclear whether the bulk modulus of the cotunnite phase is similar to that of diamond.

Here, we report the stability and the equation of state for the cotunnite phase in  $\text{TiO}_2$  up to 70 GPa under quasi-hydrostatic conditions using a diamond anvil cell combined with laser annealing.

## Experiment

In our experiments, rutile (99.9%, Soekawa Chemicals) was used as the starting material. It was mixed with a fine platinum powder, which was used as a laser absorber and a pressure calibrant. High pressures were generated using a lever-type diamond anvil cell with 350  $\mu\text{m}$  culet diamonds. The samples were sandwiched between NaCl pellets and loaded into a hole that was drilled into a rhenium gasket. The samples, together with the NaCl pellets, were dried in a drying furnace at 130°C after sampling. NaCl was employed as the pressure-transmitting medium to reduce deviatoric stresses and temperature gradients in the sample chamber. Heating was carried out by irradiating with Nd:YAG laser beams from two sides with a 50–80  $\mu\text{m}$  diameter heating spot.

Angle-dispersive X-ray diffraction (XRD) measurements were conducted at high pressure and room

temperature using the BL13A beamline at the Photon Factory of KEK, Japan. This beamline provides a collimated beam (30  $\mu\text{m}$  in diameter) of monochromatic X-ray radiation (wavelength: 0.4266 Å). The XRD spectra were recorded using an imaging plate detector. The sample–detector distance and inclination of the imaging plate were calibrated using a standard material ( $\text{CeO}_2$ ) at 1 atm. Two-dimensional XRD images were integrated as a function of  $2\theta$  to obtain conventional one-dimensional diffraction profiles.

Pressures were determined from the observed unit-cell volume of platinum using the equation of state proposed by Holmes et al. (1989), and the pressure errors were calculated from uncertainties in the unit-cell volume of platinum. The  $St$  value, an indicator of the magnitude of the uniaxial stress component in the samples, was calculated from the (111), (200), and/or (220) diffraction lines of platinum (Shim et al. 2000). The obtained  $St$  value was smaller than 0.005, which indicates that the uniaxial component was sufficiently small and that the volume measurements were performed under quasi-hydrostatic conditions (Shim et al. 2000). The experimental conditions, together with the  $St$  values, are summarized in Table 1.

## Phase relations in $\text{TiO}_2$ and stability of the cotunnite phase at high pressure

The first run was conducted in compression up to about 44 GPa; Fig. 1 shows representative XRD patterns obtained in this run. The experimental conditions and the product phases are summarized in Table 1. The starting material was compressed to 11.9 GPa at room temperature. The XRD pattern at 11.9 GPa before heating was broad and contained reflections due to rutile and the baddeleyite phase (Fig. 1a). This is in good agreement with previous studies in which the transition from rutile and anatase to the baddeleyite phase was observed at about 12 GPa without heating (Dubrovinskaia et al. 2001; Haines and Léger 1993). After heating at 2,200 K for 20 min, the pressure increased to 13.2 GPa at room temperature and the XRD pattern changed to one indicating the coexistence of the  $\alpha\text{-PbO}_2$  and baddeleyite phases with a minor amount of rutile (Fig. 1b). Then we repeated the XRD observations after heating the sample at 2,500 K at each increment of pressure. The diffraction lines from the  $\alpha\text{-PbO}_2$  phase became weak and the single phase of baddeleyite was obtained at 19.1 GPa (Fig. 1c). The XRD patterns at pressures of 22.5–28.7 GPa reveal the coexistence of the baddeleyite and OI phases (Fig. 1d). The OI phase was solely stable at 35.3–36.2 GPa (Fig. 1e). The cotunnite phase appeared, accompanied with the OI phase, at 37.4 GPa (Fig. 1f), and the OI phase

**Table 1** Experimental conditions and identified product phases at room temperature after heating

No.	Pt					P (GPa) <sup>b</sup>	T (K) <sup>c</sup>	Heating time (min)	Result
	<i>d</i> [111] (Å)	<i>d</i> [200] (Å)	<i>d</i> [220] (Å)	<i>a</i> (Å)	<i>Sr</i> <sup>a</sup>				
Compression in Run 1									
T001	2.2366(7)	1.9418(32)	1.3662(18)	3.8713(59)	0.014	11.9(22)	–	–	R + Bd
T002	2.2318(2)	1.9338(4)	1.3668(1)	3.8663(6)	0.002	13.2(2)	2,200	20	A + Bd
T004	2.2263(2)	1.9284(5)	1.3625(3)	3.8551(10)	0.002	16.2(4)	2,500	15	A + Bd
T006	2.2214(1)	1.9246(3)	1.3604(1)	3.8482(4)	0.001	18.1(2)	2,500	10	A + Bd
T008	2.2204(3)	1.9239(8)	1.3587(5)	3.8449(15)	0.003	19.1(6)	2,500	10	Bd
T010	2.2138(3)	1.9177(5)	1.3548(4)	3.8334(11)	0.002	22.5(5)	2,500	10	Bd + O
T012	2.2110(1)	1.9157(3)	1.3540(1)	3.8301(5)	0.002	23.5(2)	2,500	10	Bd + O
T014	2.2010(4)	1.9083(7)	1.3481(2)	3.8139(12)	0.003	28.7(6)	2,500	10	Bd + O
T016	2.1910(1)	1.8984(6)	1.3411(3)	3.7946(11)	0.003	35.3(6)	2,500	10	O
T018	2.1889(2)	1.8972(6)	1.3404(2)	3.7921(9)	0.003	36.2(5)	2,500	10	O
T020	2.1876(1)	1.8956(6)	1.3391(3)	3.7888(11)	0.003	37.4(6)	2,500	10	O + C
T022	2.1824(1)	1.8913(7)	1.3361(3)	3.7802(11)	0.003	40.7(6)	2,500	10	C
T024	2.1777(2)	1.8867(2)	1.3337(1)	3.7725(4)	0.001	43.6(2)	2,500	10	C
Compression in Run 2									
G004	2.1678(2)	1.8782(2)	1.3277(1)	3.7551(4)	0.001	50.7(3)	1,600	60	C
G006	2.1640(2)	1.8745(4)	1.3246(3)	3.7471(8)	0.002	54.1(5)	1,600	15	C
G008	2.1562(2)	1.8687(6)	1.3203(2)	3.7350(9)	0.003	59.6(7)	1,800	15	C
G010	2.1538(1)	1.8667(7)	1.3185(4)	3.7303(12)	0.003	61.7(9)	1,700	15	C
G012	2.1523(4)	1.8661(7)	1.3183(2)	3.7292(12)	0.003	62.3(9)	1,700	15	C
G014	2.1502(1)	1.8638(9)	1.3162(4)	3.7239(15)	0.004	64.8(11)	1,700	15	C
G016	2.1471(4)	1.8612(5)	1.3153(1)	3.7201(9)	0.003	66.6(7)	1,700	15	C
G018	2.1462(3)	1.8606(7)	1.3143(3)	3.718(12)	0.003	67.6(9)	2,000	15	C
Decompression in Run 2									
G020	2.1474(2)	1.8605(2)	1.3152(1)	3.7197(4)	0.001	66.8(3)	2,000	15	C
G022	2.1498(3)	1.8632(5)	1.3166(1)	3.7242(8)	0.002	64.7(6)	2,000	15	C
G024	2.1517(7)	1.8659(6)	–	3.7293(24)	0.004	62.2(17)	2,000	15	C
G026	2.1532(3)	1.8659(3)	1.3188(1)	3.7301(6)	0.002	61.8(4)	2,000	15	C
G028	2.1574(1)	1.8695(6)	1.3206(3)	3.7362(11)	0.003	59.0(8)	2,000	15	C
G030	2.1685(4)	1.8785(7)	1.3268(5)	3.7542(14)	0.003	51.1(9)	2,000	15	C
G034	2.1935(1)	1.9013(10)	1.3424(5)	3.7985(17)	0.004	33.9(9)	–	–	C
G035	2.2200(5)	1.9248(7)	1.3596(4)	3.8467(12)	0.004	18.6(5)	–	–	C
G036	–	–	–	–	–	0	–	–	A

A  $\alpha$ -PbO<sub>2</sub>, Bd baddeleyite, C cotunnite, O OI phase, R rutile

<sup>a</sup> *Sr*, an indicator of the magnitude of the uniaxial stress in the sample, was calculated as average value from Pt peaks (Shim et al. 2000)

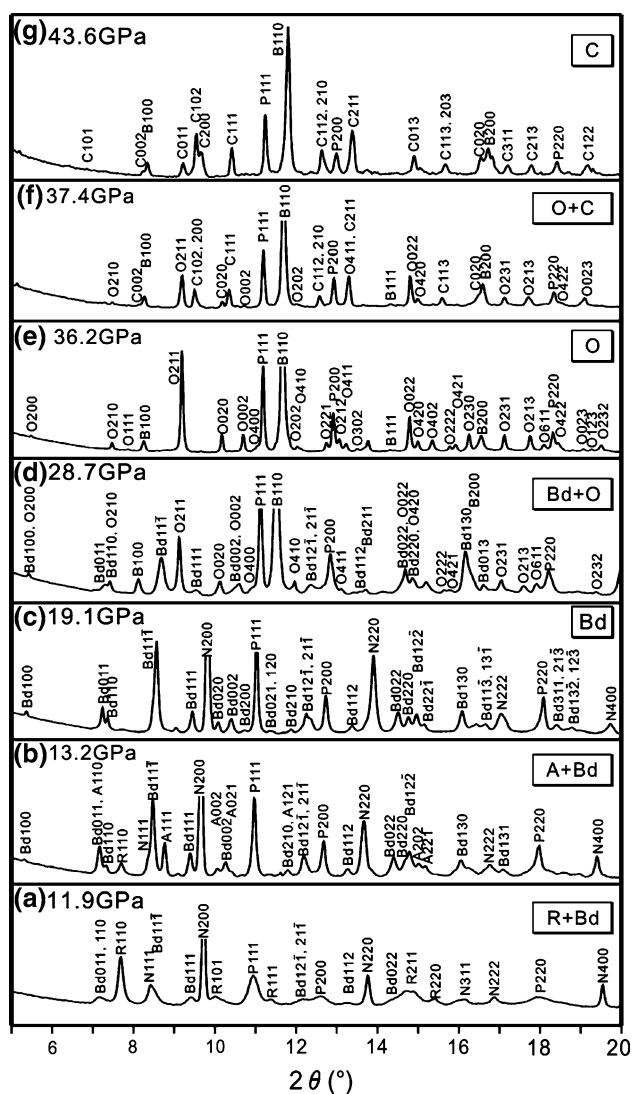
<sup>b</sup> Pressure was determined by equation of state of platinum at room temperature after or without heating (Holmes et al. 1989)

<sup>c</sup> Temperature uncertainties were about  $\pm 200$  K

disappeared at 40.7 GPa. The cotunnite phase was observed even at 43.6 GPa after heating at 2,500 K for 10 min (Fig. 1g). The fluorite-like cubic phase reported by Matte-sini et al. (2004) was not observed at all during this run.

In the second run, XRD observations were conducted during compression and decompression with and without heating. Representative XRD patterns obtained during the second run are shown in Fig. 2, and the experimental conditions and the product phases are listed in Table 1. The

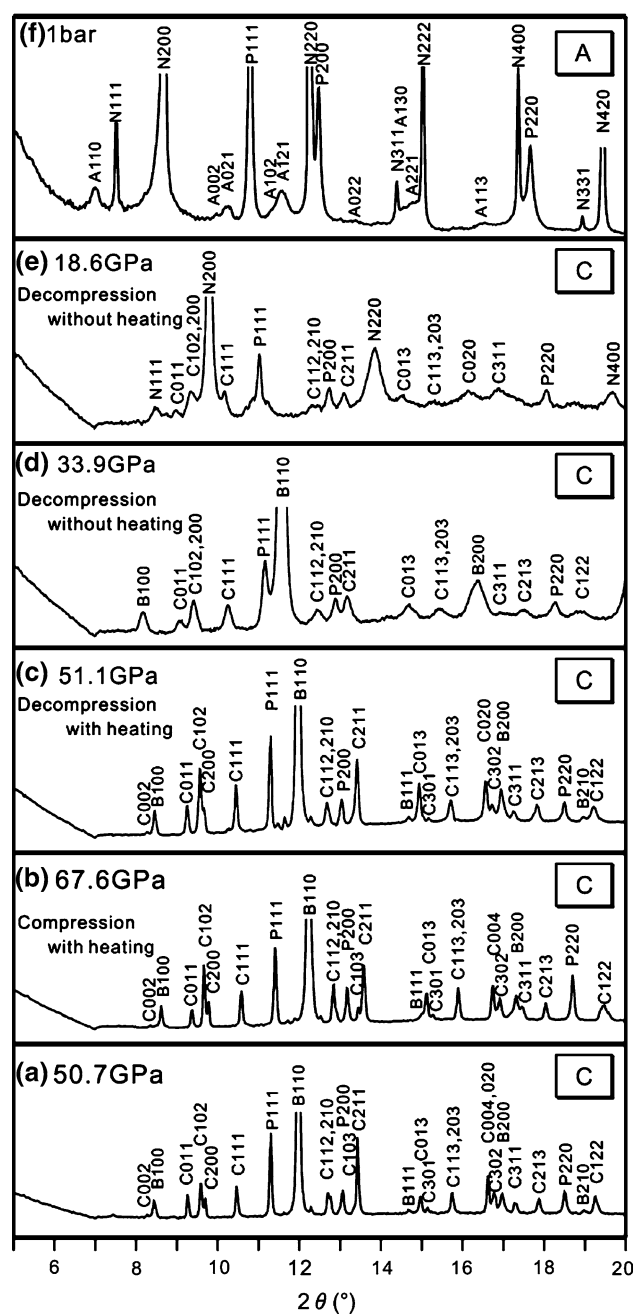
starting material was compressed to 55 GPa and then heated. After heating at 1,600 K for 60 min, the pressure dropped to 50.7 GPa and the cotunnite phase was observed (Fig. 2a). The sample was further compressed by applying a high pressure and heated at 1,600–2,000 K. Only the cotunnite phase was stable during compression up to 67.6 GPa (Fig. 2b), in agreement with previous studies that have observed the cotunnite phase up to 80 GPa (Dubrovinsky et al. 2001; Dubrovinskaya et al. 2002; Ahuja and



**Fig. 1** Representative XRD patterns ( $\lambda = 0.4266 \text{ \AA}$ ) at room temperature during compression during run 1 obtained prior to heating (a), obtained after heating at 2,200–2,500 K (b–g) (see Table 1). A  $\alpha$ -PbO<sub>2</sub>, B NaCl-B2, Bd baddeleyite, C cotunnite, N NaCl-B1, O OI, P platinum, R rutile

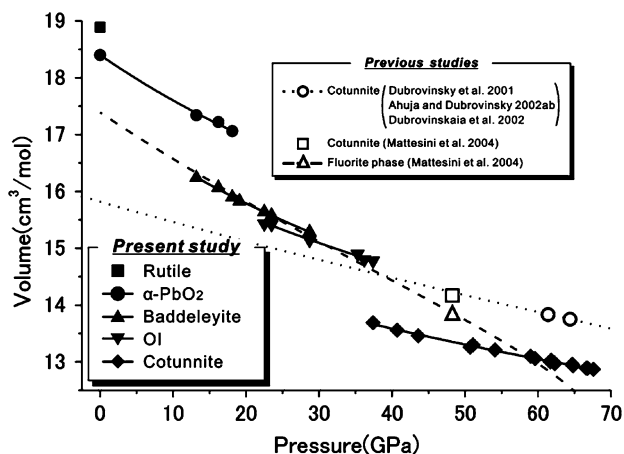
Dubrovinsky 2002a, b). On decompression and heating at 2,000 K, the cotunnite phase was stable at 51.1 GPa (Fig. 2c). The sample was further decompressed to 33.9 GPa at room temperature, and the reflections from the cotunnite phase became broad (Fig. 2d). The cotunnite phase was still observed at 18.6 GPa (Fig. 2e). In the recovered sample at ambient conditions, the cotunnite phase disappeared and only weak diffraction peaks from the  $\alpha$ -PbO<sub>2</sub> phase were observed (Fig. 2f). Once again, the fluorite-like cubic phase was not observed during this compression and decompression process.

The phase transition sequence with increasing pressure was found to be rutile  $\rightarrow$   $\alpha$ -PbO<sub>2</sub> phase  $\rightarrow$  baddeleyite phase  $\rightarrow$  OI phase  $\rightarrow$  cotunnite phase in this study. The



**Fig. 2** Representative XRD patterns ( $\lambda = 0.4266 \text{ \AA}$ ) at 300 K during compression and decompression in run 2. (a) 50.7 GPa after heating at 1,600 K, (b) 67.6 GPa after heating at 2,000 K, (c) 51.1 GPa after heating at 2,000 K, (d) 33.9 GPa without heating, (e) 18.6 GPa without heating and (f) ambient conditions. A  $\alpha$ -PbO<sub>2</sub>, B NaCl-B2, C cotunnite, N NaCl-B1, P platinum

cotunnite phase was synthesized from the OI phase at 37.4 GPa after heating at 2,500 K during the compression process in run 1 (Fig. 1). It was also synthesized directly from the starting material (rutile) at 50.7 GPa and remained stable at 67.6 GPa after heating in run 2 (Fig. 2). Our results suggest that the cotunnite phase is the most



**Fig. 3** Pressure dependence of volume of the high-pressure polymorphs of  $\text{TiO}_2$  at room temperature. *Solid symbols* represent the results of the present study obtained after laser annealing, and *solid lines* represent the compression curves for each phase obtained by fitting the second-order Birch-Murnaghan equation of state (see Table 3). *Open symbols* represent the cotunnite and fluorite phases in the previous studies (Dubrovinsky et al. 2001; Ahuja and Dubrovinsky 2002a, b; Dubrovinskaja et al. 2002; Mattesini et al. 2004). *Dotted and dashed lines* represent the compression curves for the cotunnite and fluorite phases in the previous studies, respectively

stable phase at pressures from 37.4 GPa to at least 67.6 GPa, while we could not observe the fluorite-like cubic phase that Mattesini et al. (2004) found at 48 GPa after heating at 1,900–2,100 K, which they proposed as the densest phase at pressures above 40 GPa. We measured the unit-cell volumes of each phase carefully after laser annealing, and the results are plotted in Fig. 3. The unit-cell volumes of the cubic phase reported by Mattesini et al. (2004) are larger than those of the cotunnite phase up to about 60 GPa in this study (Fig. 3). This is consistent with the cubic phase not being observed in this study. The unit-cell volume for the cubic phase becomes smaller than the cotunnite phase observed in this study at pressures above 60 GPa, suggesting that the cubic phase may form at pressures above 60 GPa; however, the cubic phase was not observed above 60 GPa in this study. Theoretical calculations (Muscat et al 2002) predict that the cotunnite phase is more stable than the fluorite phase even at 70 GPa, in good agreement with the results of the present study. Mattesini et al. (2004) discussed the stability of the cubic phase by comparing the equations of state of the cubic and cotunnite phases reported by Dubrovinsky et al. (2001). However, the equation of state for the cotunnite phase reported by Dubrovinsky et al. (2001) is quite different from the cotunnite phase observed in this study (see Fig. 3); this is discussed in detail later below. The unit-cell volume of the cotunnite phase observed in the present study also differs markedly from that reported by Mattesini et al. (2004). Since the experiments of Mattesini et al. (2004) were conducted by

**Table 2** Unit-cell parameters for  $\text{TiO}_2$  phases at high pressure and room temperature after heating

No.	P (GPa)	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	$\beta$ (°)	<i>V</i> (Å <sup>3</sup> )
$\alpha$ - $\text{PbO}_2$ phase (Pbcn)						
G036 <sup>a</sup>	0	4.547(12)	5.466(6)	4.915(3)		122.2(7)
T002	13.2(2)	4.401(7)	5.382(3)	4.864(2)		115.2(4)
T004	16.2(4)	4.389(6)	5.370(6)	4.859(2)		114.5(4)
T006	18.1(2)	4.366(4)	5.352(5)	4.853(3)		113.4(3)
Baddeleyite phase (P 2 <sub>1</sub> /c)						
T002	13.2(2)	4.645(5)	4.868(2)	4.825(5)	98.67(6)	107.8(3)
T004	16.2(4)	4.630(3)	4.858(2)	4.798(4)	98.46(5)	106.8(2)
T006	18.1(2)	4.610(3)	4.855(2)	4.769(3)	98.27(4)	105.6(2)
T008	19.1(6)	4.602(2)	4.855(1)	4.754(2)	98.18(2)	105.1(1)
T010	22.5(5)	4.587(7)	4.843(4)	4.720(5)	97.89(7)	103.9(4)
T012	23.5(2)	4.578(9)	4.842(5)	4.712(7)	97.86(9)	103.5(6)
T014	28.7(6)	4.543(8)	4.837(3)	4.665(6)	97.72(10)	101.6(4)
OI phase (Pbca)						
T010	22.5(5)	9.065(2)	4.860(2)	4.653(3)		205.0(2)
T012	23.5(2)	9.066(12)	4.839(8)	4.668(5)		204.8(9)
T014	28.7(6)	9.014(5)	4.835(3)	4.616(3)		201.2(4)
T016	35.3(6)	8.962(2)	4.814(1)	4.589(1)		198.0(2)
T018	36.2(5)	8.927(2)	4.811(1)	4.578(1)		196.6(1)
T020	37.4(6)	8.925(8)	4.808(3)	4.574(2)		196.3(4)
Cotunnite phase (Pnma)						
T020	37.4(6)	5.119(4)	2.982(2)	5.957(5)		90.9(3)
T022	40.7(6)	5.081(4)	2.978(3)	5.952(4)		90.1(3)
T024	43.6(2)	5.072(4)	2.970(2)	5.937(3)		89.4(2)
G004	50.7(3)	5.051(1)	2.949(1)	5.913(1)		88.1(1)
G030	51.1(9)	5.055(3)	2.952(2)	5.921(3)		88.4(2)
G006	54.1(5)	5.050(3)	2.943(2)	5.904(4)		87.8(2)
G028	59.0(8)	5.031(3)	2.932(2)	5.901(3)		87.0(2)
G008	59.6(7)	5.028(1)	2.930(1)	5.889(1)		86.7(1)
G010	61.7(9)	5.022(2)	2.924(1)	5.882(2)		86.4(1)
G026	61.8(4)	5.024(3)	2.925(2)	5.888(2)		86.5(2)
G012	62.3(9)	5.016(2)	2.921(2)	5.877(2)		86.1(2)
G024	62.2(17)	5.021(3)	2.921(2)	5.883(3)		86.3(2)
G022	64.7(6)	5.016(2)	2.919(1)	5.876(2)		86.1(1)
G014	64.8(11)	5.013(1)	2.917(1)	5.873(1)		85.9(1)
G016	66.6(7)	5.008(2)	2.915(2)	5.867(1)		85.6(2)
G020	66.8(3)	5.007(2)	2.914(2)	5.869(2)		85.6(2)
G018	67.6(9)	5.004(2)	2.913(2)	5.865(2)		85.5(2)

<sup>a</sup> Recovered from 51.1 GPa (No. G030) to ambient conditions without heating

directly compressing the powdered sample, the cubic phase reported by Mattesini et al. (2004) could be the metastable phase obtained under non-hydrostatic conditions. Therefore, we can conclude that the cotunnite phase rather than the fluorite-like cubic phase is the most stable phase at pressures from 40 GPa to at least 70 GPa.



**Table 3** Equation of state parameters for the TiO<sub>2</sub> polymorphs

$V_0$ (cm <sup>3</sup> /mol)	$K_0$ (GPa)	$K_0'$	P-medium	Annealing	P-scale	References
<b><math>\alpha</math>-PbO<sub>2</sub> phase</b>						
18.40 (fixed)	206(4)	4 (fixed)	NaCl	2,200–2,500 K	Pt–H	This study
18.40	98	5 (fixed)	Silicon oil	–	Ruby-M	Haines and L�ger (1993)
18.42	260	4 (fixed)	M–E	–	Ruby-M	Gerward and Olsen (1997)
18.42	258	4.05	NaCl	–	NaCl-D	Olsen et al. (1999)
18.42	258	4.1	M–E–W	–	Ruby-M	Arlt et al. (2000)
18.39	253	4 (fixed)	NaCl	1,800	NaCl-SH	Al-Khatatbeh et al. (2009)
<b>Baddeleyite phase</b>						
17.36(4)	175(5)	4 (fixed)	NaCl	2,200–2,500 K	Pt–H	This study
? <sup>a</sup>	522	5 (fixed)	Silicon oil	–	Ruby-M	Haines and L�ger (1993)
16.89	290	4 (fixed)	M–E	–	Ruby-M	Gerward and Olsen (1997)
16.89	290	4 (fixed)	NaCl	–	NaCl-D	Olsen et al. (1999)
16.88	290	4 (fixed)	M–E–W	–	Ruby-M	Arlt et al. (2000)
16.63	303	3.9	Ar	600 K	Ruby <sup>a</sup>	Swamy et al. (2002)
16.90	304	3.9	–	–	? <sup>a</sup>	Dubrovinsky et al. (2001), Ahuja and Dubrovinsky (2002a, b)
16.9	298	4 (fixed)	NaCl	1,800	NaCl-SH	Al-Khatatbeh et al. (2009)
<b>OI phase</b>						
16.83(10)	222(14)	4 (fixed)	NaCl	2,500 K	Pt–H	This study
16.42	318	4 (fixed)	–	600–1,000 K	Pt or Au <sup>a</sup>	Dubrovinskaia et al. (2001)
16.58	314	4 (fixed)	NaCl	1,800	NaCl-SH	Al-Khatatbeh et al. (2009)
<b>Cotunnite phase</b>						
15.11(5)	306(9)	4 (fixed)	NaCl	1,600–2,500 K	Pt–H	This study
15.14(5)	294(9)	4.25(fixed)	NaCl	1,600–2,500 K	Pt–H	This study
15.82	431	1.35	–	–	? <sup>a</sup>	Dubrovinsky et al. (2001), Ahuja and Dubrovinsky (2002a, b), Dubrovinskaia et al. (2002)
15.22	312	4 (fixed)	NaCl	1,800	NaCl-SH	Al-Khatatbeh et al. (2009)

M–E 4:1 methanol–ethanol mixture, M–E–W 16:3:1 methanol–ethanol–water mixture

Ruby-M Mao et al. (1978), Pt–H Holmes et al. (1989), NaCl-D Decker (1971), NaCl-SH Sato-Sorensen (1983) or Heinz and Jeanloz (1984)

<sup>a</sup> The detail was not described in the reference(s)

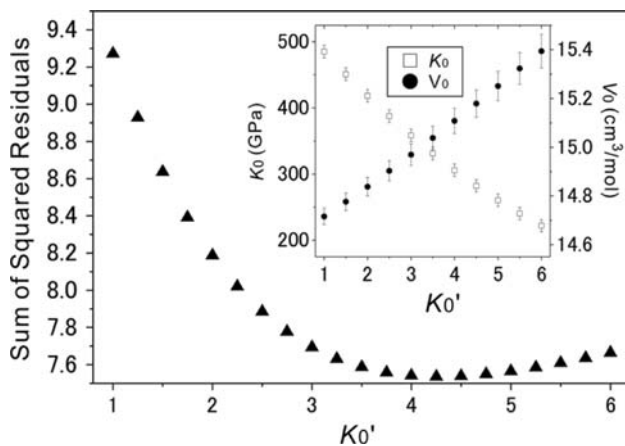
### Equation of state for the cotunnite phase

The unit-cell volumes for the TiO<sub>2</sub> polymorphs at room temperature observed in the present study are shown in Fig. 3 together with those reported previously (Dubrovinsky et al. 2001; Dubrovinskaia et al. 2002; Ahuja and Dubrovinsky 2002a, b; Mattesini et al. 2004). The unit-cell parameters of each phase after laser annealing are listed in Table 2. The hydrostaticity of the applied pressure can be checked from the consistency of the  $d$  values of a different index, which is expressed by the value of  $St$  (Shim et al. 2000). We can conclude that our volume data were obtained under quasi-hydrostatic conditions (Shim et al. 2000), because the  $St$  values calculated from the present diffraction data are smaller than 0.005 (Table 1). The volume data for the TiO<sub>2</sub> polymorphs were fitted using the third-order Birch-Murnaghan equation of state, as given by

$$P = 3/2K_0 \left[ (V/V_0)^{-7/3} - (V/V_0)^{-5/3} \times \left\{ 1 + 3/4(K_0' - 4) \left[ (V/V_0)^{-2/3} - 1 \right] \right\} \right] \quad (1)$$

where  $V_0$  is the volume at zero pressure,  $K_0$  is the isothermal bulk modulus, and  $K_0'$  is the first pressure derivative of the isothermal bulk modulus. If we fix  $K_0'$  at 4, we obtain the second-order Birch-Murnaghan equation of state. The fitted results for the TiO<sub>2</sub> polymorphs are summarized in Table 3, where they are also compared with previously reported results.

The cotunnite phase is unquenchable under ambient conditions, and thus the fitting parameters are  $V_0$ ,  $K_0$ , and  $K_0'$ . However, since the fitting of three parameters produces large uncertainties, we calculated  $V_0$  and  $K_0$  by fixing  $K_0'$ . Figure 4 shows the fitted  $V_0$  and  $K_0$  values and the sum of squared residuals (SSR) obtained by using different



**Fig. 4** SSR after fitting  $V_0$  and  $K_0$  by varying the value of  $K_0'$  based on the third-order Birch-Murnaghan equation of state for the cotunnite phase. The inset shows the variation in  $V_0$  and  $K_0$  for different selections of  $K_0'$

$K_0'$  values based on Eq. (1). Very high  $K_0$  values (419–485 GPa) can be obtained if we assume very small  $K_0'$  values (1–2) (Fig. 4), but a large SSR remains in this case. SSR was minimized when  $K_0'$  was fixed as 4.25 (Fig. 4). The third-order Birch-Murnaghan equation of state at  $K_0' = 4.25$  yields  $V_0 = 15.14(5)$  cm<sup>3</sup>/mol and  $K_0 = 294(9)$ , while the second-order Birch-Murnaghan equation of state yields  $V_0 = 15.11(5)$  cm<sup>3</sup>/mol and  $K_0 = 306(9)$  (Table 3). These results are consistent with those predicted by GGA calculations ( $V_0 = 15.28$  cm<sup>3</sup>/mol and  $K_0 = 281$  at  $K_0' = 4.8$ ) performed by Caravaca et al. (2009) and obtained by experiment ( $V_0 = 15.22$  cm<sup>3</sup>/mol and  $K_0 = 312$  at  $K_0' = 4$ ) reported by Al-Khatatbeh et al. (2009).

The parameters of the equation of state for the cotunnite phase obtained in the present study ( $V_0 = 15.11$ – $15.14$  cm<sup>3</sup>/mol,  $K_0 = 294$ – $306$  GPa and  $K_0' = 4$ – $4.25$ ) are quite different from those reported in previous experimental studies ( $V_0 = 15.82$  cm<sup>3</sup>/mol,  $K_0 = 431$  GPa, and  $K_0' = 1.35$ ) (Dubrovinsky et al. 2001; Dubrovinskaia et al. 2002; Ahuja and Dubrovinsky 2002a, b). Although the amount of numerical data reported in previous studies is quite limited, a few unit-cell volumes for the cotunnite phase at around 50–60 GPa reported in previous studies (Dubrovinsky et al. 2001; Ahuja and Dubrovinsky 2002a, b; Dubrovinskaia et al. 2002; Mattesini et al. 2004) are plotted in Fig. 3. Figure 3 clearly shows that not only the equation of state parameters but also the absolute values of the unit-cell volumes are quite different, and the volumes at high pressure differ by more than 5% from those of the present study. In previous studies, the volume data were collected by varying the pressure at room temperature without using a pressure medium and without annealing. These experimental procedures are likely to generate large stress inhomogeneities in samples. Moreover, the earlier

studies do not mention anything about the pressure scales used. Although it is difficult to believe that the stress state and the pressure scale alone are responsible for such a large discrepancy in the unit-cell volume, further analysis is impossible because of the lack of detailed information in the previous studies (Dubrovinsky et al. 2001; Dubrovinskaia et al. 2002; Ahuja and Dubrovinsky 2002a, b; Mattesini et al. 2004). On the other hand, we carefully annealed the sample and checked the stress state by calculating the  $St$  value, which indicates that our X-ray measurements were performed under quasi-hydrostatic conditions. Therefore, we can say that the measurements in the present study are more reliable and that the isothermal bulk modulus,  $K_0$ , for the cotunnite phase lies within the range of about 294–306 GPa. These values are significantly smaller than that of diamond (444 GPa) (Sung and Sung 1996), and thus we conclude that the bulk modulus for the cotunnite phase of TiO<sub>2</sub> is not comparable to that of diamond.

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