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Abstract
Despite great technological importance and many investigations, a material
with a measured hardness comparable to that of diamond or cubic boron
nitride has yet to be identified. Our combined theoretical and experimental
investigations led to the discovery of a new polymorph of titanium dioxide,
where titanium is ninefold coordinated to oxygen in the cotunnite (PbCl$_2$)
structure. Hardness measurements on this phase, synthesized at pressures above
60 GPa and temperatures above 1000 K, reveal that this material is the hardest
oxide yet discovered. Furthermore, it is one of the least compressible (with
a measured bulk modulus of 431 GPa) and hardest (with a microhardness of
38 GPa) polycrystalline materials studied so far.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

A number of experimental and theoretical studies [1–11] indicate that titanium dioxide
could have a series of high-pressure phases with their hardness possibly approaching that
of diamond. For example, the baddeleyite-type TiO$_2$ has a K_{300} of 290 GPa [9], a value
that is close to the bulk modulus of stishovite. The monoclinic baddeleyite-type structure
(MI, space group $P2_1/c$) is common among sevenfold-coordinated dioxides and is known to
transform, upon further compression, through an intermediate orthorhombic (OI, space group
$Pbca$) structure to another orthorhombic (OII, space group $Pnma$) cotunnite-type phase [11].
Cotunnite-structured ZrO$_2$ and HfO$_2$ possess extremely high bulk moduli of 444 and 340 GPa,
respectively [11]. If TiO$_2$ could also exist in the cotunnite structure, one could expect such a
material to be very incompressible and hard.

Previous *ab initio* simulations have successfully modelled the structural, elastic, and
energetic properties of a number of well characterized TiO$_2$ phases including rutile, anatase, and
the columbite-type (space group $Pbcn$) TiO$_2$-II [10, 12]. In this study, we performed *ab initio*
simulations using the full-potential linear muffin-tin orbital (FPLMTO) method. We have also

conducted a series of experiments in laser- or electrically heated diamond anvil cells (DACs) in order to determine whether or not it is possible to synthesize cotunnite-structured TiO$_2$.

2. Method

In order to study high-pressure properties of TiO$_2$, we have used the FPLMTO method. These calculations were based on the local-density approximation and we used the Hedin–Lundqvist parametrization for the exchange and correlation potential [13, 14]. Basis functions, electron densities, and potentials were calculated without any geometrical approximation. These quantities were expanded in combinations of spherical harmonic functions (with a cut-off $l_{max} = 6$) inside non-overlapping spheres surrounding the atomic sites (muffin-tin spheres) and in a Fourier series in the interstitial region. The radial basis functions within the muffin-tin spheres are linear combinations of radial wavefunctions and their energy derivatives, computed at energies appropriate to their site and principal as well as orbital atomic quantum numbers, whereas outside the spheres the basis functions are combinations of Neuman or Hankel functions [15]. In the calculations reported here, we made use of pseudo-core 3p and valence band 4s, 4p, and 3d basis functions for Ti, and valence band 2s, 2p, 3d basis functions for O with two corresponding sets of energy parameters, one appropriate for the semi-core 3p states, and the other appropriate for the valence states. The resulting basis formed a single, fully hybridizing basis set. For sampling the irreducible wedge of the Brillouin zone, we used the special-k-point method [16].

The details of experiments in electrically and laser-heated DACs are described in Dubrovinsky *et al* [17–19]. We obtained powder x-ray diffraction data with a Siemens x-ray system consisting of a Smart CCD Area Detector and a direct-drive rotating-anode x-ray generator (18 kW). Mo Kα radiation (tube voltage 50 kV, tube current 24 mA) focused with a capillary x-ray optical system to a diameter of 40 μm FWHM was used. The Rietveld refinements of powder x-ray diffraction data were carried out using the GSAS program [20].

3. Results and discussion

We have performed *ab initio* simulations of reasonable structures at pressures to 100 GPa to identify possible structures that TiO$_2$ could adopt under increased pressure. The various structures simulated are rutile, anatase, TiO$_2$-II, MI, pyrite ($Pa\bar{3}$), fluorite ($Fm3m$), OI, and OII. The simulations predict the cotunnite-structured phase of TiO$_2$ to be more stable than other structures proposed to date including the fluorite and pyrite modifications above 50 GPa (figure 1). Significantly, the *ab initio* calculations predict a remarkably high value for the bulk modulus for this phase: 386(10) GPa, from FPLMTO calculations.

We conducted a series of experiments in laser- or electrically heated DACs in order to determine whether or not it is possible to synthesize cotunnite-structured TiO$_2$. Anatase or rutile (99.99% TiO$_2$) was used as the starting material. At applied pressures of about 12 GPa or above, both rutile and anatase transformed to the baddeleyite ($P2_1/c$) phase, in good agreement with previous observations [7–9] (figure 2). On further compression, reflections due to the MI phase could be followed to over 60 GPa. Unit-cell parameters of the MI phase were determined at pressures of 15–42 GPa and the molar volume (V) versus pressure (P) data were fitted to a third-order Birch–Murnaghan equation of state [21]:

$$P = 1.5K_{300}[(V_0/V)^{7/3} - (V_0/V)^{5/3}][1 - 0.75(4 - K'){(V_0/V)^{2/3} - 1}] \tag{1}$$

where K_{300}, K', and V_0 are the bulk modulus, its pressure derivative, and the molar volume at zero pressure and 300 K, respectively. This yielded values of K_{300} and K' of 304(6)
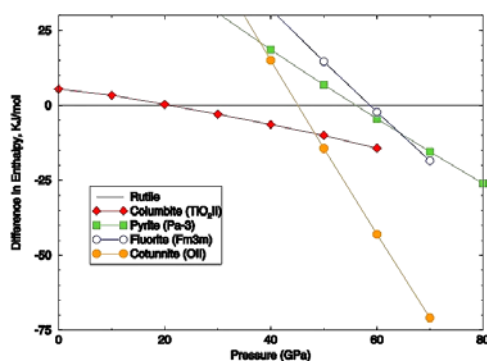
Figure 1. The stabilities of various known and hypothetical TiO$_2$ polymorphs relative to rutile as a function of pressure obtained by *ab initio* calculations at $T = 0$ K.
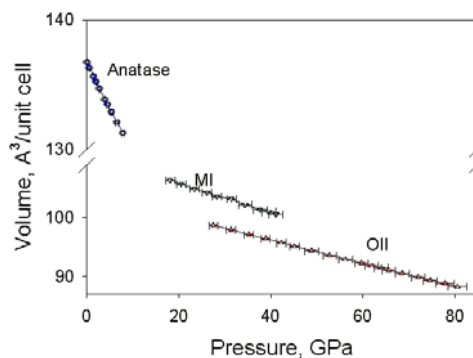
Figure 2. Pressure dependences of the volumes of anatase, baddeleyite-type, and cotunnite-type phases of TiO$_2$. Birch–Murnaghan equations of state (equation (1)) are plotted as solid lines with parameters $K_{300} = 178(1)$ GPa, $K' = 4$ (fixed), and $V_0 = 20.59(1)$ cm^3 mol^{-1} for anatase; $K_{300} = 304(6)$ GPa, $K' = 3.9(2)$, and $V_0 = 16.90(3)$ cm^3 mol^{-1} for the MI phase; and $K_{300} = 431(10)$ GPa, $K' = 1.35(10)$, and $V_0 = 15.82(3)$ cm^3 mol^{-1} for the cotunnite-type (OII) phase.
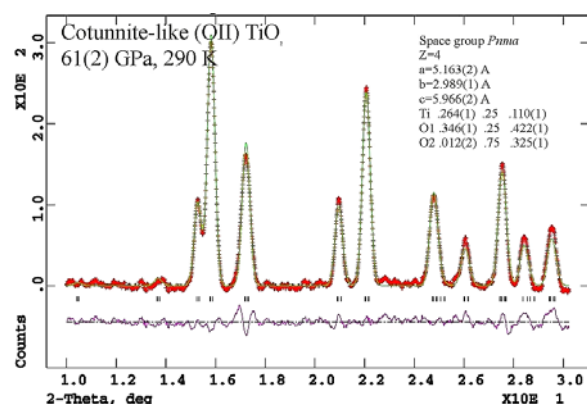

Figure 3. An example of profile-fitted x-ray diffraction data obtained from a cotunnite-structured TiO$_2$ sample at 290 K. The sample was synthesized in the electrically heated DAC at 61(2) GPa and 1100(25) K and subsequently temperature quenched to 290 K.

and 3.9(2) respectively, in good agreement with the values reported by Olsen *et al* [9] ($K_{300} = 290(20)$ GPa at a fixed $K' = 4$). At pressures above about 45 GPa, however, the quality of the diffraction pattern decreased drastically and at about 60 GPa the material became translucent. We observed that at pressures above 50 GPa, TiO$_2$ absorbs Nd:YAG laser radiation and the laser-heated areas of the sample became black. After heating at 1600–1800 K by laser for 40 min at pressures between 60 and 65 GPa, the material transformed to a new phase as evidenced by the x-ray diffraction spectra (figure 3). All reflections of the new phase could be indexed in an orthorhombic cotunnite-type cell. Rietveld refinement of the x-ray powder diffraction data [20] from a sample synthesized in an electrically heated DAC (see below) at 61(2) GPa and 1100(25) K (figure 3) yielded atomic positions within the *Pnma* space group similar to those of PbCl$_2$ [22] and cotunnite-type ZrO$_2$ [11]. The transition from the MI to OII structure results in an increase in the coordination number of titanium atoms from 7 to 9, with oxygen atoms forming elongated tricapped trigonal prisms containing the titanium atoms.

Table 1. Bulk moduli (GPa) and Vickers hardnesses (GPa) for some polycrystalline hard materials.

Material	Bulk modulus	Hardness
B_4C	200	30(2)
SiC	248	29(3)
Al_2O_3	252	20(2)
SiO_2, stishovite	291	32(2)
WC	421	30(3)
Cubic BN	369	32
Cotunnite-type TiO_2[a]	431	38(3)
Sintered diamond	444	50

[a] Measurements at 157(2) K.

Once synthesized at high temperature and at pressures above 60 GPa, the cotunnite-type TiO_2 phase could, at ambient temperature, be compressed to at least 80 GPa, decompressed to below 30 GPa, and then 'recompressed' to higher pressures again (figure 2). Fitting the P–V data collected at ambient temperature to equation (1) gave values of $K_{300} = 431(10)$ GPa, $K' = 1.35(10)$, and $V_0 = 15.82(3)$ cm^3 mol^{-1}. A comparison of the molar volumes of rutile (the stable form of TiO_2 at ambient conditions) and the MI phase with that of the cotunnite-structured TiO_2 shows that the newly discovered phase is 15.9% denser than rutile and 6.9% denser than the MI phase. This is consistent with previous observations for ZrO_2 and HfO_2 [11] where the differences in density between the phase stable at ambient conditions (MI) and the high-pressure OII phase is about 13%. We also note that the bulk modulus of cotunnite-type TiO_2 when extrapolated to ambient conditions is just slightly lower than that of diamond.

On decompression at ambient temperature to pressures below 25 GPa, the OII phase transformed to the MI phase, and the latter transformed to TiO_2-II upon further decompression to between 8 and 12 GPa. Rapid decompression (within a second) from 60 GPa to ambient pressure in liquid nitrogen at a temperature of 77 K (using the cryogenic recovery technique similar to that described by Leinenweber *et al* [23]), however, led to the preservation of the cotunnite structure (figure 3). On heating at ambient pressure to temperatures between 175 and 180 K, the quenched OII phase transformed to TiO_2-II.

We carried out hardness tests on the cotunnite-structured TiO_2 at a temperature of 155–160 K using the Vickers microhardness tester (Shimadzu Type M) with loads of 25, 50, 100, 150, and 300 g.

The reliability of the hardness measurements was tested by determining the hardness of a number of polycrystalline materials (B_4C, Al_2O_3, SiC, WC, TiC, and stishovite) sintered in a DAC at 9–11 GPa and 770(25) K and subsequently quenched. The results of our measurements presented in table 1 are in good agreement with the data in the literature. Samples of cotunnite-structured TiO_2 for the hardness measurements were synthesized by heating anatase or rutile to 1100(25) K at pressures of 60–70 GPa in an electrically heated DAC for 7–8 h. It is very difficult to achieve complete phase transition of the sample using a laser-heated DAC due to temperature gradients, particularly at the sample–diamond interface, whereas in an electrically heated DAC, the material is heated homogeneously throughout the whole pressure chamber [24]. After synthesis, the samples of cotunnite-type TiO_2 were cryogenically recovered at 77 K. As a consequence of performing the experiment in an electrically heated DAC, the samples are cylindrical in shape with a diameter of 250–280 μm and a thickness of 40–60 μm with clean, flat surfaces suitable for hardness measurements. We conducted nine independent indentation measurements of the hardness of cotunnite-type TiO_2 and found the hardness to be independent of the load. All the measurements indicated a high hardness, ranging from 36.8 to 40.7 GPa, with an average value of 38 GPa.

The polycrystalline high-pressure cotunnite-structured phase of titanium dioxide is the hardest oxide discovered to date. This material is harder than stishovite and boron oxide and much harder than alumina [3, 25]. Polycrystalline cubic boron nitride and sintered diamond are approximately two times softer than their corresponding single-crystal equivalents [3, 26]. This suggests that the cotunnite-type TiO$_2$ is among the hardest known polycrystalline materials.

So far we have been able to preserve the cotunnite-type TiO$_2$ under ambient pressure only at low temperatures (below 170 K). By contrast, the cotunnite-type modifications of ZrO$_2$ and HfO$_2$ have been quenched to ambient conditions. As with the cotunnite-type TiO$_2$, these latter phases are found to be very incompressible [7, 11]. Thus, doping of TiO$_2$ with Zr or Hf would, probably, lead to the synthesis of superhard oxides stable at ambient conditions.

4. Conclusions

Combined theoretical and experimental investigations led to the discovery of a new polymorph of titanium dioxide with titanium ninefold coordinated to oxygen in the cotunnite (PbCl$_2$) structure. Hardness measurements on the cotunnite-structured TiO$_2$ synthesized at pressures above 60 GPa and temperatures above 1000 K reveal that this material is the hardest oxide yet discovered. Furthermore, it is one of the least compressible (with a measured bulk modulus of 431 GPa) and hardest (with a microhardness of 38 GPa) polycrystalline materials studied thus far.

References

[1] Dubrovinsky L, Dubrovinskaia N A, Swamy V, Muscat J, Harrison N M, Ahuja R, Holm B and Johansson B 2001 *Nature* **410** 653
[2] Riedel R 1994 *Adv. Mater.* **6** 549
[3] C M Sung and Sung M 1996 *Mater. Chem. Phys.* **43** 1
[4] M L Cohen 1994 *Solid State Commun.* **92** 45
[5] Léger J M, Haines J and Blanzat B 1994 *J. Mater. Sci. Lett.* **13** 1688
[6] Lundin U, Fast L, Nordstrom L, Johansson B, Wills J M and Eriksson O 1998 *Phys. Rev.* B **57** 4979
[7] Léger J M, Haines J, Atouf A and Tomaszewski P 1994 *High Pressure Science and Technology—1993* ed S C Schmidt, J W Shaner, G A Samara and M Ross (New York: American Institute of Physics) p 363
[8] Haines J and Léger J M 1993 *Physica* B **192** 232
[9] Olsen J S, Gerward L and Jiang J Z 1999 *J. Phys. Chem. Solids* **60** 229
[10] Dewhurst J K and Lowther J E 1996 *Phys. Rev.* B **54** R3673
[11] Desgreniers S and Lagarec K 1999 *Phys. Rev.* B **59** 8467
[12] Muscat J 1999 The phase stability, surface structure and defect chemistry of titanium dioxide from first principles techniques *PhD Thesis* University of Manchester
[13] Wills J M and Cooper B R 1987 *Phys. Rev.* B **36** 3809
[14] Hedin L and Lundqvist B L 1971 *J. Phys. C: Solid State Phys.* **4** 2064
[15] Skriver H L 1984 *The LMTO Method* (Berlin: Springer)
[16] Froyen S 1989 *Phys. Rev.* B **39** 3168
[17] Dubrovinsky L S, Saxena S K, Lazor P, Ahuja R, Eriksson O, Wills J M and Johansson B 1997 *Nature* **388** 362
[18] Dubrovinsky L S, Saxena S K, Tutti F and Le Bihan T 1999 *High Pressures–High Temp.* **31** 553
[19] Dubrovinsky L S, Saxena S K, Tutti F and Le Bihan T 2000 *Phys. Rev. Lett.* **84** 1720
[20] Larson A C and Von Dreele R B 1994 *Los Alamos National Laboratory Report* LAUR 86
[21] Anderson O L *Equations of State of Solids for Geophysics and Ceramic Science* (Oxford: Oxford University Press) p 405
[22] Sahl K and Zeeman J 1961 *Naturwissenschaften* **20** 641
[23] Leinenweber K, Schuelke U, Ekundit S and McMillan P F 1998 *Properties of Earth and Planetary Materials at High Pressure and Temperature (Geophysics Monograph)* vol 101, ed M H Manghnani and T Yagi (Washington, DC: American Geophysical Union) p 97
[24] Rekhi S, Dubrovinsky L S and Saxena S K 1999 *High Pressures–High Temp.* **31** 299
[25] Srikanth V, Roy R, Graham E K and Voigt D E 1991 *J. Am. Ceram. Soc.* **74** 3145
[26] Léger J M, Haines J, Schmidt M, Petitet J P, Pereira A S and da Jornada J A H 1996 *Nature* **383** 401