

Cotunnite-structured titanium dioxide: the hardest known oxide

Despite great technological importance and many investigations¹⁻⁶, 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 nine-coordinated to oxygen in the cotunnite (PbCl₂) 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.

It has been recognized that the hardness of ionic and covalent materials is related to elastic properties and increases with bulk modulus (K_T) and shear modulus (G)^{1,5,7-9} (Table 1). A number of experimental and theoretical studies¹⁰⁻¹¹ indicate that titanium dioxide could have a series of high-pressure phases with hardness possibly approaching that of diamond. Cotunnite-structured (OII, space group *Pnma*) ZrO₂ and HfO₂ have extremely high bulk moduli of 444 and 340 GPa, respectively⁶. If TiO₂ also could exist in the cotunnite structure, one can expect that such a material will be very incompressible and hard.

Table 1. Bulk moduli and Vickers hardness for some polycrystalline hard materials.

Material	Bulk modulus, GPa	Hardness*, GPa	Source
B ₄ C	200	30 (30)	3
SiC	248	29 (29)	3
Al ₂ O ₃	252	20 (19)	7
SiO ₂ , stishovite	291	32 (33)	7
WC	421	30 (30)	8
Cubic BN	369	(32)	3

Cottunite-type TiO ₂ **	431	38	
Sintered diamond	444	(50)	3

*Literature data given in parentheses. Uncertainty in measured hardness is less than 3 GPa

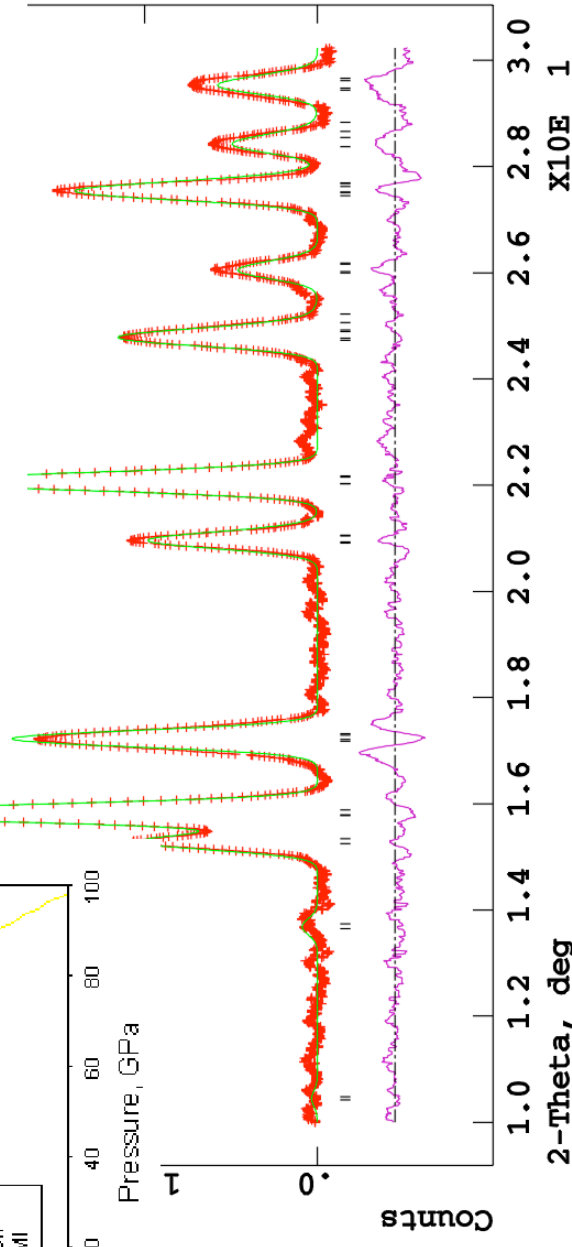
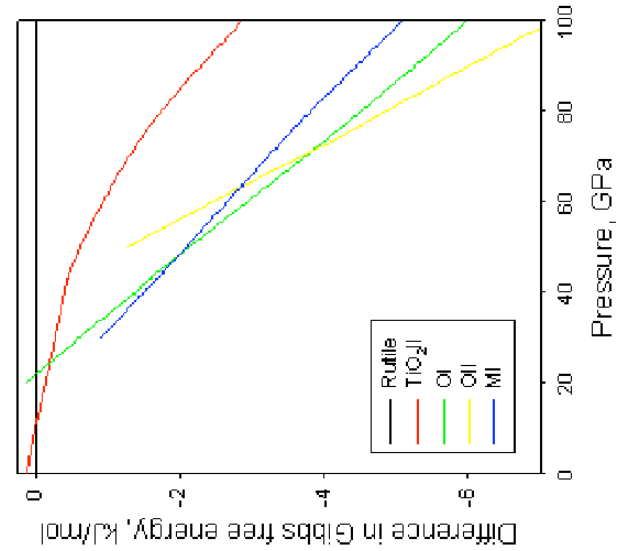
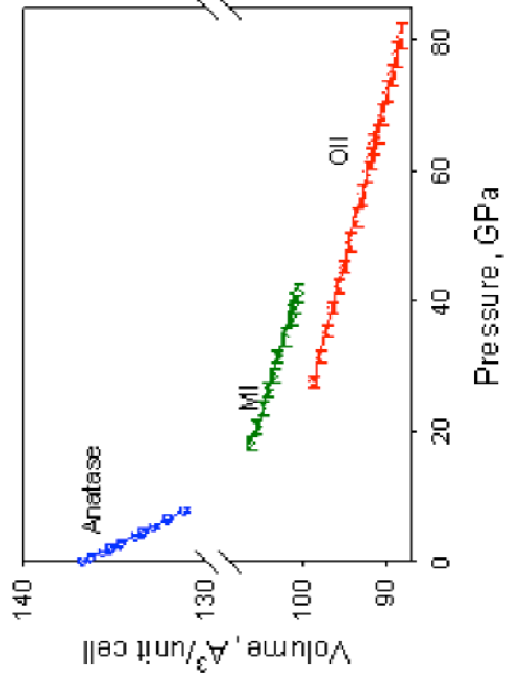
**Measurements at 157(2) K

We performed lattice dynamic (LD) and *ab initio* [linear combination of atomic orbitals periodic Hartree-Fock (LCAO-HF) and Full-Potential Linear-Muffin-Tin Orbital (FPLMTO)] simulations for a number of reasonable structures at pressures up to 100 GPa to identify possible structures that TiO₂ could adopt under high pressure conditions. The various structures simulated are rutile, anatase, TiO₂-II, baddeleyite-type (MI, space group $P2_1/c$), pyrite ($Pa\bar{3}$), fluorite (Fm3m), OI (space group $Pbca$), and OII^{6,10-11}. The simulations predict that the cotunnite-structured TiO₂ is more stable than the other structures proposed to date above 50 GPa (Fig. 1). Most significantly, the *ab initio* calculations predict a remarkably high bulk modulus value for this phase: 380(20) GPa by the LCAO-HF and 386(10) GPa by the FPLMTO calculations.

We 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 TiO₂. Anatase or rutile (99.99% TiO₂) was used as the starting material. At applied pressures of about 12 GPa or above, both rutile and anatase transformed to the baddeleyite structure, in good agreement with previous observations¹⁰⁻¹¹ (Fig. 1). On further compression, reflections due to the MI phase could be followed up to over 60 GPa. Unit cell parameters of the MI phase were determined at pressures of 15 to 42 GPa and the molar volume (V) versus pressure (P) data were fitted to a third-order Birch-Murnaghan equation of state (Fig. 1). This gave values for bulk modulus K_{300} and its pressure derivative K' of 304(6) and 3.9(2) respectively, in good agreement with the values reported by Olsen et al.¹¹ ($K_{300}=290\pm 20$ 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. After heating at 1600-1800 K by laser for 40 minutes at pressures between 60 and 65 GPa, the material transformed to a new phase as evidenced by the X-ray diffraction spectra (Fig. 1). Rietveld refinement of the X-ray

powder diffraction data¹² from a sample synthesized in an electrically-heated DAC (**see below**) at 61(2) GPa and 1100(25) K (Fig. 1) yielded atomic positions within the *Pnma* space group similar to those of PbCl₂ and cotunnite-type ZrO₂⁶. The transition from MI to OII structure results in an increase of the coordination number of the titanium atoms from 7 to 9, with oxygen atoms forming elongated tricapped trigonal prisms containing the titanium atoms.

Figure 1. An example of profile-fitted X-ray diffraction data obtained from a cotunnite-structured TiO₂ sample (space group *Pnma*, *Z*=4, *a*=5.163(2) Å, *b*=2.989(1) Å, *c*=5.966(2) Å, Ti (0.264(1);0.25;0.110(1)), O1 (0.346(1); 0.25; 0.422(1)), O2 (0.012(2); 0.75; 0.325(1)). The sample was synthesized in an electrically-heated DAC at 61(2) GPa and 1100(25) K and subsequently temperature-quenched to 290 K. The GSAS program package¹² was used in the Rietveld refinement (*wR_p*=1.9%, *R_p*=1.6%, χ^2 =0.49). Inset on the left shows the stability of various known and hypothetical TiO₂ polymorphs relative to rutile as a function of pressure obtained by lattice dynamics at T=300 K. Inset on the right shows pressure dependence of the volume for the anatase, baddeleyite, and cotunnite phases of TiO₂. Birch-Murnaghan equations of state are plotted as solid lines with parameters *K*₃₀₀=178(1) GPa, *K*'=4 (fixed), and *V*₀=20.59(1) cm³/mol for anatase; *K*₃₀₀=304(6) GPa, *K*'=3.9(2), and *V*₀=16.90(3) cm³/mol for baddeleyite-type; and *K*₃₀₀=431(10) GPa, *K*'=1.35(10), and *V*₀=15.82(3) cm³/mol for the cotunnite-type (OII) phase.



Once synthesized at high temperature and at pressures above 60 GPa, the cotunnite-type TiO₂ phase could, at ambient temperature, be compressed to at least 80 GPa, decompressed to below 30 GPa, and then “recompressed” to higher pressures again (Fig. 1). Fitting the P-V data collected at ambient temperature to a third-order Birch-Murnaghan equation of state gave values of $K_{300}=431(10)$ GPa, $K'=1.35(10)$, and $V_0=15.82(3)$ cm³/mol. Note that the bulk modulus of cotunnite-type TiO₂ when extrapolated to ambient conditions is only 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 TiO₂-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.¹³), however, led to the preservation of the cotunnite-structure. Upon heating at ambient pressure to temperatures between 175 and 180 K, the quenched OII phase transformed to TiO₂-II.

We carried out hardness tests on the cotunnite-structured TiO₂ 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 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 TiO₂ for the hardness measurements were synthesized by heating anatase or rutile to 1100(25) K at pressures of 60 to 70 GPa in an electrically-heated DAC for 7 to 8 hours. It is very difficult to achieve a 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. After synthesis, the samples of the cotunnite-type TiO₂ were cryogenically recovered at 77 K. As a consequence of performing the experiments in an electrically-heated DAC, the samples are cylindrical in shape with a diameter of 250-280 μ m and a thickness of 40 to 60 μ m with clean, flat surfaces suitable for hardness measurements. We conducted nine independent indentation measurements of the hardness of cotunnite-type TiO₂ and found the hardness to be

independent of the load. All the measurements showed 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^{3,10}. Polycrystalline cubic boron nitride and sintered diamond are approximately two-times softer than their corresponding single crystal equivalents^{3,7}. This suggests that the cotunnite-type TiO₂ is among the hardest known polycrystalline materials.

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