

Experimental and Theoretical Identification of a New High-Pressure TiO₂ Polymorph

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Our combined theoretical and experimental investigations have led to the discovery of a new polymorph of titanium dioxide, where titanium is seven-coordinated to oxygen in the orthorhombic OI (*Pbca*) structure. The zero-pressure bulk modulus of the new phase measured in the pressure range 19 to 36 GPa is 318(3) GPa. We demonstrate that the group IVa dioxides (TiO₂, ZrO₂, HfO₂) on compression at ambient temperature all follow the common path: rutile → α -PbO₂-type → baddeleyite-type (MI) → orthorhombic OI (*Pbca*) structure → cotunnite-type (OII).

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Outstanding properties of some of the titania (TiO₂) polymorphs have not only made those phases extremely useful in many applications, but they have also identified them as prime materials for experimental and theoretical studies. TiO₂ is of particular interest because of its use in a wide variety of commercial applications including pigment, catalysis, electronics, electrochemical, and ceramic industries and also because of the multiplicity of polymorphs it forms under varying chemical, temperature, and pressure conditions. High-pressure transformations of TiO₂ have attracted special attention because this material is regarded as a low-pressure analog of SiO₂, the most abundant component of the Earth's mantle.

A number of experimental and theoretical studies [1–5] indicate that titanium dioxide has a series of high-pressure phases. It is well known that titanium dioxide at high pressure attains phases that are isostructural with columbite (orthorhombic α -PbO₂) and baddeleyite (monoclinic ZrO₂) [6–8]. High-pressure, high-temperature treatment of titanium dioxide yields the α -PbO₂ modification (also called TiO₂II), which can be quenched to ambient conditions.

The monoclinic baddeleyite-type structure (MI, space group *P2₁/c*) is common among sevenfold coordinated dioxides and has for a number of systems been observed to transform, upon further compression, through an intermediate orthorhombic (OI, space group *Pbca*) structure to another orthorhombic (OII, space group *Pnma*) cotunnite-type phase [9,10]. Such a sequence of transformations has been found, in particular, for structural and chemical analogs of titania—ZrO₂ and HfO₂ [9,10]. Recently, cotunnite-structured TiO₂ with extremely high bulk modulus (431 GPa) and hardness (38 GPa) was synthesized at pressures above 60 GPa and at high temperatures [11]. However, the intermediate OI phase of TiO₂ has not been found so far. In the present Letter we present the results of theoretical and experimental identification of this new orthorhombic high-pressure titania polymorph.

Previous *ab initio* and semiempirical simulations have successfully modeled the structural, elastic, and energetic properties of a number of well characterized TiO₂ phases including rutile, anatase, brookite, and the columbite-type (space group *Pbcn*) TiO₂II [4,5,12]. In the present study, we perform lattice dynamic (LD) and *ab initio* full-potential linear-muffin-tin-orbital (FPLMTO) simulations of reasonable TiO₂ structures at pressures up to 100 GPa in order to identify the possible structures that TiO₂ can adopt under increased pressures. The various simulated structures are rutile, anatase, brookite, TiO₂-II, MI, pyrite (*Pa $\bar{3}$*), fluorite (*Fm $\bar{3}m$*), OI, and OII. Although *ab initio* treatments have to be preferred relative to empirical methods, the choice of the simulation technique is often determined by the complexity of the problem. Structurally simpler polymorphs with unit cells containing a small number of atoms, for example, rutile and anatase, are easily treated with *ab initio* techniques. More complex polymorphs such as the baddeleyite-type TiO₂ or brookite (which represent a low crystallographic symmetry with a larger number of atoms in the unit cell) are not easily amenable to *ab initio* treatments on a regular basis because of the very high demand on the computer resources. For the latter kind of polymorphs, it may be computationally expedient to pursue empirical methods for now. The details of the lattice dynamics simulations have been described in our previous work [13,14]. In quasiharmonic approximation, equilibrium crystal structure at given *P, T* can be obtained by minimization of the following functional [13–15]:

$$G_{P,T} = E + kT \sum_i^M \left\{ \frac{\hbar\omega_i}{2kT} + \ln \left[1 - \exp\left(-\frac{\hbar\omega_i}{2kT}\right) \right] \right\} + PV, \quad (1)$$

where *E* is the cohesive energy, *k* is the Boltzmann

constant, h is the Planck constant, M is the total number of phonon frequencies, ω_i is the frequency, and V is the molar volume.

For every given vector of the reciprocal lattice \vec{q} within the first Brillouin zone a set of frequencies ω_i is obtained as a result of the solution of the corresponding determinant equation.

$$|D(\vec{q}) - I\omega^2(\vec{q})| = 0, \quad (2)$$

where $D(\vec{q})$ is the dynamic matrix [15] and I is the identity matrix.

In the simulations we used the empirical Ti-O interatomic potential model of Matsui and Akaogi [16]. All calculations were performed at 300 K using a 64-point mesh in the first Brillouin zone. No symmetry conditions were applied (assuming $P1$ space group). The starting structural models for the high-pressure hypothetical polymorphs were taken from Haines *et al.* [17].

The FPLMTO static lattice calculations were based on the local-density approximation and we used the Hedin-Lundqvist parametrization for the exchange and correlation potential [18,19]. Basis functions, electron densities, and potentials were calculated without any geometrical approximation. These quantities were expanded in combinations of spherical harmonic functions (with a cutoff $l_{\max} = 6$) inside nonoverlapping 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 wave functions 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 [20]. In the calculations reported here, we made use of pseudocore $3p$ 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 semicore $3p$ 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 [21].

In good agreement with experimental observations and with the results of previous theoretical studies we found that the lowest energy among the tested TiO_2 polymorphs has the rutile structure. It is also predicted that the cotunnite-structured phase of TiO_2 is more stable than other structures proposed to date including the fluorite, pyrite, and OI modifications above 70 GPa (Fig. 1). According to the lattice dynamics and FPLMTO calculations at ambient temperature the expected sequence of the phase transformation of TiO_2 is rutile \rightarrow TiO_2II \rightarrow MI \rightarrow OI \rightarrow OII. Experiments [11] have already confirmed the existence of the cotunnite-type TiO_2 structure at pressures above 55 GPa. The orthorhombic OI phase is predicted theoretically for the pressure range 50 to 70 GPa

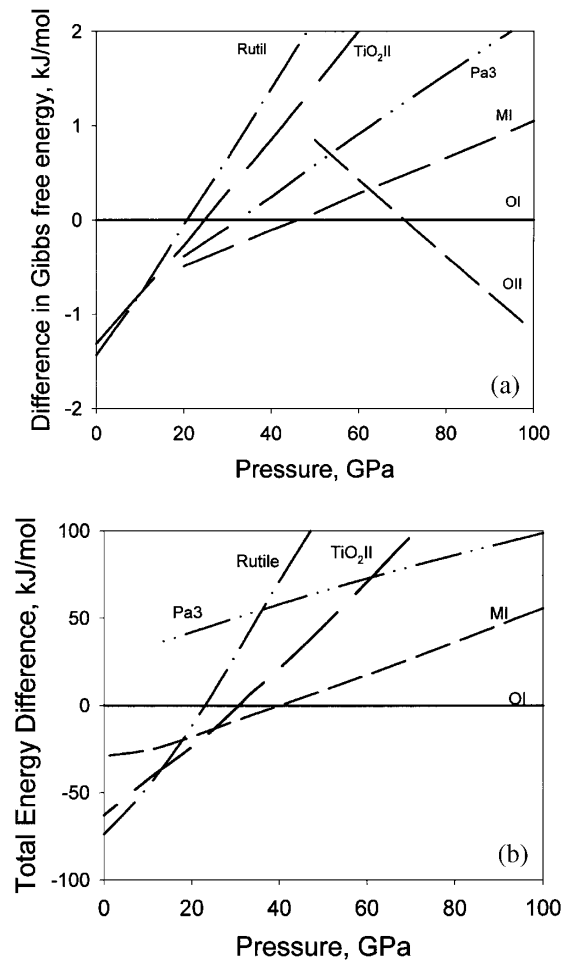


FIG. 1. The stabilities of various known and hypothetical TiO_2 polymorphs relative to rutile as a function of pressure obtained by LD at $T = 300$ K (a) and by *ab initio* FPLMTO static lattice calculations at $T = 0$ K (b). The designation of the phases follows Ref. [9]: $\text{TiO}_2\text{-II}$ has the $\alpha\text{-PbO}_2$ structure, and MI has the baddeleyite structure, OI is orthorhombic with the $Pbca$ space group, and OII is a cotunnite-type structure. In LD simulations the MI and Pa3 phases were traced only to 20 GPa and OII only to 4 GPa because at lower pressures the MI, Pa3, and OII phases relaxed to the $\text{TiO}_2\text{-II}$ structure.

by LD simulations and above 25 GPa by FPLMTO calculations. We conducted a number of experiments aiming to synthesize this theoretically predicted new titania polymorph.

The details of the experiments performed with electrically and laser-heated diamond anvil cells are described by Dubrovinsky *et al.* [22–24]. Powder x-ray diffraction data were obtained with a Siemens x-ray system consisting of a smart CCD area detector and a direct-drive rotating anode x-ray generator (18 kW). MoK_α radiation (tube voltage 50 kV; tube current 24 mA) focused with a capillary x-ray optical system to 40 μm diameter FWHM was used. At European Synchrotron Radiation Facility (beam line BM01) power diffraction data were collected with the MAR345 detector using an x-ray beam of 0.6996 \AA

at 600–650 K for 3 h or by scanning the sample with a Nd:YAG laser at 1000(100) K for 30 min. The molar volume (V) versus pressure (P) data were fitted to a third-order Birch-Murnaghan equation of state [26]:

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

(K_{300} , K' , and V_0 are the bulk modulus, its pressure derivative, and the molar volume at zero pressure and 300 K temperature, respectively).

The fit gave values for K_{300} and V_0 of 318(3) GPa and 16.42(1) cm³/mol, respectively ($K' = 4$ was fixed). The bulk modulus of the OI phase is slightly higher than the bulk modulus of MI [290(20) GPa [3], 304(6) GPa [11]] and significantly lower than for the OII phase [431(10) GPa [11]]. Extrapolated to zero pressure, the molar volume of the OI phase is 2.8% lower than V_0 of the MI phase and 3.8% higher than V_0 of the OII phase [11].

Rietveld refinement [25] of the x-ray powder diffraction data collected after laser heating of the sample at 27–29 GPa (Fig. 3a) yielded atomic positions within the $Pbca$ space group similar to those for the partially structurally refined PbO₂ [17]. To our knowledge, this is the first full structural refinement of the OI structural type found so far for a number of different compounds (for example, ZrO₂, HfO₂, MnF₂, EuI₂, PbO₂) [4,9,10,17,27]. Structural refinement reveals that there is a close link between the modified fluorite (space group $Pa\bar{3}$) and the OI structures. In fact, in the OI structure the titanium atoms are displaced less than 0.2 Å from the position in the fluorite-derived cell. Seven oxygen atoms are placed at distances in the range 1.87 to 2.07 Å (mean Ti-O distance is 1.97 Å) and form “one-capped trigonal prism” [28] (with a rectangular face capped). These polyhedrons are combined in “zigzag” chains similar to the chains in α -PbO₂ (or TiO₂II), which, in turn, form a 3D structure (Fig. 3b).

This study of TiO₂ together with earlier work on the group IVa dioxides (TiO₂, ZrO₂, HfO₂) [1–4,9–11] show that on compression at ambient temperature the structure follows the common path: rutile \rightarrow α -PbO₂-type \rightarrow baddeleyite-type (MI) \rightarrow orthorhombic OI ($Pbca$) structure \rightarrow cotunnite-type (OII). In other words, the orthorhombic OI phase with seven-coordinated cations is an intermediate phase between the MI and OII structures for the IVa dioxides. It should be noted that the group IVb dioxides follow another path and, in particular, instead of the baddeleyite-type structure they transform into the modified fluorite structured cubic phase [11,17,29,30].

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