Theoretical and Experimental Evidence for a New Post-Cotunnite Phase of Titanium Dioxide with Significant Optical Absorption

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We report the discovery of a post-cotunnite phase of TiO_2 by both density-functional *ab initio* calculations and high-pressure experiments. A pressure-induced phase transition to a hexagonal Fe_2P-type structure (space group $P\bar{6}2m$) was predicted to occur at 161 GPa and 0 K and successfully observed by *in situ* synchrotron x-ray diffraction measurements at 210 GPa and 4000 K with a significant increase in opacity. This change in opacity is attributed to a reduction of band gap from 3.0 to 1.9 eV across the phase change. The Fe_2P-type structure is proved to be the densest phase in major metal dioxides.

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The high-pressure and temperature phase transition of dioxides is of fundamental interest in solid-state physics, chemistry, and geosciences. In many dioxides, TiO_2 is well known as an important wide-gap oxide semiconductor with various industrial applications such as electrochemical solar cells and photocatalyst due to the characteristic high refractive index [1–9]. Apart from those technological aspects, high-pressure transformations of TiO_2 have attracted special attention as a low-pressure analog of SiO_2, the most abundant component of the Earth's mantle. A number of experimental and theoretical studies have revealed many crystalline polymorphs of TiO_2 at high pressures and high temperatures [10–14]. At ambient conditions, rutile is the most stable phase of TiO_2. Anatase and brookite are also known as natural minerals. All of these phases transform to an α-PbO_2-type, to an orthorhombic-I-type, then finally to a cotunnite-type structure at approximately 50 GPa [11,14]. The cotunnite-type polymorph is identified as the highest-pressure phase, as in many dioxides [15]. Although the analogy of the phase change to the cotunnite structure was applied to SiO_2 [16,17], a very recent *ab initio* study predicted a different phase transition from the pyrite-type structure to an unexpected Fe_2P-type structure (hexagonal, space group $P\bar{6}2m$) (Fig. 1) at 690 GPa, bypassing the cotunnite-type phase stability at low temperature [18]. Since no dioxides or difluorides with this crystal structure were reported, physical and chemical properties of this new class of oxide are still unknown. Although the extremely high transition pressure predicted in SiO_2 seems unreachable in the laboratory, TiO_2 shows significantly lower transition pressures. For instance, the α-PbO_2 phase stabilizes at ∼10 GPa in TiO_2, while the same phase at 100 GPa in SiO_2. High-pressure behavior of TiO_2 is therefore a key to understanding the rich polymorphism in the metal dioxide systems, in particular, the post-cotunnite phase relations. However, all the studies performed on TiO_2 were limited below 100 GPa, and no post-cotunnite phase has been identified. In this study, we investigate the applicability of the Fe_2P-type structure to TiO_2 both theoretically and experimentally.

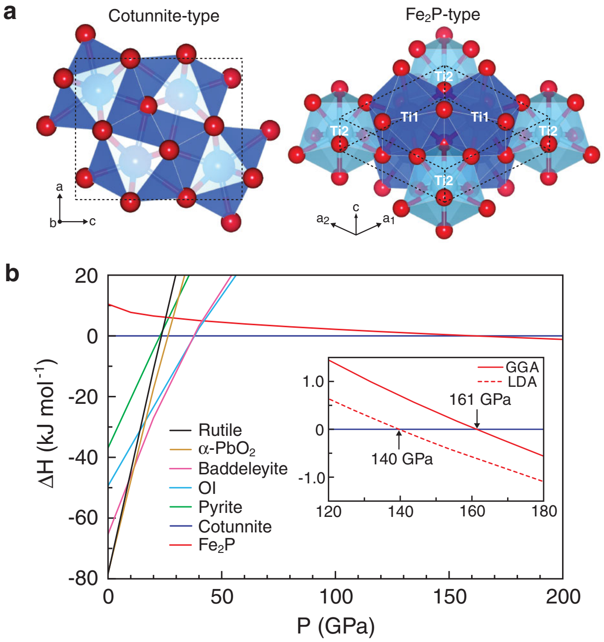

FIG. 1 (color). Crystal structures of two high-pressure phases of TiO_2 and enthalpy relationships among several phases. (a) The orthorhombic cotunnite-type (left) and hexagonal Fe_2P-type structures (right). The red and blue spheres represent oxygen and titanium atoms, respectively. Two different kinds of TiO_9 polyhedra are colored in blue (Ti1) and light blue (Ti2) for the Fe_2P-type structure. (b) Static enthalpy differences relative to the cotunnite-type phase as a function of pressure. Those between the Fe_2P-type and cotunnite-type are focused in the inset along with the results within the LDA.

Our *ab initio* calculations are based on the density-functional theory with the local density approximation (LDA) and the generalized gradient approximation (GGA) [19]. Static enthalpy differences (ΔH) calculated relative to the cotunnite-type structure are plotted in Fig. 1(b) as a function of pressure. As in previous calculations [20], the enthalpy of rutile-type is found to be slightly larger than that of α-PbO_2-type at ambient pressure. Structural phase transitions occur with increasing pressure from α-PbO_2-type to baddeleyite-type at 11 GPa, to orthorhombic-I-type at 36 GPa, and to cotunnite-type at 38 GPa. This phase sequence is in close agreement with the experimental one [11,12,14]. We then found another phase transition at further higher pressure. The calculations clearly indicate that the Fe_2P-type structure becomes more stable than cotunnite-type at 161 (within the GGA) and 140 GPa (LDA). The LDA predicts a lower transition pressure than the GGA as is often seen for the high-pressure phase transitions [18,21]. These transition pressures are notably lower than those predicted for SiO_2 (~ 690 GPa).

Structural parameters of the cotunnite-type and Fe_2P-type phases calculated with the GGA at the transition pressure are summarized in Ref. [19], which are identical to those reported for SiO_2 [18]. The substantial differences in the transition pressures in SiO_2 and TiO_2 should be related to the different electronic characteristics of the cation-oxide bondings. The static enthalpy has two different components represented as $H(P) = E_{\mathrm{tot}}(P) + PV$, where E_{tot}, P, and V are the electronic total energy, hydrostatic pressure, and volume, respectively. Examining contributions from these two terms separately, we found that the differences in E_{tot} and PV terms between the cotunnite-type and Fe_2P-type phases both decreased almost equally with increasing pressure as ΔE_{tot} and $\Delta(PV)$ of $+5.441$ and -4.751 (kJ mol^{-1}) at 140 GPa and of 5.082 and -5.047 (kJ mol^{-1}) at 160 GPa, respectively. This means that the enthalpy crossover associated with the transition to Fe_2P-type structure is achieved both by the electronic energy gain and by the volume reduction.

To prove the post-cotunnite phase transition in TiO_2 experimentally, *in situ* x-ray diffraction (XRD) studies were performed at the synchrotron beam line BL10XU, SPring-8. High-(P, T) conditions were achieved by using a laser-heated diamond-anvil cell (DAC) technique with double fiber lasers. Rutile was used as a starting material. The sample was mixed with fine platinum powder, which served as both an internal pressure standard [22] and a laser absorber, and loaded in the sample chamber together with insulation layers of NaCl. Other details were the same as a previous study [23]. When the sample was compressed to 154 GPa at room temperature, weak diffraction peaks of the cotunnite-type phase were observed. These became slightly sharper during laser heating at 177 GPa and 2000 K, indicating that the cotunnite-type phase is stable at these P, T conditions. On the other hand, when the sample was heated at 200 GPa and 3000 K, 10 new peaks appeared in addition to those from the cotunnite phase. These new peaks grew and sharpened with further heating at 210 GPa and 4000 K, and the diffraction peaks from the cotunnite-type phase almost disappeared. The XRD spectrum after temperature quenching is shown in Fig. 2(a). The two-dimensional XRD image shows clear circular Debye rings of the new diffraction lines. We found that they can successfully be assigned to the Fe_2P-type structure. This is the first crucial experimental evidence on the phase transition to the Fe_2P-type structure in all metal dioxides.

High-temperature thermodynamic properties including the Clapeyron boundary were also determined by *ab initio* lattice dynamics calculations combined with the quasiharmonic approximation [19]. Compression curves of the cotunnite-type and Fe_2P-type structures obtained within the GGA and the LDA at 300 K are plotted in Fig. 2(b) along with the experimental volumes for the cotunnite-type [10–12] and Fe_2P-type (this study) phases. The GGA provides excellent agreement with the experimental volumes, while the volumes by the LDA are distinctly ($\sim 4.5\%$) smaller. For the cotunnite-type TiO_2, only the earliest experimental results by Dubrovinsky *et al.* [10] show distinct discrepancies from other data. The present zero-pressure bulk modulus (B_0) calculated for the cotunnite-type phase (245.9 GPa) [19] is also much smaller than Dubrovinsky *et al.*'s value (431 GPa) [10] but agrees with more recent ones (220–300 GPa) [11,12,20]. Cotunnite-type TiO_2 is therefore less prospective for a potential ultrahard material. Figure 2(b) also demonstrates that the experimental volume of Fe_2P-type again coincides quite excellently with the calculated one even at the extreme pressure of $\sim$190 GPa.

The phonon spectra possess no soft modes, clearly indicating the Fe_2P-type TiO_2 to be both vibrationally and mechanically stable [Fig. 2(c)]. The high-(P, T) phase boundary between the cotunnite-type and Fe_2P-type phases was determined from the quasiharmonic approximation free energy balance. The zero-temperature transition pressure shifts slightly from 161 to 168 GPa by the quantum zero-point vibration effect. The Clapeyron boundary (dP_t/dT, where P_t is the transition pressure) becomes nearly constant above 300 K with a value of $+8.0$ MPa/K. This phase boundary is quite consistent with our experimental results. The LDA gives lower transition pressures but a comparable Clapeyron slope. We also examined the stability of this new phase at low pressure, but the Fe_2P-type structure was found dynamically unstable below 60 GPa. Special treatments such as chemical doping are required to recover it down to ambient conditions like metal-doped stabilized ZrO_2 [24].

Both phases have similar electronic band structures at the transition pressure [Fig. 3(a)], as the O $2p$ component

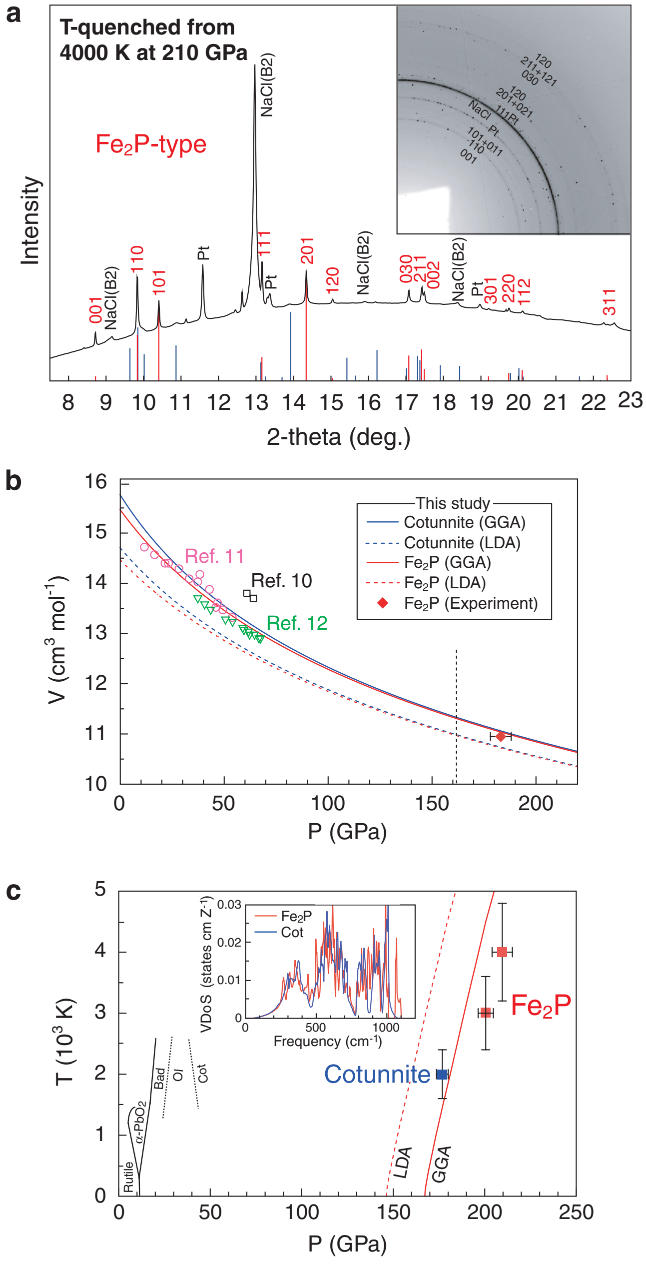

FIG. 2 (color). (a) An *in situ* XRD profile of Fe$_2$P-type TiO$_2$ after heating with a two-dimensional image presenting circular Debye rings (inset). Simulated patterns for Fe$_2$P-type (red) and cotunnite-type (blue) are also provided. (b) Volume compression curves of the cotunnite-type and Fe$_2$P-type phases at 300 K calculated with the GGA (solid lines) and the LDA (dashed line). The red diamond represents the experimental volume of a Fe$_2$P-type phase (present study), and open symbols represent those of a cotunnite-type phase [10–12]. A vertical line represents the static GGA transition pressure. (c) High-(P, T) phase diagram of TiO$_2$ with phase boundaries between the cotunnite-type and Fe$_2$P-type phases calculated within the GGA (red solid line) and LDA (dashed line). Blue and red squares represent the present experimental conditions where the cotunnite-type phase and Fe$_2$P-type, respectively, were observed. The vibrational density of states of the cotunnite-type (blue) and Fe$_2$P-type (red) phases calculated at 160 GPa within the GGA (inset).

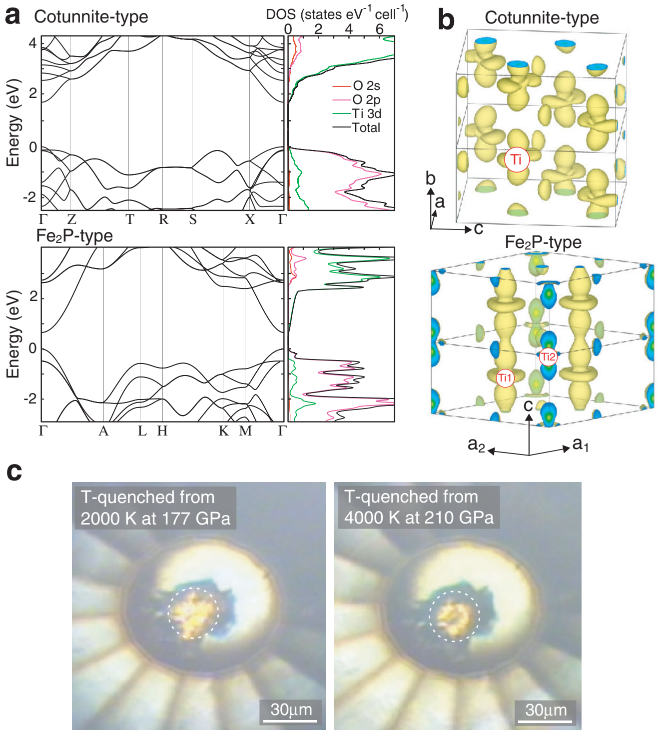

FIG. 3 (color). Electronic properties of the two high-pressure polymorphs of TiO$_2$. (a) Electronic band structures calculated at 160 GPa within the GGA for the cotunnite-type (upper) and Fe$_2$P-type (lower) structures. The top of valence bands is set to zero. (b) Kohn-Sham probability densities ($|\phi|^2$) of a Ti 3d state at the conduction band bottoms in the cotunnite-type and Fe$_2$P-type phases at 160 GPa. Dashed cubes show the unit cells. (c) Optical images of a sample in the DAC before the phase transition (left) and after synthesis of Fe$_2$P-type TiO$_2$ (right). Dashed circles represent the sample chamber. The center of the sample chamber (gray opaque area in the right panel) was heated by lasers.

and Ti 3d component are dominant for the valence and conduction bands, respectively. However, a substantial contrast in their energy gaps (E_g) is found. E_g of the Fe$_2$P-type phase is 0.66 eV, which is smaller than half of E_g of the cotunnite-type phase (1.79 eV). This small E_g of the Fe$_2$P-type is achieved by the low energy level of the conduction band bottom at the Γ point, which dominantly consists of Ti 3d electrons. The one-electron probability densities ($|\phi|^2$) of the Ti 3d state at the conduction band bottom [Fig. 3(b)] indicate that $d\gamma$-like orbitals between Ti1 atoms substantially overlap each other along the c direction in the Fe$_2$P-type, while more distorted $d\gamma$-like orbitals with marginal overlapping between neighboring Ti atoms, i.e., more localizing, form in the cotunnite-type. This bonding-type interaction is responsible for some energy gain of the conduction band bottom, leading to the significant decrease in E_g of the Fe$_2$P-type structure. This difference in E_g should also be detectable experimentally via a change in transparency. However, since the standard density-functional approaches, both the LDA and the GGA, are widely known to substantially underestimate E_g of insulators [25], here we apply a simple correction to E_g based on the systematics found in the GGA calculations (see [19] for more details). E_g at 160 GPa is corrected to 1.9 and 3.0 eV for the Fe_2P-type and cotunnite-type phases, corresponding to a ~650 nm and ~410 nm light wavelength, respectively.

These wavelengths fall in the visible light range. Thus, some discriminable change in opacity is expected across the phase transition. Optical microscope images of the sample in the DAC before and after the phase transition shown in Fig. 3(c) clearly indicate a characteristic change in transparency. Although the sample was highly transparent before the phase transition, it became opaque clearly when Fe_2P-type TiO_2 was synthesized. This supports the substantial decrease in E_g calculated and is the first evidential result on the TiO_2 polymorph with large visible light absorbance. The present discovery of the new post-cotunnite phase transition in TiO_2 unambiguously demonstrates that the Fe_2P-type structure is the densest phase in major dioxides with a particular optoelectronic property.

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