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# Stability of rutile-type TiO<sub>2</sub> under high pressure

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## Abstract

The high-pressure phases of TiO<sub>2</sub> have been investigated theoretically on the basis of first-principles density functional theory. Both the equation of states of the low-pressure phase and the structural phase transitions (the rutile-to- $\alpha$ -PbO<sub>2</sub>-type and  $\alpha$ -PbO<sub>2</sub>-to-baddeleyite transitions) were successfully explained in agreement with previous experiments. The calculation suggests the possibility that the high-pressure phase next to the baddeleyite phase does not have the brookite structure, which has been observed in ZrO<sub>2</sub> and HfO<sub>2</sub>. Furthermore, the stability of the low-pressure phases in TiO<sub>2</sub> was discussed on the basis of the atomic electronic structure.

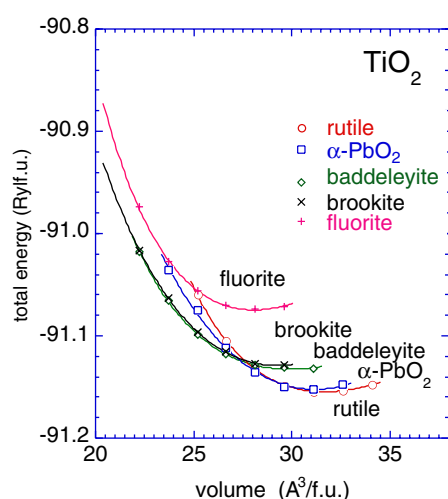
(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

The various structures of TiO<sub>2</sub>, ZrO<sub>2</sub>, and HfO<sub>2</sub> have been exhibited under high pressure, experimentally. The stable phase at ambient conditions of TiO<sub>2</sub> is the rutile type and it transforms to the  $\alpha$ -PbO<sub>2</sub> type and baddeleyite structures on applying pressure [1]. This sequence is in contrast with that of ZrO<sub>2</sub> and HfO<sub>2</sub>, whose stable structure is the baddeleyite type at ambient conditions [2]. In this paper, a theoretical study of the structural phase transition of TiO<sub>2</sub> is reported, in which first-principles electronic structure calculations were performed. This study provides the explanation for the stability of the normal phase of TiO<sub>2</sub>, and the difference in stable form between these oxides from the point of view of the electronic structures.

## 2. Calculation methods

The total energies have been calculated as a function of volume within the density functional theory. The exchange–correlation energy was evaluated with the generalized gradient approximation [3]. The pseudopotential method [4] was used to solve the Kohn–Sham equations. Since the transferability of the pseudopotential of the 3d transition metal elements cannot be expected to be as good as that for simple elements, the pseudopotential for Ti was constructed for the electron configuration of the ground state of Ti<sup>4+</sup>. This type of configuration



**Figure 1.** Total energies of the rutile,  $\alpha$ -PbO<sub>2</sub>, baddeleyite, brookite, and fluorite structures of TiO<sub>2</sub>. The points indicate calculated energies and the solid lines are fits to the Murnaghan equation of state.

was qualitatively observed in a previous calculation [5]. Some of the electrons, however, still occupy the 3d orbitals in the crystal, whose charge density has an overlap with the inner 3s and 3p orbitals. Thus, the partial core correction [6] was incorporated in the evaluation of the exchange–correlation energy.

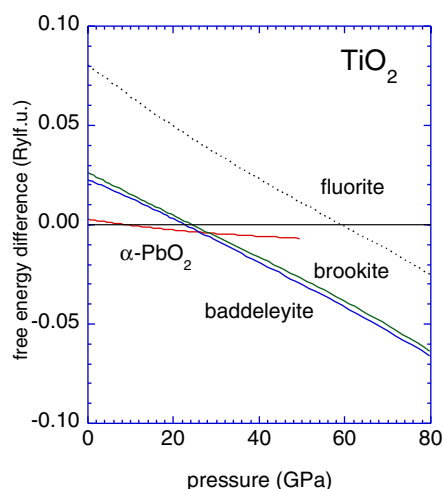
The wavefunctions were described in terms of the plane-wave basis sets for which the kinetic energy is less than 90 Ryd. The  $k$ -space integration was performed with the special-point method. The error was estimated to be about 1 mRyd fu<sup>-1</sup> in the total energy.

The atomic positions and the shape of the unit cell have been optimized at each volume for each structure with the help of force and stress calculations.

### 3. Results and discussion

Figure 1 shows the total energies calculated as a function of the volume for various structures, and fits to the Murnaghan equation of state and its parameters are listed in table 1. It can be seen that the rutile structure is the most stable structure among the structures calculated here, which is consistent with the experimental findings. The next high-pressure phase was calculated to be the  $\alpha$ -PbO<sub>2</sub> type, and the baddeleyite one follows it. The measured equations of state for the two low-pressure phases are compared with the present results in table 1. The agreement between theory and measurements is excellent, as can be seen also for many other materials. The linear compressibilities of the  $\alpha$ -PbO<sub>2</sub> phase have been measured along each axis. The calculated values are  $1.20 \times 10^{-3}$ ,  $1.25 \times 10^{-3}$ , and  $1.04 \times 10^{-3}$  GPa<sup>-1</sup> for the  $a$ -,  $b$ -, and  $c$ -axis, respectively, which are in agreement with experimental values:  $1.18 \times 10^{-3}$ ,  $1.50 \times 10^{-3}$ , and  $1.08 \times 10^{-3}$  GPa<sup>-1</sup> [9]. The fluorite structure, which was regarded as the prototype of the baddeleyite structure for ZrO<sub>2</sub>, is about 50 mRyd fu<sup>-1</sup> higher in total energy than the baddeleyite structure.

The brookite structure is the high-pressure phase of the baddeleyite structure for ZrO<sub>2</sub> and HfO<sub>2</sub>. In the present study, the total energy of the brookite structure is 2–3 mRyd fu<sup>-1</sup> higher than that of the baddeleyite structure at 22 Å<sup>3</sup> fu<sup>-1</sup> or larger volumes.



**Figure 2.** Free energies relative to that for the rutile phase.

**Table 1.** Calculated parameters for the equation of state for various structures of TiO<sub>2</sub>:  $V_0$ ,  $B_0$ , and  $B'$  are the equilibrium volume, the bulk modulus at zero pressure, and its pressure derivative, respectively.

Structure		$V_0$ ( $\text{\AA}^3 \text{fu}^{-1}$ )	$B_0$ (GPa)	$B'$
Rutile	Present	31.68	190	5.07
	Experiment <sup>a</sup>	31.22	216	6.76
$\alpha$ -PbO <sub>2</sub>	Present <sup>b</sup>	30.96	257	1.99
	Experiment <sup>c</sup>	30.65	253	4
Baddeleyite		29.90	148	4.21
Brookite		29.27	214	2.33

<sup>a</sup> References [7] and [8].

<sup>b</sup> The data between 26 and 33  $\text{\AA}^3 \text{fu}^{-1}$  were used.

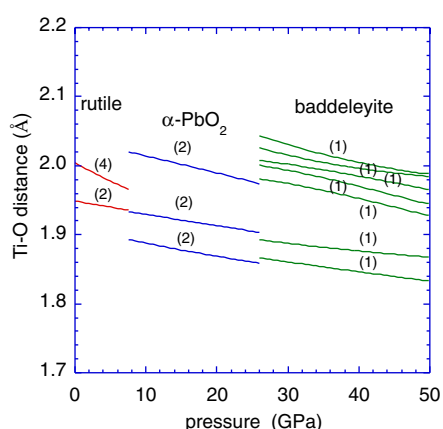
<sup>c</sup> Reference [9].

Figure 2 shows the free energy converted from the total energy by using the Murnaghan equation of state. The results indicate that the pressure of the transition from the rutile to the  $\alpha$ -PbO<sub>2</sub>-type phase was 7.5 GPa. This type of transition has not been observed directly at low temperatures. The phase boundary at 600–100 K lies near 6 GPa [10], close to the calculated value.

The pressure of the  $\alpha$ -PbO<sub>2</sub>-to-baddeleyite transition was calculated to be 26 GPa. This type of transition has been observed at 12 GPa at room temperature, and high-temperature data indicate a decrease of the transition pressure at lower temperature.

The brookite structure, which appears as the high-pressure phase of the baddeleyite structure for ZrO<sub>2</sub> and HfO<sub>2</sub>, does not appear up to 90 GPa in the present calculation, as mentioned above. According to the preliminary result for the cotunnite structure, the pressure of the transition from the baddeleyite to the cotunnite structure is about 60 GPa. Thus the brookite phase of TiO<sub>2</sub> would be a metastable phase at low temperature as discussed by Jamieson and Olinger [11] and/or the direct transition to the cotunnite phase would be exhibited bypassing the brookite transition.

The position of the O atoms is very difficult to determine with x-ray diffraction under high pressure. The calculated pressure change of the O distribution around the Ti atom is depicted



**Figure 3.** The pressure change of the distribution of O atoms around the Ti atom. The numbers in parentheses indicate the numbers of O atoms.

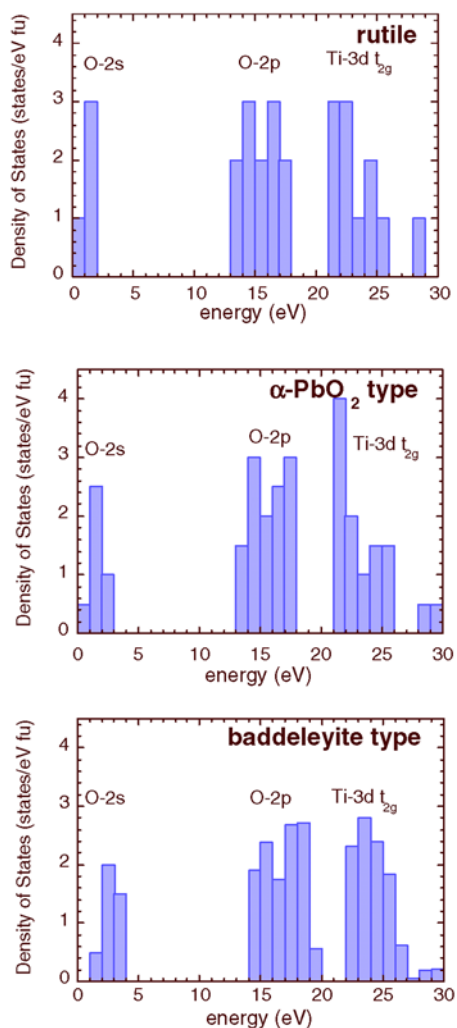
in figure 3. The figure shows that the sixfold coordination is preserved in the low-pressure phases and the baddeleyite phase has sevenfold coordination. The eighth-neighbour O atom is located about 3 Å from the Ti atom. Although the symmetry of the baddeleyite structure is low and the degree of freedom of the atomic position is large, the calculated coordination of the O atoms is as expected in  $\text{ZrO}_2$  and  $\text{HfO}_2$ .

The characteristic feature of  $\text{TiO}_2$  is the existence of the rutile and  $\alpha\text{-PbO}_2$ -type structures, as compared with  $\text{ZrO}_2$  and  $\text{HfO}_2$ . As can be seen in figure 1, the rutile and  $\alpha\text{-PbO}_2$  structures tend to have lower energy than the baddeleyite and brookite structures. Figure 4 shows a rough approximation of the density of states of  $\text{TiO}_2$  in the rutile,  $\alpha\text{-PbO}_2$ , and baddeleyite structures. In all three structures, the highest occupied band mainly made up of O 2p orbitals is separated from the lowest unoccupied band of Ti 3d orbitals. The major difference can be seen in the shape of the O 2p band: first, the bandwidth for the baddeleyite structure is rather larger than those for the rutile and the  $\alpha\text{-PbO}_2$  structures; second, the shape of the band of the rutile structure is rather symmetric in comparison with that of the  $\alpha\text{-PbO}_2$  structure. The first point can be understood by considering the fact that the two lower-pressure structures have sixfold O coordination around the Ti atom while the baddeleyite structure has sevenfold coordination. The second point indicates that the degree of covalency in the Ti–O bond is larger in the rutile structure than in the  $\alpha\text{-PbO}_2$  structure.

The apparent difference in atomic electronic structure between Ti and Zr or Hf can be seen in the core: the Zr and Hf atoms have d orbitals in their cores while this is not the case for the Ti. It follows that the inner d orbitals push the valence d orbitals up in energy due to the orthogonalization effect. Thus, the stabilization of the rutile structure due to the p–d hybridization cannot be expected in  $\text{ZrO}_2$  and  $\text{HfO}_2$ . Similar hybridization is considered to exist also in the  $\alpha\text{-PbO}_2$  structure of  $\text{TiO}_2$  despite its weakness arising from the Ti–O distance, as depicted in figure 3. Therefore, the difference between the low-pressure phases of the  $\text{TiO}_2$  and  $\text{ZrO}_2$  or  $\text{HfO}_2$  can be considered to be due to the electronic structure in the core of the cations.

#### 4. Conclusions

In this study, the high-pressure phases of  $\text{TiO}_2$  were investigated theoretically on the basis of first-principles density functional calculations. In addition to the equation of states of the low-



**Figure 4.** Rough approximation of the density of states for the rutile,  $\alpha$ -PbO<sub>2</sub>, and baddeleyite structures at around 0 GPa.

pressure phase, the structural phase transitions were successfully explained, in agreement with previous experiments. The present calculation suggests the possibility that the high-pressure phase next to the baddeleyite structure is not the brookite structure, which was observed in ZrO<sub>2</sub> and HfO<sub>2</sub>. However, the energy difference between these two phases is so small that further investigation is necessary. Finally, the stability of the low-pressure phases in TiO<sub>2</sub> was discussed on the basis of the atomic electronic structure.

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