First-principles study of ground-state properties and high pressure behavior of ThO$_2$

Bao-Tian Wang$^{a,b}$, Hongliang Shi$^{1,b,c}$, Wei-Dong Li$^a$, Ping Zhang$^{b,*}$

$^a$Institute of Theoretical Physics and Department of Physics, Shanxi University, Taiyuan 030006, People’s Republic of China
$^b$LCP, Institute of Applied Physics and Computational Mathematics, P.O. Box 8009, Beijing 100088, People’s Republic of China
$^c$State Key Laboratory for Superlattices and Microstructures, Institute of Semiconductors, Chinese Academy of Sciences, P.O. Box 912, Beijing 100083, People’s Republic of China

Abstract

The mechanical properties, electronic structure and phonon dispersion of ground state ThO$_2$ as well as the structure behavior up to 240 GPa are studied using first-principles density-functional theory. Our calculated elastic constants indicate that both the ground-state fluorite structure and high pressure cotunnite structure of ThO$_2$ are mechanically stable. The bulk modulus, shear modulus, and Young’s modulus of cotunnite ThO$_2$ are all smaller by approximately 25% compared with those of fluorite ThO$_2$. The Poisson’s ratios of both structures are approximately equal to 0.3 and the hardness of fluorite ThO$_2$ is 22.4 GPa. The electronic structure and bonding nature of fluorite ThO$_2$ are fully analyzed, and show that the Th–O bond displays a mixed ionic/covalent character. The phase transition from the fluorite to cotunnite structure is calculated to occur at the pressure of 26.5 GPa, consistent with recent experimental measurement by Idiri et al. [1]. For the cotunnite phase it is further predicted that an isostructural transition takes place in the pressure region of 80–130 GPa.

1. Introduction

Besides uranium and plutonium, thorium is also an important nuclear material. Thorium metal and its compounds have been widely investigated both experimentally and theoretically since metal thorium was discovered in 1828. Among thorium compounds, thorium dioxide ThO$_2$, which is a stable diamagnetic transparent insulating solid, has attracted special attention. In addition to its usage as nuclear fuel material, thorium dioxide has also been used as a solid-state electrolyte. In particular, due to its prominent hardness, ThO$_2$ has potential interest as an optical component material and laser host.

Recently, a series of experimental reports on pressure-induced phase transition of ThO$_2$ [1–3] were reported in the literature. At ambient pressure, ThO$_2$ crystallizes in the (CaF$_2$-type) fluorite structure with space group $Fm\bar{3}m$ (No. 225). By using the energy dispersive X-ray diffraction method, Dancausse et al. [3] reported that at 40 GPa, ThO$_2$ undergoes a phase transition to the orthorhombic structure of cotunnite (PbCl$_2$) type with space group $Pnma$ (No. 62). Later, through improved experimental measurement technique, Idiri et al. [1] observed that this phase transition really begins around 30 GPa, and that the two phases coexist in a wide pressure range of nearly 20 GPa. Additional high-pressure Raman spectroscopy measured by Jayaraman et al. [2] also suggested that ThO$_2$ starts to transform into the cotunnite structure at around 30 GPa.

In contrast to the above-mentioned extensive experimental investigations, only one theoretical study on the phase transition of ThO$_2$ at high pressure was reported recently by Boettger [4] who employing the relativistic linear combinations of Gaussian type orbitals-fitting function (LCGTO-FF) technique predicted a transition pressure of around 27.5 GPa. In addition, considering the obvious discrepancy between two works performed by one experimental group [1,3] involving the transition pressure, one more theoretical investigation from basis quantum mechanics is not only complementary but also indispensable. Motivated by this observation, in this paper, we present a first-principles study by calculating the total energies and enthalpies of ThO$_2$ at its experimentally established crystalline phases. Our calculation shows that the transition pressure is around 26.5 GPa, consistent with the recent experiment by Idiri et al. [1] and theoretical study by Boettger [4].

The other task for this paper is to theoretically present a thorough description of physical, mechanical and chemical bonding properties of ThO$_2$ at its ground state of the fluorite phase. To date, theoretical studies of the ground-state behavior of ThO$_2$ are very scarce in literature [5–11] and some of them are even inconsistent with the experimental data to a large extent. For example, without taking into account the 5f state, Kelly et al. [5] calculated the bulk modulus $B$ of ThO$_2$ to be 290 GPa, which is far from the experimental value of 198 GPa. On the other hand, based on a purely ionic model, Harding et al. [6] obtained $B = 175$ GPa, which, compared to the experimental data, clearly underestimated the binding interaction in the material to a large extent. This as whole encourages us to theoretically report a systematic investigation on the
ground-state properties of ThO$_2$ at its ambient phase. Besides the consistency with the existing experimental data, we expect that the new results for the first time predicted in this paper and experimentally inaccessible at present, such as the hardness, the phonon spectrum, and the charge transfer of the Th–O bond, will be of great help for a primary understanding of ThO$_2$. The rest of this paper is arranged as follows. In Section 2, the computational method is briefly described. In Sections 3 and 4, we present our calculated results, some of which are made comparison with available experimental and theoretical results. In Section 5, we summarize the conclusions of this work.

2. Computational method

Our total energy calculations are carried out by employing the plane-wave basis pseudopotential method as implemented in Vienna ab initio simulation package [12]. The exchange and correlation effects are described by the density-functional theory (DFT) within the generalized gradient approximation (GGA) [13]. The electron and core interactions are included using the frozen-core projected augmented wave approach which combines the accuracy of augmented-plane-wave methods with the efficiency of the pseudo-potential approach [14]. The thorium 6s$^2$7s$^2$6p$^6$6d$^1$5f$^1$ and the oxygen 2s$^2$2p$^4$ electrons are treated as valence electrons. Note that although the 5f state are empty in elemental Th, this level evolves into a hybridization with O 2p state in the valence band, as well as contributes prominently to the conduction band (see Fig. 3 below). We use a 9 × 9 × 9 k-point grid with Monkhorst–Pack scheme [15] for fluorite ThO$_2$ and 9 × 15 × 9 k-point grid for cotunnite structure. The electron wave function is expanded in plane waves up to a cutoff energy of 500 eV, and all atoms are fully relaxed until the quantum mechanical forces become less than 0.02 eV/Å.

To obtain optimized lattice constants of ground state ThO$_2$, first, we calculated several total energies at different lattice constants around the experimental value. Then we fitted the energy-volume data to the third-order Birch–Murnaghan equation of state (EOS) [16] to give the theoretical equilibrium volume, minimum energy, bulk modulus $B$, and pressure derivative of the bulk modulus $B'$. On the other hand, the bulk modulus $B$, shear modulus $G$, Young’s modulus $E$, Poisson’s ratio $\nu$, can also be derived from the elastic constants. We found that the bulk modulus $B$ obtained by these two ways are in good agreement, indicating that our calculations are self-consistent. In order to investigate the high pressure behavior of ThO$_2$, we have optimized the structural parameters of its $Fm\bar{3}m$ and $Pnma$ phases at different pressures by using GGA method. To avoid the Pulay stress problem, we performed the structure relaxation calculations at fixed volumes rather than constant pressures. For $Fm\bar{3}m$ phase, due to its high symmetry, the structure relaxation calculations are performed at fixed volumes with no relaxation of coordinates. However, for $Pnma$ phase, the coordinates of atoms and the cell shape are necessary to be optimized due to their internal degrees of freedom.

3. Ground state properties for fluorite-type thorium dioxide

3.1. Atomic structure and mechanical properties

At ambient condition thorium dioxide crystallizes in a CaF$_2$-like ionic structure. Its cubic unit cell is composed of four ThO$_2$ formula units with the thorium atoms and the oxygen atoms in 4a and 8c sites, respectively (see Fig. 1a). Each Th atom is surrounded by eight O atoms forming a cube and each O connects with four Th atoms to build a tetragon. A particular feature of this structure is the presence of a large octahedral hole sited at position ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$). The present optimized lattice constant ($a_0$) is 5.62 Å (see Table 1), in good agreement with the experimental [1,7] value of 5.6 Å.

Elastic constants can measure the resistance and mechanical features of crystal to external stress or pressure, thus describing the stability of crystals against elastic deformation. For small strains Hooke’s law is valid and the crystal energy $E$ is a quadratic function of strain [17]. Thus, to obtain the total minimum energy for calculating the elastic constants to second-order, a crystal is strained and all the internal parameters are relaxed. Consider a symmetric 3 × 3 nonrotating strain tensor $\epsilon$ which has matrix elements $\epsilon_{ij}(i,j = 1, 2, 3)$ defined by

$$
\epsilon_{ij} = \begin{pmatrix}
\epsilon_1 & \epsilon_{12} & \epsilon_{13} \\
\epsilon_{12} & \epsilon_2 & \epsilon_{23} \\
\epsilon_{13} & \epsilon_{23} & \epsilon_3
\end{pmatrix}.
$$

Such a strain transforms the three lattice vectors defining the unstrained Bravais lattice (a$_{k}$, $k = 1, 2, 3$) to the strained vectors [18] (a’$_{k}$) as defined by

$$a'_k = (I + \epsilon) a_k,
$$

where I is a unit 3 × 3 matrix. Each lattice vector $a_k$ or $a'_k$ is a 3 × 1 matrix. The change in total energy due to above strain (1) is [17]...
and
\[ G_V = (C_{11} - C_{12} + 3C_{44})/5. \]

Under Reuss approximation [21], the Reuss bulk modulus \( B_R \) and Reuss shear modulus \( G_R \) are
\[ B_R = B_V \]
(6)
and
\[ G_R = 5(C_{11} - C_{12})C_{44}/[4C_{44} + 3(C_{11} - C_{12})]. \]
(7)

The bulk modulus \( B \) and shear modulus \( G \), based on the Hill approximation [22], are arithmetic average of Voigt and Reuss elastic modulus, i.e., \( B = 1/2(B_V + B_R) \) and \( G = 1/2(G_V + G_R) \). The Young's modulus \( E \) and Poisson's ratio \( \nu \) for an isotropic material are given by [24]
\[ E = \frac{9BG}{3B + G}, \]
(8)
and
\[ \nu = \frac{3B - 2G}{2(3B + G)}. \]
(9)

The calculated results for these moduli and Poisson's ratio for the fluorite ThO\(_2\) are listed in Table 1. Note that we have also calculated the bulk modulus \( B \) by fitting the EOS. The derived bulk modulus turns out to be exactly the same as that from the above VRH approximation, which again indicates that our calculations are consistent and reliable. For comparison, other theoretical results [7,4,9] and available experimental data [1,7,19] are also shown in Table 1. It can be seen that on the whole, our present results compare well with those previous experimental and FP-LMTO/FLAPW theoretical results. Concerning the Poisson’s ratio, it is well known that for the common materials that have much smaller shear moduli compared with the bulk moduli, their Poisson’s ratio is close to 1/3. For the present ThO\(_2\) system, our calculated shear modulus \( G \) is much lower than the bulk modulus \( B \). Thus, our calculated result of 0.302 for the Poisson’s ratio, as well as the derived result of 0.285 according to the experimentally determined elastic constants [19] and using Eq. (9), can be well understandability.

Furthermore, hardness is also one fundamental physical quantity when considering the phase stability and mechanical properties. Note that the hardness is important for the applications of ThO\(_2\) as both nuclear material and optical components. So here we calculate the hardness of ThO\(_2\) by using the approach raised by Simunek et al. [25]. In the case of two atoms 1 and 2 forming one bond of strength \( s_{12} \) in a unit cell of volume \( V \), the expression for hardness has the form [25]
\[ H = (C/\Omega)b_{12}s_{12}e^{-\sigma_1}, \]
(10)
where
\[ s_{12} = \sqrt{(e_1e_2)/(n_1n_2d_{12})}, \quad e_i = Z_i/r_i \]
(11)
and
\[ f_2 = \left(\frac{e_2 - e_1}{e_1 + e_2}\right)^2 = 1 - \left[\sqrt{(e_1e_2)/(e_1 + e_2)}\right]^2 \]
(12)
are the strength and ionicity of the chemical bond, respectively, and \( d_{12} \) is the interatomic distance; \( C = 1550 \) and \( \sigma \) are 4 constants. The radius \( r_i \) is chosen to make sure that the sphere centered at atoms \( i \) in a crystal contains exactly the valence electronic charge \( Z_i \). For the fluorite structure of ThO\(_2\), \( b_{12} = 32 \) counts the interatomic bonds between atoms Th (1) and O (2) in the unit cell, \( n_1 = 8 \) and \( n_2 = 4 \) are coordination numbers of atom Th and O, respectively, \( r_1 = 1.81 \) (Å) and \( r_2 = 1.00 \) (Å) are the atomic radii for Th and O.

### Table 1

| Property | This study | Previous calculation | Experiment |
|----------|------------|----------------------|------------|
| \( a_0 \) (Å) | 5.62 | 5.61\(^a\), 5.62\(^b\), 5.62\(^c\), 5.60\(^d\), 5.60\(^e\) | 5.6001(3)\(^f\) |
| \( C_{11} \) (GPa) | 349.5 | 376.0\(^a\), 314.5\(^b\) | 367\(^c\) |
| \( C_{12} \) (GPa) | 111.4 | 109.8\(^a\), 73.1\(^b\) | 106\(^c\) |
| \( C_{44} \) (GPa) | 70.6 | 68.1\(^a\), 75.7\(^b\) | 79\(^c\) |
| \( B \) (GPa) | 191 | 198\(^b\), 192.8\(^b\), 184.5\(^b\), 198\(^b\) | 199/2\(^c\), 195/2\(^c\) |
| \( G \) (GPa) | 87.1 | 94.1\(^a\), 94.5\(^b\) | 97\(^c\) |
| \( E \) (GPa) | 226.8 | 243.8\(^a\), 243.7\(^b\) | 249\(^c\) |
| \( \nu \) | 0.302 | 0.295\(^a\), 0.289\(^b\) | 0.285\(^c\) |
| Hardness (GPa) | 22.4 | | |
| \( E_1(\text{eV}) \) | 4.673 | 4.60\(^a\), 4.52\(^b\) | 6\(^b\) |

\(^a\) Ref. [9].
\(^b\) Ref. [10].
\(^c\) Ref. [4].
\(^d\) Ref. [11].
\(^e\) Ref. [1].
\(^f\) Ref. [19].
\(^g\) Ref. [7].
\(^h\) Ref. [26].
atoms, respectively, \( Z_1 = 12 \) and \( Z_2 = 6 \) are valence charge for Th and O atoms, respectively, \( d_{ij} = 2.43 \) (Å) is the interatomic distance, and \( \Omega = 145.53 \) (Å\(^3\)) is the volume of unit cell. Using Eqs. (10)–(12), we obtain \( s_{1z} = 0.081 \) and \( f_2 = 0.0025 \). The hardness of ThO\(_2\) at its ground-state fluorite structure is thus given by \( H = 22.4 \) (GPa). This indicates that the fluorite ThO\(_2\) is a hard material and approaches to a superhard material (hardness > 40 GPa). The high hardness of this crystal can be understood from the dense crystal structure, which results in high valence electron density and short bond distances. The unusual mixture of covalent and ionic components in the Th–O chemical bond will be discussed in the following subsection.

3.2. Electronic structure and charge distribution

Almost all the macroscopical properties of materials, such as hardness, elasticity, and conductivity, originate from their electronic structure properties as well as the nature of the chemical bonding. Therefore it is necessary to perform the electronic structure analysis of ThO\(_2\). The calculated band structure (left panel) and total density of states (DOS, right panel) of fluorite ThO\(_2\) are shown in Fig. 2. The present calculated energy band gap of 4.673 eV (listed in Table 1), which is consistent with previous FLAPW (FT-LMTO) theoretical result of 4.60 (4.522) eV [10,7], indicates that ThO\(_2\) is a typical insulator. The underestimation of band gap compared with experimental value of 6 eV [26] is due to the drawback of the exchange-correlation approximation (GGA). As a comparison, the orbital-resolved partial densities of states (PDOS) for one Th atom and two O atoms in a unit cell are also presented in Fig. 3. One can see that the low bands covering from \(-18.33 \) to \(-11.22 \) eV mainly consist of O 2s and Th 6p states which shows a clear hybridization. The high valence bands located just below the Fermi level are mainly contributed by O 2p states with a little Th 6d and 5f states and have a band width of 3.79 eV. This illustrates a significant charge transfer from Th 6d and 5f states to O 2p states. In addition, the covalency of ThO\(_2\) comes from the mixing of Th 5f, 6d, and p states into the O 2p valence bands. As for the conduction bands, the DOS is mainly featured by Th 5f states, mixed with a little Th 6d and O 2p states and has a width of 1.78 eV.

In order to gain more insight into the bonding nature of ground state ThO\(_2\), we also investigate the valence charge density distribution. The calculated valence charge density map of the (1 1 0) plane is plotted in Fig. 4. It is obvious from Fig. 4 that the charge density around Th and O ions are all near spherical distributions with slight deformation toward the direction of their nearest neighboring atoms. Furthermore, the charge density around Th and O ions is high while there is almost no valence charge in the large octahedral-hole interstitial region. This suggests remarkable ionization for thorium and oxygen ions and significant insulating property in ThO\(_2\). In order to describe the covalency quantitatively and more clearly, we plot in the inset the line charge density distribution along the nearest Th–O bond. The charge density of Th atoms decreases to approximately equal to zero near the Th nucleus. This is due to the fact that our calculations of charge density only include the valence charge. Therefore, the arrow in the inset indicates the charge density minimum (0.45 e/Å\(^2\)) along the Th–O bond. Although this value is smaller than 0.7 e/Å\(^2\) for Si covalent bond, it is prominently higher than 0.05 e/Å\(^2\) for Na–Cl bond in typical ionic crystal NaCl. Therefore, the Th–O bond has evident covalent property. To see the ionicity of Th–O bond, we have performed the Bader analysis [27,28]. The charge enclosed within the Bader volume is a good approximation to the total electronic charge of an atom. Note that although we have included the core charge in charge density calculations, since we do not expect variations as far as the trends are concerned, only the valence charge...
are calculated. After calculation, we find that there are 9.34 electrons around Th and 7.33 electrons around O. Therefore, about 2.66 electrons transfer from each Th atom to O atom. So, the ionicity of Th–O bond is also evident. Based on the PDOS and charge density analysis, therefore, we derive that the Th–O bond is a mixture of covalent and ionic components. From this aspect, it is now understandable that the previous full-ionic model [6] has largely underestimated the bulk modulus of ThO₂.

3.3. Phonon dispersion curve

The calculation of phonon frequencies of the crystalline structure is one of the basic aspects when considering the phase stability, phase transformations, and thermodynamics of crystalline materials. By using the Hellmann–Feynman theorem and the direct method [29], we have calculated the phonon curves along some high-symmetry directions in the Brillouin zone, together with the phonon density of states. For the phonon dispersion calculation, we used the 2 × 2 × 2 fcc supercell containing 96 atoms and the 4 × 4 × 4 Monkhorst-Pack k-point mesh for the Brillouin zone integration. In order to calculate the Hellmann–Feynman forces, we displace four atoms (two Th and two O atoms) from their equilibrium positions and the amplitude of all the displacements is 0.03 Å. The calculated phonon dispersion curves along the Γ–X–W–L–Γ directions are displayed in Fig. 5. The Γ–X, X–W, and L–Γ lines are along (001), (102), and (111) directions, respectively.

For ThO₂ in the CaF₂-structure primitive cell, there are only three atoms. Therefore, nine phonon modes exist in the dispersion relations. One can see that there is no gap between the optic modes and the acoustic branches and the LO–TO also has no splitting at Γ point. Due to the fact that thorium is heavier than oxygen atom, the vibration frequency of thorium atom is lower than that of oxygen atom. Therefore, the phonon density of states can be viewed as two parts. One is the part lower than 5.5 THz where the main contribution comes from the thorium sublattice, while the other part higher than 5.5 THz is dominated by the dynamics of the light oxygen atoms.

4. High pressure behavior of ThO₂

The optimized structural lattice parameters a, b, and c for the Pnma phase at 0 GPa are 6.174, 3.776, and 7.161 Å, respectively, giving V = 167.0 Å³. This volume, comparable to the value of 164.4 Å³ from previous LCGTO-FF calculations [4] is prominently smaller than the equilibrium volume of 177.5 Å³ for the Fm3m phase. Using the same method as that has been employed in our previous work on orthorhombic BeH₂ [30], we have applied the strains and calculated the elastic constants, various moduli, and Poisson’s ratio v for cotunnite-type ThO₂ at 0 GPa. The results are collected in Table 3. From Table 3 the following prominent features can be seen: (i) The orthorhombic ThO₂ at zero pressure is mechanically stable because its elastic constants satisfy the following mechanical stability criteria [31].

\[
\begin{align*}
C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23}) &< 0, \\
(C_{11} + C_{22} - 2C_{12}) &> 0, & (C_{11} + C_{33} - 2C_{13}) &> 0, \\
(C_{22} + C_{33} - 2C_{23}) &> 0.
\end{align*}
\]

In fact, one can see from Table 3 that the calculated C_{12}, C_{33}, and C_{13} are largely smaller than C_{11}, C_{22}, and C_{33}. Therefore, the mechanical stability criteria is easily satisfied; (ii) Although the equilibrium volume of cotunnite-type ThO₂ is distinctly compressed, its bulk modulus, shear modulus, and Young’s modulus are all smaller by approximately 25% than those in fluorite-type ThO₂. This intriguing behavior has also been observed in the UO₂ system [32], which, like ThO₂, will undergo a Fm3m → Pnma phase transition. Since the 5f orbital band is occupied in UO₂, while it is almost empty in ThO₂, thus this similarity of the softening in moduli upon phase transition for the two systems is clearly unrelated with the 5f orbitals. From this aspect, we speculate that most actinide dioxides share this phase transition involved similarity. Again, we have confirmed for the Pnma phase that the bulk modulus B calculated by fitting the EOS equals to that through VRH approximation. We notice that recent LCGTO-FF calculations [4] gave the bulk modulus B to be 206.8 GPa and the pressure derivative of the bulk modulus B’ to be 4.94. The difference between LCGTO-FF calculations and our results can be attributed either to the type of equation of state used and/or to differences in the exchange and correlation functionals; and (iii) The Poisson’s ratio v of ThO₂ in Pnma phase is nearly the same as in Fm3m phase, i.e., close to 1/3. This is understandable since the shear modulus is much smaller than the bulk modulus in the both two phases.

Now let us discuss the phase transition energetics of ThO₂. The total energies (per unit cell) of the two phases at different volumes are calculated and shown in Fig. 6. Obviously, the Fm3m phase is stable under ambient pressure while under high pressure the Pnma phase becomes stable. According to the rule of common tangent of two energy curves, a phase transition at 26.5 GPa is predicted by the slope shown in the inset of Fig. 6. Besides, we also determine the phase transition pressure by comparing the Gibbs free energy as a function of pressure. At 0 K, the Gibbs free energy is equal to the enthalpy H, expressed as \( H = E + PV \). Fig. 7 shows the relative enthalpies of the cotunnite phase phase with respect to the fluorite phase as a function of pressure. The crossing between the two enthalpy curves in Fig. 7 readily gives phase transition pressure of

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**Fig. 5.** Calculated phonon dispersion curves along the high-symmetry directions (left panel) and total density of states (DOS, right panel) for ground state ThO₂.

**Table 3**

Calculated elastic constants, bulk modulus B, pressure derivative of the bulk modulus B', shear modulus G, Young's modulus E, Poisson’s ratio v for cotunnite-type ThO₂ at 0 GPa. Except B' and Poisson’s ratio, all other values are in units of GPa.

| C₁₁ | C₁₂ | C₁₃ | C₂₂ | C₂₃ | C₃₃ | C₄₄ | C₅₅ | C₆₆ | B   | B'   | G    | E    | v    |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|------|------|------|------|------|
| 299.3 | 256.3 | 235.6 | 37.4 | 54.9 | 84.9 | 73.7 | 95.5 | 104.8 | 148  | 7.8   | 65.9  | 172.2 | 0.307 |
26.5 GPa, which is fully consistent with the above result in terms of the common-tangent-rule. This value is well close to the experimental measurement by Idiri et al. [1] and by Jayaraman et al. [2] as ~30 GPa. Here, the minor theoretical underestimation by ~5.0 GPa is speculated to be caused by the possible existence of an energy barrier with an amplitude of $D_w$. To overcome this energy barrier, the external pressure $P_0$ should be larger than the conventional common-tangent-rule determined pressure $P$ by an amount $\Delta P = P - P$. According to the experimentally measured transition pressure $P$ [1] and our theoretically obtained common tangent curve in Fig. 6, we deduce the energy barrier amplitude to be ~0.06 eV (per formula unit). This value is too small to maintain the $Pnm\bar{a}$ phase to ambient conditions, which is consistent with the fact that to date, the $Pnm\bar{a}$ phase of ThO$_2$ has only been observed under high pressures.

Table 4 lists the calculated lattice parameters, atoms site in Wyckoff notation of orthorhombic ThO$_2$ at 37 GPa. Available experimental values have been presented for comparison where the data from [3] is at 41.2 GPa and data from [1] at 36 GPa.

![Fig. 6. Comparison of total energy vs. the cell volume for ThO$_2$ in $Fm\overline{3}m$ and $Pnm\bar{a}$ phases. A phase transition at 26.5 GPa is predicted by the slope of the common-tangent-rule, as shown in the inset.](image)

![Fig. 7. Calculated enthalpy differences of $Pnm\bar{a}$ phase with respect to $Fm\overline{3}m$ phase as a function of pressure.](image)

Table 4

| Property | This study | Experiment |
|----------|------------|------------|
| $a$      | 5.852      | 5.90$^{a}$, 5.898(8)$^{b}$ |
| $b$      | 3.580      | 3.58$^{a}$, 3.600(3)$^{b}$ |
| $c$      | 6.840      | 6.81$^{a}$, 6.862(7)$^{b}$ |
| Volume ($\text{Å}^3$) | 141.27 | 143.84$^{a}$, 145.7(3)$^{b}$ |
| Atoms site | | |
| Th (4c)  | (0.250, 0.25, 0.111) | (0.261, 0.25, 0.111)$^{b}$ |
| O$_1$ (4c) | (0.142, 0.25, 0.431) | (0.163, 0.25, 0.449)$^{b}$ |
| O$_2$ (4c) | (0.472, 0.75, 0.328) | (0.12, 0.75, 0.27)$^{b}$ |

$^{a}$ Ref. [3].  $^{b}$ Ref. [1].

![Fig. 8. Calculated compression curves of ThO$_2$ compared with experimental measurements. The volume collapses at our predicted phase transition point 26.5 GPa and experimental phase transition pressure 37 GPa are labeled.](image)
To see the change of electronic structure of ThO$_2$ under high pressure, we present in Fig. 10 the orbital-resolved PDOS for the $Fm\overline{3}m$ and $Pnma$ phases at the theoretical transition pressure of 26.5 GPa. One can see that there occurs an understandable narrowing in the band gap (4.6 eV for the $Fm\overline{3}m$ phase and 3.15 eV for the $Pnma$ phase). The valence and conduction bands carry a sizeable downward shift to stabilize the high-pressure $Pnma$ phase. In addition, the valence and conduction bands are more widened and smooth in the $Pnma$ phase. However, these changes in the electronic structure are trivial and thus cannot be associated with the exotic transition-accompanied volume collapse in ThO$_2$ and other actinide dioxides. Concerning the 5f electron effect, here we would like to present our viewpoint as follows. First, the 5f orbital is almost empty for both two phases of ThO$_2$. Therefore, the transition-accompanied volume collapse in ThO$_2$ is irrelevant to the 5f orbital effect. Second, in other actinide dioxides, such as PuO$_2$, although taking into account the 5f electronic interaction is crucial to obtain more reasonable ground state [33], this local correlation effect is not expected to play a role in explaining the transition-accompanied volume collapse in these 5f-occupied actinide dioxides. The reason is simply because that inclusion of 5f electronic localization will weaken the binding of cations and anions, causing an increase instead of a decrease in the volume of system. Therefore, the phenomenon of volume collapse during high-pressure phase transition of the actinide dioxides is mainly attributed to the ionic (instead of electronic) response to the external compression.

5. Conclusion

In summary, the ground-state properties as well as the high pressure behavior of ThO$_2$ were studied by means of the first-principles DFT-GGA method. The elastic constants and their derived moduli and Poisson’s ratio were calculated for both the ambient $Fm\overline{3}m$ and the high-pressure $Pnma$ phases of ThO$_2$ and were shown to agree well with recent reliable experiments. Based on these results, the mechanical stability of the $Pnma$ phase at zero pressure was predicted. The hardness, lattice vibration dynamics, and the Th–O chemical bond of the ambient phase were calculated and analyzed in order to support the practical application of ThO$_2$. We showed that the Th–O bond displays a mixed ionic/covalent character. Here the ionicity is mainly featured by charge transfer from Th 6d/5f states to O 2p states, while the covalency is manifested by hybridization of thorium 5f, 6d and p states into oxygen 2p states. This mixed ionic/covalent feature makes ThO$_2$ a hard material, with its hardness calculated in this paper to be ~22 GPa. As another main task, we studied phase transition of ThO$_2$ under high pressure. Our calculated $Fm\overline{3}m \to Pnma$ transition pressure is 26.5 GPa, according well with recent experimental results of ~30 GPa. Our calculated transition-accompanied volume collapse of 5.9% is also in good agreement with the experimental data of 6.1%. At higher pressure, we further found that an isostructural transition occurs between 80 and 130 GPa for the $Pnma$ phase, which is to be experimentally verified in future.

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